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# Advancements in nitrous oxide abatement: a review of direct catalytic decomposition and selective catalytic reduction

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Nitrous oxide (N<sub>2</sub>O) emissions pose significant environmental and regulatory challenges, which necessitates a need for advancements in catalytic abatement methods. This review evaluates catalytic systems with insights for industrial applications, covering three catalyst types: supported metal catalysts (Rh/CeO<sub>2</sub>, Ru/γ-Al<sub>2</sub>O<sub>3</sub>, Rh/Al<sub>2</sub>O<sub>3</sub>, and Pd/Al<sub>2</sub>O<sub>3</sub>), transition metal oxides (Co<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub>, CuO, and NiO), and ion-exchanged zeolites (Fe-, Co-, and Cu- on ZSM-5, BEA, SSZ-13, FER, and MOR). For direct decomposition reactions, the catalytic performance is influenced by the redox and oxygen desorption properties, as well as by the inclusion of promoters. For SCR applications, iron-based zeolites (e.g., Fe-MFI, Fe-MOR, Fe-BEA, and Fe-SSZ-13) offer high activity, low cost, and low toxicity. Among the reductants, CO and hydrocarbons demonstrate superior efficiency when compared to H<sub>2</sub> and NH<sub>3</sub> for Fe-BEA zeolites. The presence of O<sub>2</sub> and H<sub>2</sub>O was shown to inhibit both reaction pathways, while SO<sub>2</sub> can cause irreversible deactivation. For SCR, NO demonstrates competitive adsorption, which inhibits the reaction with CO and hydrocarbon reductants. Additionally, transient kinetic studies and density functional theory were highlighted in terms of how they inform reaction mechanisms. Furthermore, high-throughput experimentation and machine learning can be leveraged to overcome the current and future industrial shortcomings of N<sub>2</sub>O abatement processes.

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## 1 Introduction

Nitrous oxide (N<sub>2</sub>O) is a detrimental pollutant that accounts for ~6.2% of the anthropogenic greenhouse gas emissions.<sup>1</sup> N<sub>2</sub>O has an atmospheric lifetime of ~131 years, which leads to prolonged harmful effects on the environment (*i.e.*, contributing to ozone depletion). Fig. 1 summarizes the natural and anthropogenic sources of N<sub>2</sub>O. While natural sources are the primary contributors of N<sub>2</sub>O emissions, industrial processes have led to a rapid increase in the emissions (as shown in the inset of Fig. 1).<sup>2–5</sup> Consequently, abatement methodologies should be considered in processes that emit N<sub>2</sub>O and treat NO<sub>x</sub> emissions, such as adipic acid production and the industrial oxidation of ammonia (NH<sub>3</sub>), which accounted for 76% of N<sub>2</sub>O emissions from chemical

industries in 2020 alone.<sup>6,7</sup> Emissions from industrial applications alone warrant the implementation of abatement strategies to address the continuously rising emissions.<sup>8–16</sup>

Among the various N<sub>2</sub>O abatement approaches, direct catalytic decomposition and selective catalytic reduction (SCR) of N<sub>2</sub>O have been extensively studied in the literature, are widely applied in industry, and serve as the primary focus of this review. Although several recent comprehensive reviews

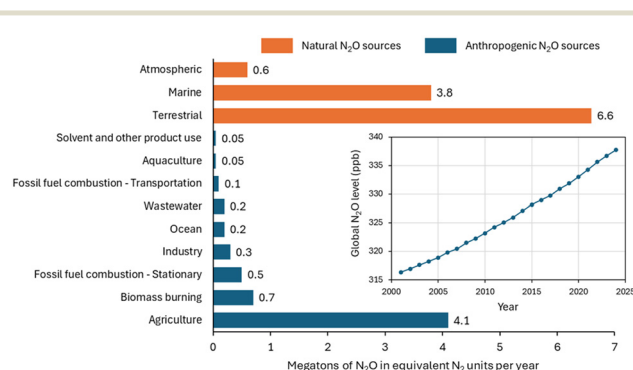


Fig. 1 Quantification of natural and anthropogenic sources of N<sub>2</sub>O emissions by category with globally averaged atmospheric abundance over time (inset). Data from ref. 2 and 4.

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have analyzed  $\text{N}_2\text{O}$  abatement strategies, this review uniquely emphasizes the most commonly used catalytic systems for both direct decomposition and SCR of  $\text{N}_2\text{O}$ .<sup>8–13</sup>

A systematic comparison of  $T_{50}$  values for the direct decomposition and SCR of  $\text{N}_2\text{O}$ , as reported in the literature, was performed based on the feed conditions provided. To enable further comparisons across the systems, gas hourly space velocity (GHSV), weight hourly space velocity (WHSV), and/or weight to volumetric flow ( $W/F$ ) values were calculated (if not explicitly reported for each reference and the data was available). This standardization allows for the evaluation of catalyst performance under varying reaction conditions. Supported metals, metal oxides, and zeolites form the primary catalyst classes compared in this review, with reported or extracted  $T_{50}$  values contextualized based on their respective GHSV, WHSV, and/or  $W/F$  values reported herein. Additionally, emerging catalysts, such as single-atom catalysts and high-entropy oxides (HEOs), are discussed. This review also considers the use of both conventional and unconventional reductants, as well as the effects of impurity gases, in  $\text{N}_2\text{O}$  abatement processes. Studies on catalyst durability remain limited, regardless, oxide-based and zeolite-type catalysts stability will be discussed in sections 2.5 and 3.5.

Beyond catalyst performance evaluations, this review delves into key reaction mechanisms and considers insights gained at a molecular level from advanced tools such as density functional theory (DFT) and temporal analysis of products (TAP) studies. Furthermore, this review provides a forward-looking perspective on leveraging machine learning (ML) approaches and high-throughput experimentation (HTE) to accelerate catalyst discovery. These innovative methodologies have the potential to guide the development of novel catalysts, provide fundamental mechanistic insights, and enable rapid catalyst screening, to guide the field toward efficient industrial  $\text{N}_2\text{O}$  abatement.

### 1.1 Thermo-catalytic performance definitions

For  $\text{N}_2\text{O}$  abatement, a variety of metrics exist to analyze catalytic activity and track reaction performance. Conversion efficiency is used to track the reaction progress over a range of temperatures for a catalytic system and is reported as the fraction of reactants (*i.e.*,  $\text{N}_2\text{O}$ ) that were converted to products. Gas chromatography (GC), Fourier-transform infrared spectroscopy (FTIR), and mass spectrometry (MS) are commonly used to quantify conversion efficiency for the gaseous analytes.

The  $T_{50}$  number (also known as the light-off temperature) is also commonly reported for  $\text{N}_2\text{O}$  abatement. The  $T_{50}$  number is the temperature at which conversion efficiency reaches 50% completion (*i.e.*, the center of an  $S$ -curve conversion *vs.* temperature plot), where a lower  $T_{50}$  number represents a more active catalyst system.

Conversion efficiency and  $T_{50}$  alone do not account for the intrinsic properties of the catalyst and are easily impacted by

temperature, metal loading, and gas flow rate.<sup>17</sup> Therefore, the additional knowledge of the GHSV allows for a better comparison between catalysts by accounting for the volumetric flow rate of reactants to the catalyst bed with respect to the volume of the catalyst utilized. Similarly, the WHSV is also commonly reported and expresses the mass flow rate of reactants to the catalyst bed with respect to the weight of the catalyst. The ratio of the amount of catalyst to the flow rate ( $W/F$ ) is also commonly reported. The GHSV, WHSV, and  $W/F$  help to provide additional insights when comparing reported catalytic conversion efficiencies and  $T_{50}$  values of a system (*e.g.*, larger flowrates with lower masses of catalyst will result in a larger space velocity, resulting in a lower apparent activity).

The  $T_{50}$  numbers at specified flow conditions will be the main metric reported to compare  $\text{N}_2\text{O}$  abatement catalysts. Furthermore, turnover frequency is not reported herein, due to difficulties in determining the number of active sites, as well as a lack of reporting in literature.<sup>18</sup>

### 1.2 Overview and application-based considerations

The use of direct decomposition reaction schemes *versus* the SCR of  $\text{N}_2\text{O}$  presents distinct challenges and considerations. Direct decomposition enables the abatement of  $\text{N}_2\text{O}$  into  $\text{N}_2$  and  $\text{O}_2$  without additional reactants, whereas SCR adds additional reductants such as CO, hydrocarbons,  $\text{NH}_3$ , or  $\text{H}_2$  to aid in decomposition. An overview of the performance of various catalyst systems (supported metals, metal oxides, and zeolites) is shown in Fig. 2, highlighting  $T_{50}$  values for direct decomposition (Fig. 2B) and SCR of  $\text{N}_2\text{O}$  (Fig. 2C). The figure categorizes the values reported in literature based on whether  $\text{H}_2\text{O}$  and  $\text{O}_2$  are included or omitted from the feeds of each system. The SCR values are further classified according to the four most commonly studied reductants: CO, hydrocarbons,  $\text{NH}_3$  and  $\text{H}_2$ . Due to the inclusion of reductants in the SCR feed, direct decomposition of  $\text{N}_2\text{O}$  generally requires higher operating temperatures (300–600 °C) compared to the SCR of  $\text{N}_2\text{O}$  (150–500 °C), as shown in  $T_{50}$  values plotted in Fig. 2.<sup>12,13</sup>

Direct  $\text{N}_2\text{O}$  decomposition offers several industrial advantages, especially when  $\text{N}_2\text{O}$  emissions originate from high-temperature processes.<sup>12</sup> For example,  $\text{N}_2\text{O}$  emissions are often associated with the agricultural industry, ammonia combustion, adipic acid production, or fossil fuel combustion.<sup>19</sup> For these systems, direct decomposition may be favorable when emissions are released from high-temperature equipment, such as stoves/furnaces,<sup>12,19</sup> or following an ammonia combustion process.<sup>20</sup> Additionally, direct decomposition is often preferred in scenarios where introducing additional compounds into the system is undesirable. For instance, the addition of CO or  $\text{NH}_3$  may elevate the risk of toxicity exposure hazards, create a stream of unreacted reactants that would require further processing, or result in the generation of additional greenhouse gas emissions.



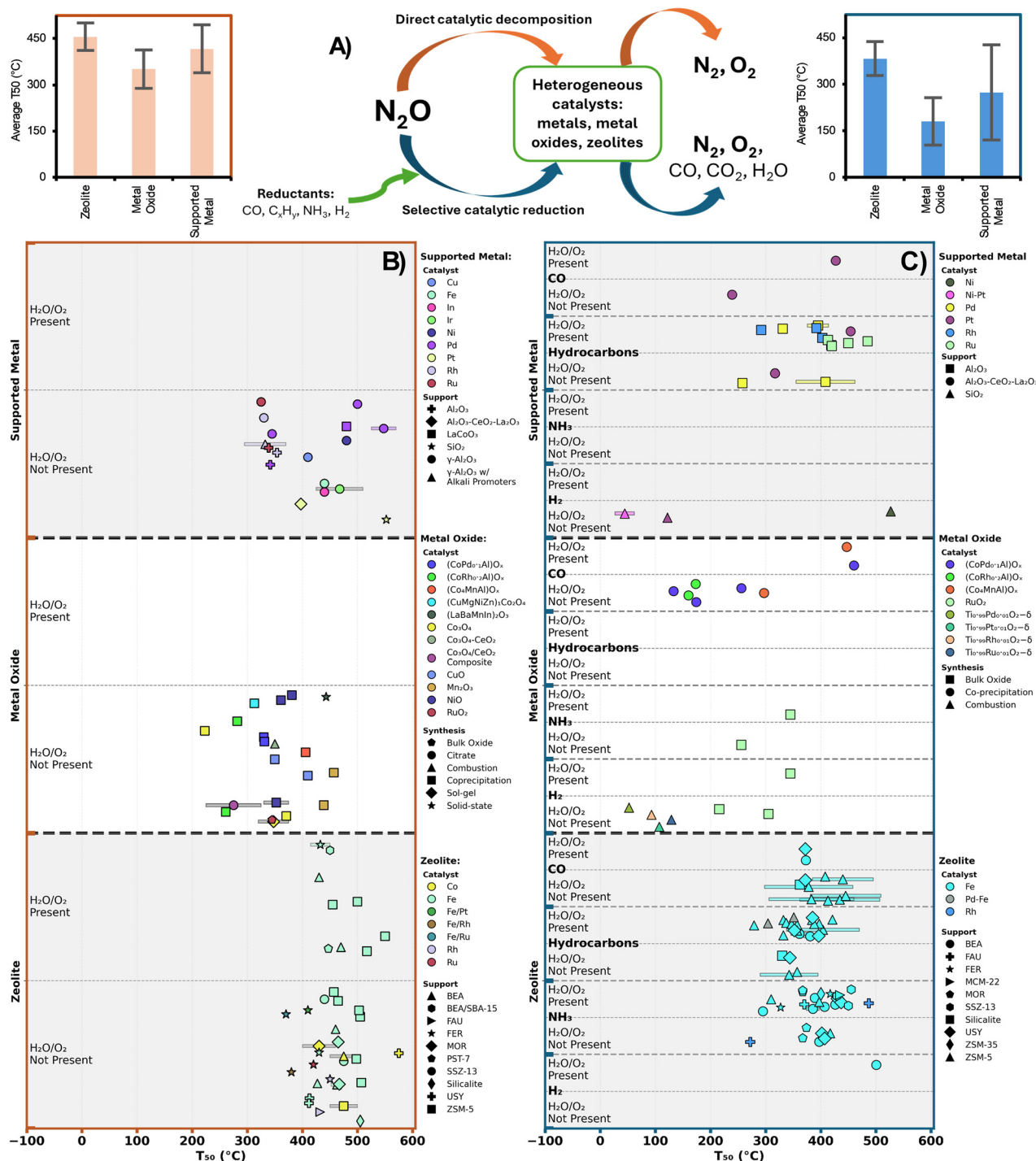


Fig. 2 (A) Reaction schemes for direct catalytic decomposition and SCR.  $T_{50}$  values for (B) direct decomposition (orange) and (C) SCR catalysts (blue). Note: three letter codes are given by the International Zeolite Association.

However, SCR of  $N_2O$  may be preferable for applications that require lower operating temperatures or in industrial processes where suitable reductants are co-produced in tandem with  $N_2O$ . Moreover, some studies suggest that SCR reactions may be more applicable for treating exhaust from stationary or automotive sources.<sup>8</sup>

The choice of catalyst introduces additional considerations. Noble metal catalysts are known to show high activity, with Rh/ $CeO_2$  being considered as one of the most active catalysts for this reaction.<sup>21,22</sup> However, these catalysts are limited by their high cost, abundance in nature, and global production constraints.<sup>23</sup> Cost-effective alternatives include transition metal oxides or zeolites, which have been



shown to achieve low  $T_{50}$  values (as shown in Fig. 2). Many of the metals used in these catalysts are more abundant than noble metals, making metal oxides and zeolite catalysts attractive.<sup>23</sup> Zeolites offer further advantages, such as hydrothermal stability (in some applications) as well as acidity, which may offer beneficial catalytic properties.<sup>24–26</sup>

## 2 Direct nitrous oxide decomposition

Abatement *via* direct decomposition of  $N_2O$  proceeds without a reducing agent to produce  $N_2$  and  $O_2$  (eqn (1)).



$N_2O$  gas-phase catalytic mechanisms generally occur by having  $N_2O$  adsorb onto the catalyst active site (\*) *via* the oxygen atom (eqn (2)). The N–O bond is then cleaved, releasing  $N_2$  and leaving oxygen adsorbed on the surface.<sup>27,28</sup> The adsorbed oxygen removal process is slow in comparison.<sup>29</sup> Subsequently, the Eley–Rideal (E–R) or Langmuir–Hinshelwood (L–H) mechanism proceeds. For the E–R mechanism, an additional  $N_2O$  molecule interacts with the adsorbed atomic oxygen to produce  $O_2$  and  $N_2$  (eqn (3) and (4), Fig. 3). For the L–H mechanism, two adsorbed oxygen atoms recombine and then release  $O_2$  (eqn (5), Fig. 3).



The Mars–van Krevelen mechanism is commonly suggested for many redox reactions, but it is not often observed in the direct decomposition of  $N_2O$ . By employing *in situ* XPS and DFT methods, Sun *et al.* demonstrated that the direct  $N_2O$  decomposition over single-atom Ru on  $CeO_2$  nanorods proceeds *via* the Mars–van Krevelen mechanism.<sup>30</sup> Notably, oxygen desorption and oxygen vacancy formation are facilitated by the recombination of oxygen atoms that dissociate from  $N_2O$  with adjacent lattice oxygen. The Mars–van Krevelen mechanism is discussed more in section 3 and

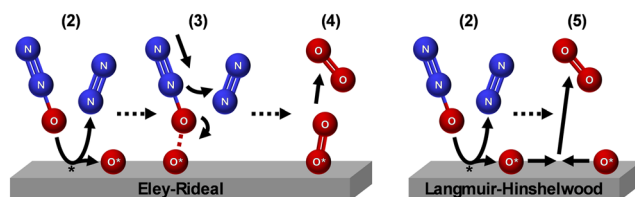


Fig. 3 Schematics of the Eley–Rideal and Langmuir–Hinshelwood mechanisms for  $N_2O$  decomposition. (“\*” denotes surface site or adsorbed species). The numbers refer to the equations found in the text.

depicted in Fig. 7B, where an oxygen vacancy is created by a reductant to facilitate the  $N_2O$  reaction.

Regardless of the mechanism, the  $O_2$  desorption step is crucial to the catalyst performance for  $N_2O$  decomposition due to the inhibitory effects of  $O_2$ . Multiple studies report decreased conversion and reaction rates with excess  $O_2$  present across various catalysts.<sup>31–33</sup>  $O_2$  often competes for binding sites and is slow to desorb from the catalyst. Therefore, catalyst discovery is necessary to aid in the desorption of oxygen from the surface of the catalyst to obtain increased conversion.

Several different catalyst designs have been utilized and modified in attempts to decompose  $N_2O$  and are considered by the following main categories: supported metal, metal oxide, and zeolite catalysts. These three types of catalysts will be discussed for  $N_2O$  decomposition, and a summary of the catalysts with corresponding activities is shown in Table 1 and Fig. 2B.

### 2.1 Supported metal catalysts

Many studies have suggested that  $Rh/CeO_2$  is one of the more active catalysts for the direct decomposition of  $N_2O$ .<sup>21</sup> In one comprehensive study conducted by Li *et al.*, the researchers found that the synthesis of  $Rh/CeO_2$  catalysts was important to increase activity.<sup>21</sup> The authors found that the calcination temperature of the supported  $Rh/CeO_2$  catalysts led to an increase in activity (by a decrease in  $T_{50}$  value from  $\sim 355$  °C for catalysts calcined at 500 °C to  $\sim 325$  °C for catalysts calcined at 800 °C). They found further enhancement of catalytic activity by first calcining the support ( $CeO_2$ ) at 800 °C where the  $T_{50}$  value was further reduced to  $\sim 310$  °C.<sup>21</sup> Furthermore, Zhang *et al.* found that steam treating the catalyst allowed for a more water tolerant  $Rh/CeO_2$  catalyst.<sup>22</sup> Though it is generally accepted that Rh is the most active metal for the abatement of  $N_2O$ , previous studies have looked at the activity of the different platinum group metals (*i.e.*, Rh, Pt, Pd, Ru, and Ir) and compared them to the activity of transition metals, which may provide cheaper alternatives. Pekridis *et al.* analyzed the impact of utilizing Pd, Rh, Ru, Cu, Fe, In, and Ni at 2 wt% supported on  $\gamma-Al_2O_3$  (Fig. 4A).<sup>32</sup> It was found that the three noble metals (Pd, Ru, and Rh) exhibited the highest activity with the lowest  $T_{50}$  of  $\sim 325$  °C. Of the transition metals, Cu exhibited the highest activity with a  $T_{50}$  of  $\sim 400$  °C. Though the Cu-supported catalyst outperformed the other transition metal-supported catalysts, the noble metal catalysts still showed superior activity.<sup>32</sup> The authors attributed the difference in activity to the strength of oxygen adsorption on the surface. When testing noble metal catalysts in a reactant feed with excess  $O_2$ , all  $T_{50}$  values shifted towards higher temperatures; however, the increase in  $T_{50}$  for the noble metals was about 25 °C compared to the shift of 50 °C for the transition metals, which is likely a result of the higher electron density of the noble metals to efficiently facilitate oxygen desorption.<sup>32</sup>



**Table 1** Summary of N<sub>2</sub>O direct decomposition catalysts, grouped by catalyst type: supported metal catalysts (top), metal oxide catalysts (middle), and zeolite catalysts (bottom). *T*<sub>50</sub> represents the temperature at which 50% conversion is reached, with flow conditions being defined by the gas hourly space velocity (GHSV), weight hourly space velocity (WHSV), or ratio of catalyst weight to volumetric gas flow rate (*W/F*). Note: GHSV, WHSV, and *W/F* were standardized based on feed conditions presented in the literature source for further comparison

Metal	Support	Catalyst synthesis	Reaction pretreatment	Feed composition	GHSV (h <sup>-1</sup> )	WHSV (h <sup>-1</sup> )	<i>W/F</i> (g s mL <sup>-1</sup> )	<i>T</i> <sub>50</sub> (°C)	Ref.
Rh (1 wt%)	CeO <sub>2</sub>	Dry impregnation followed by steam treatment		0.3% N <sub>2</sub> O/He			0.018	~273	22
Rh (1 wt%)	CeO <sub>2</sub>	Dry impregnation		200 ppm N <sub>2</sub> O/5% CO <sub>2</sub> /N <sub>2</sub>	30 000			~310	21
Ru (2 wt%)	γ-Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He: 600 °C/1 h	0.12% N <sub>2</sub> O/He	35 000			~325	32
Rh (2 wt%)	γ-Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He: 600 °C/1 h	0.12% N <sub>2</sub> O/He	35 000			~330	32
Pd (2 wt%)	γ-Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He: 600 °C/1 h	0.12% N <sub>2</sub> O/He	35 000			~345	32
Cu (2 wt%)	γ-Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He: 600 °C/1 h	0.12% N <sub>2</sub> O/He	35 000			~410	32
Fe (2 wt%)	γ-Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He: 600 °C/1 h	0.12% N <sub>2</sub> O/He	35 000			~440	32
In (2 wt%)	γ-Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He: 600 °C/1 h	0.12% N <sub>2</sub> O/He	35 000			~440	32
Ni (2 wt%)	γ-Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He: 600 °C/1 h	0.12% N <sub>2</sub> O/He	35 000			~480	32
Pt (0.25–1 wt%)	γ-Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He: 600 °C/1 h	0.1% N <sub>2</sub> O/He	40 000				33
Ir (0.25–1 wt%)	γ-Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He: 600 °C/1 h	0.1% N <sub>2</sub> O/He	40 000			425–510	33
Pd (0.25–1 wt%)	γ-Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He: 600 °C/1 h	0.1% N <sub>2</sub> O/He	40 000			525–570	33
Rh (0.5 wt%)	CeO <sub>2</sub>	Dry impregnation		1000 ppm N <sub>2</sub> O/He	10 000				27
Rh (0.5 wt%)	γ-Al <sub>2</sub> O <sub>3</sub>	Dry impregnation		1000 ppm N <sub>2</sub> O/He	10 000				27
Pd (1 wt%)	LaCoO <sub>3</sub>	Impregnation		1000 ppm N <sub>2</sub> O/1000 ppm NO/He			0.168	~480	34
Pd (1 wt%)	γ-Al <sub>2</sub> O <sub>3</sub>	Impregnation		1000 ppm N <sub>2</sub> O/1000 ppm NO/He			0.168	~500	34
Rh (1 wt%)	γ-Al <sub>2</sub> O <sub>3</sub>	Dry impregnation		200 ppm N <sub>2</sub> O/5% O <sub>2</sub> /N <sub>2</sub>	30 000				35
Rh (1 wt%)	CeO <sub>2</sub>	Dry impregnation		200 ppm N <sub>2</sub> O/5% O <sub>2</sub> /N <sub>2</sub>	30 000				35
Rh (0.1 wt%)	γ-Al <sub>2</sub> O <sub>3</sub> with alkali promoters	Impregnation		1% N <sub>2</sub> O/N <sub>2</sub>	4000			295–370	36
Rh (2 wt%)	ZrO <sub>2</sub> with Pd as a promoter	Impregnation		1000 ppm N <sub>2</sub> O/He			0.02	307	37
Pt (0.5 wt%)	Al <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub> -La <sub>2</sub> O <sub>3</sub>	Co-precipitation, impregnation	H <sub>2</sub> /He, 400 °C, 1 hHe, 400 °C, 1 h	0.1% N <sub>2</sub> O, He balance	10 000			397	38
Ru (2 wt%)	Al <sub>2</sub> O <sub>3</sub>	Dry impregnation		500 ppm N <sub>2</sub> O, He balance			0.12	339	39
Rh (2 wt%)	Al <sub>2</sub> O <sub>3</sub>	Dry impregnation		500 ppm N <sub>2</sub> O, He balance			0.12	354	39
Pd (2 wt%)	Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He, 100 cm <sup>3</sup> min <sup>-1</sup> , 600 °C, 1 h	0.12% N <sub>2</sub> O, He balance	35 000			342	40
Pt (2 wt%)	SiO <sub>2</sub>	Incipient wetness impregnation	H <sub>2</sub> , 400 °C, 1 h	1250 ppm N <sub>2</sub> O, He balance	25 000			552	41

Oxide	Dopant/promoter	Catalyst synthesis	Reaction pretreatment	Feed composition	GHSV (h <sup>-1</sup> )	WHSV (h <sup>-1</sup> )	<i>W/F</i> (g s mL <sup>-1</sup> )	<i>T</i> <sub>50</sub> (°C)	Ref.
MnO			He: 120 °C/45 min then 500 °C/90 min	0.066 atm N <sub>2</sub> O/N <sub>2</sub>	2000				42
Mn <sub>3</sub> O <sub>4</sub>			He: 120 °C/45 min then 500 °C/90 min	0.066 atm N <sub>2</sub> O/N <sub>2</sub>	2000				42
Mn <sub>2</sub> O <sub>3</sub>			He: 120 °C/45 min then 500 °C/90 min	0.066 atm N <sub>2</sub> O/N <sub>2</sub>	2000				42
MnO <sub>2</sub>			He: 120 °C/45 min then 500 °C/90 min	0.066 atm N <sub>2</sub> O/N <sub>2</sub>	2000				42



Table 1 (continued)

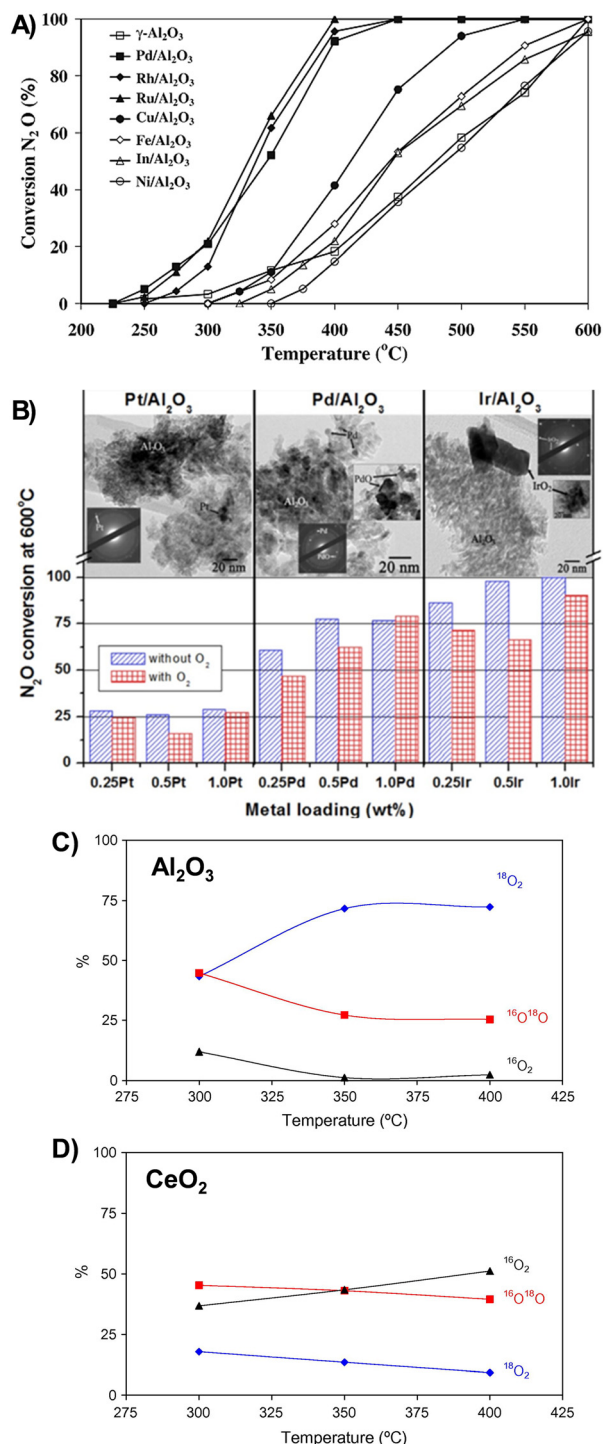
Oxide	Dopant/promoter	Catalyst synthesis	Reaction pretreatment	Feed composition	GHSV (h <sup>-1</sup> )	WHSV (h <sup>-1</sup> )	W/F (g s mL <sup>-1</sup> )	T <sub>50</sub> (°C)	Ref.
Co <sub>3</sub> O <sub>4</sub>				5% N <sub>2</sub> O/Ar	80 000			<700	31
CuO	CeO <sub>2</sub> (nanorods)	CeO <sub>2</sub> : hydrothermal CuO/CeO <sub>2</sub> : precipitation	Ar: 400 °C/1 h	2500 ppm N <sub>2</sub> O/Ar					43
Co <sub>3</sub> O <sub>4</sub> /CeO <sub>2</sub> composite oxide	Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba	Citrate method	20% O <sub>2</sub> /Ar: 400 °C/30 min	1000 ppm N <sub>2</sub> O/Ar			0.2	225–325	44
Co <sub>3</sub> O <sub>4</sub>	Cs	Coprecipitation		1000 ppm N <sub>2</sub> O/N <sub>2</sub>	30 000			223	45
CuO	Cs	Coprecipitation		1000 ppm N <sub>2</sub> O/N <sub>2</sub>	30 000			350	45
NiO		Coprecipitation		1000 ppm N <sub>2</sub> O/N <sub>2</sub>	30 000			361	45
Co <sub>3</sub> O <sub>4</sub>		Coprecipitation		1000 ppm N <sub>2</sub> O/N <sub>2</sub>	30 000			371	45
NiO	Cs	Coprecipitation		1000 ppm N <sub>2</sub> O/N <sub>2</sub>	30 000			381	45
CuO		Coprecipitation		1000 ppm N <sub>2</sub> O/N <sub>2</sub>	30 000			410	45
Mn <sub>2</sub> O <sub>3</sub>		Coprecipitation		1000 ppm N <sub>2</sub> O/N <sub>2</sub>	30 000			439	45
Mn <sub>2</sub> O <sub>3</sub>	Cs	Coprecipitation		1000 ppm N <sub>2</sub> O/N <sub>2</sub>	30 000			457	45
Co <sub>3</sub> O <sub>4</sub> -CeO <sub>2</sub>	Rb	Combustion method employing urea	N <sub>2</sub> : 500 °C/1 h	500 ppm N <sub>2</sub> O/N <sub>2</sub>			0.15	~350	46
Co <sub>3</sub> O <sub>4</sub>	Sm	Sol-gel method with citric acid and urea		1000 ppm N <sub>2</sub> O/N <sub>2</sub>			0.06	~320–375	47
NiO	Pr	Coprecipitation		800 ppm N <sub>2</sub> O/N <sub>2</sub>			0.06	~330–375	48
Co <sub>3</sub> O <sub>4</sub>	Ce-Pr	Coprecipitation		800 ppm N <sub>2</sub> O/N <sub>2</sub>	60 000			317	49
Co <sub>3</sub> O <sub>4</sub>	K-Dy	Sol-gel	Ar: 400 °C/30 min	2000 ppmv N <sub>2</sub> O/Ar	20 000			~225–240	50
Co <sub>3</sub> O <sub>4</sub>	K-Dy	Co-precipitation and impregnation	Ar: 500 °C/30 min	2000 ppmv N <sub>2</sub> O/Ar	20 000			~225	51
Co <sub>3</sub> O <sub>4</sub>	Bi	Sol-gel	Ar: 400 °C/30 min	2000 ppmv/Ar			0.24	~250	52
Co <sub>3</sub> O <sub>4</sub>	F	Co-precipitation		1000 ppm/Ar	10 000			310	53
Co <sub>3</sub> O <sub>4</sub>	N	g-C <sub>3</sub> N <sub>4</sub> -modified thermal decomposition		1000 ppmv N <sub>2</sub> O/Ar	10 000			~260	54
Co <sub>3</sub> O <sub>4</sub>	NiO-Y <sub>2</sub> O <sub>3</sub>	Co-precipitation		1000 ppmv N <sub>2</sub> O/Ar	10 000			~275	55
RuO <sub>2</sub>		Bulk oxide	He, 400 °C, 1 h	N <sub>2</sub> O (1.5 mbar), He balance		5.4		345	56
(CuMgNiZn) <sub>1</sub> Co <sub>2</sub> O <sub>4</sub>		Coprecipitation		1000 ppm N <sub>2</sub> O/N <sub>2</sub>	60 000			313	57
La <sub>0.7</sub> Ba <sub>0.3</sub> Mn <sub>0.8</sub> In <sub>0.2</sub> O <sub>3</sub> (CoRh <sub>0.2</sub> Al) <sub>x</sub> mixed oxide		Solid-state Co-precipitation of hydrotalcite-type precursors	N <sub>2</sub> , 500 °C, >3 h	10% N <sub>2</sub> O/He 12 500 ppm N <sub>2</sub> O, N <sub>2</sub> balance	30 000		3.0	~443 261	58 59
(CoPd <sub>0.1</sub> Al) <sub>x</sub> mixed oxide		Co-precipitation of hydrotalcite-type precursors	N <sub>2</sub> , 500 °C, >3 h	12 500 ppm N <sub>2</sub> O, N <sub>2</sub> balance	30 000			330	59
(Co <sub>4</sub> MnAl) <sub>x</sub> mixed oxide		Co-precipitation of hydrotalcite-type precursors	He, 450 °C, 1 h	0.1 mol% N <sub>2</sub> O, He balance			0.06	406	60
(CoRh <sub>0.2</sub> Al) <sub>x</sub> mixed oxide		Co-precipitation of hydrotalcite-type precursors		12 500 ppm N <sub>2</sub> O, N <sub>2</sub> balance	30 000			274–290	61
(CoPd <sub>0.1</sub> Al) <sub>x</sub> mixed oxide		Co-precipitation of hydrotalcite-type precursors		12 500 ppm N <sub>2</sub> O, N <sub>2</sub> balance	30 000			328–334	61
	Zeolite Metal base	Catalyst synthesis	Reaction pretreatment	Feed composition	GHSV (h <sup>-1</sup> )	WHSV (h <sup>-1</sup> )	W/F (g s mL <sup>-1</sup> )	T <sub>50</sub> (°C)	Ref.
	Cu SSZ-13	Ion exchange	Air: 500 °C/30 min	500 ppm N <sub>2</sub> O/N <sub>2</sub>			0.0031		28



Table 1 (continued)

Metal	Zeolite base	Catalyst synthesis	Reaction pretreatment	Feed composition	GHSV (h <sup>-1</sup> )	WHSV (h <sup>-1</sup> )	W/F (g s mL <sup>-1</sup> )	T <sub>50</sub> (°C)	Ref.
Co	SSZ-13	Ion exchange	Air: 500 °C/30 min	500 ppm N <sub>2</sub> O/N <sub>2</sub>			0.0031		28
Fe	SSZ-13	Ion exchange	Air: 500 °C/30 min	500 ppm N <sub>2</sub> O/N <sub>2</sub>			0.0081		28
Co	MOR	Wet ion exchange	He: 600 °C/1 h	5000 ppm N <sub>2</sub> O/He	30 000			~400–460	62
Co	ZSM-5	Wet ion exchange	He: 600 °C/1 h	5000 ppm N <sub>2</sub> O/He	30 000			~450–500	62
Co	BEA	Wet ion exchange	He: 600 °C/1 h	5000 ppm N <sub>2</sub> O/He	30 000			~450–500	62
Co	USY	Wet ion exchange	He: 600 °C/1 h	5000 ppm N <sub>2</sub> O/He	30 000			~575	62
Fe/Ru	FER	Ion exchange		1000 ppm N <sub>2</sub> O/He	90 000			~360	63
Fe/Rh	FER	Ion exchange		1000 ppm N <sub>2</sub> O/He	90 000			~380	63
Fe/Pt	FER	Ion exchange		1000 ppm N <sub>2</sub> O/He	90 000			~410	63
Ru	FER	Ion exchange		1000 ppm N <sub>2</sub> O/He	90 000			~420	63
Fe	FER	Ion exchange		1000 ppm N <sub>2</sub> O/He	90 000			~430	63
Rh	FER	Ion exchange		1000 ppm N <sub>2</sub> O/He	90 000			>450	63
Fe	FER	Ion exchange	Air: 550 °C/2 h	0.2% N <sub>2</sub> O/3.0% O <sub>2</sub> /He	35 000			~417–437	64
Fe	BEA	Ion exchange	Air: 550 °C/2 h	0.2% N <sub>2</sub> O/3.0% O <sub>2</sub> /He	35 000			~467–477	64
Fe	ZSM-5	Ion exchange	Air: 550 °C/2 h	0.2% N <sub>2</sub> O/3.0% O <sub>2</sub> /He	35 000			~497–507	64
Fe	SSZ-13	Ion exchange	14% O <sub>2</sub> /N <sub>2</sub> : 500 °C/1 h	540 ppm N <sub>2</sub> O/N <sub>2</sub>	200 000			~440	24
Fe	BEA	Ion exchange	14% O <sub>2</sub> /N <sub>2</sub> : 500 °C/1 h	540 ppm N <sub>2</sub> O/N <sub>2</sub>	200 000			~460	24
Fe	PST-7	Hydrothermal	Air: 550 °C/2 h	1000 ppm N <sub>2</sub> O/4% O <sub>2</sub> /He	42 000			447	65
Fe	ZSM-5	Hydrothermal	Air: 550 °C/2 h	1000 ppm N <sub>2</sub> O/4% O <sub>2</sub> /He	42 000			517	65
Fe	SBA-15	Ion exchange	He: 550 °C/1 h	5000 ppm N <sub>2</sub> O/45 000 ppm O <sub>2</sub> /He			0.12		26
Fe	BEA	Ion exchange	He: 550 °C/1 h	5000 ppm N <sub>2</sub> O/45 000 ppm O <sub>2</sub> /He			0.12	~430	26
Fe	BEA/SBA-15	Ion exchange	He: 550 °C/1 h	5000 ppm N <sub>2</sub> O/45 000 ppm O <sub>2</sub> /He			0.12	~450 °C	26
Fe	ZSM-5	Wet ion exchange + alkaline treatment of zeolite	Ar: 500 °C/30 min	5000 ppm N <sub>2</sub> O/5% O <sub>2</sub> /Ar	30 000			~455	66
Fe	ZSM-5	Wet ion exchange	Ar: 500 °C/30 min	5000 ppm N <sub>2</sub> O/5% O <sub>2</sub> /Ar	30 000			~550	66
Fe	BEA	Ion exchange	3% H <sub>2</sub> /Ar, 13 cm <sup>3</sup> min <sup>-1</sup> , ramp from 80–700 °C at 10 °C min <sup>-1</sup>	0.2% N <sub>2</sub> O, He balance	35 000			452–473	67
Fe	Silicalite	Hydrothermal, ion exchange, steam activation	N <sub>2</sub> O/He, 450 °C, 1 h	N <sub>2</sub> O (1.5 mbar), He balance		11.3		505	68
Fe	ZSM-5	Hydrothermal, ion exchange, steam activation	N <sub>2</sub> O/He, 450 °C, 1 h	N <sub>2</sub> O (1.5 mbar), He balance		11.3		505	68
Fe	ZSM-5	Sublimation	N <sub>2</sub> O/He, 450 °C, 1 h	N <sub>2</sub> O (1.5 mbar), He balance		10.8		465	69
Fe	ZSM-5	Isomorphous substitution, steam activation	N <sub>2</sub> O/He, 450 °C, 1 h	N <sub>2</sub> O (1.5 mbar), He balance		10.8		498	69
Fe	ZSM-5	Hydrothermal, ion exchange, steam activation	He, 450 °C, 2 h	N <sub>2</sub> O (1.5 mbar), He balance	90 000			507	70
Fe	ZSM-5	Isomorphous substitution, ion exchange, steam activation	He, 450 °C, 2 h	N <sub>2</sub> O (1.5 mbar), He balance	90 000			503	71
Fe	USY	Ion exchange	He, 600 °C, 1 h	5000 ppm N <sub>2</sub> O, He balance	30 000			413	72
Fe	USY	Ion exchange	He, 600 °C, 1 h	5000 ppm N <sub>2</sub> O, He balance	30 000			412	73
Fe	BEA	Ion exchange	He, 600 °C, 1 h	5000 ppm N <sub>2</sub> O, He balance	30 000			427	73
Fe	MOR	Ion exchange	He, 600 °C, 1 h	5000 ppm N <sub>2</sub> O, He balance	30 000			465	73
Fe	ZSM-5	Ion exchange	He, 600 °C, 1 h	5000 ppm N <sub>2</sub> O, He balance	30 000			457	73
Fe	MOR	Ion exchange	He, 600 °C, 1 h	5000 ppm N <sub>2</sub> O, He balance	30 000			467	74
Rh	FAU	Impregnation	Air, 500 °C	0.2% N <sub>2</sub> O, He balance	30 000			432	75





**Fig. 4** (A) Comparison of catalytic activity for various  $\text{Al}_2\text{O}_3$ -supported metal catalysts (2 wt% metal tested at a GHSV =  $35\,000\ \text{h}^{-1}$  with  $P_{\text{N}_2\text{O}} = 0.12\%$  and a balance in He). Reprinted from ref. 32 with permission from Springer Nature. (B)  $\text{N}_2\text{O}$  conversion at  $600\ ^\circ\text{C}$  with and without  $\text{O}_2$  for Pt, Pd, and Ir on alumina catalysts with insight to surface morphology. Reprinted from ref. 33 with permission from Elsevier. Oxygen content produced from isotopic  $^{15}\text{N}_2^{18}\text{O}$  pulse experiment on 0.5 wt% Rh on (C)  $\text{Al}_2\text{O}_3$  and (D)  $\text{CeO}_2$  to show the evolution of oxygen species, highlighting the oxygen donating role of the  $\text{CeO}_2$  support. C and D Reprinted from ref. 27 with permission from Elsevier.

Pachatouridou *et al.* investigated the impact of the weight loading of noble metals on the decomposition of  $\text{N}_2\text{O}$ . The effect of Pt, Pd, and Ir supported on  $\gamma\text{-Al}_2\text{O}_3$  at various weight loadings showed that an increased metal loading led to increased  $\text{N}_2\text{O}$  conversion at lower temperatures, thus resulting in lower  $T_{50}$  numbers.<sup>33</sup> The Ir metal catalyst was found to have the highest activity in the absence of  $\text{O}_2$ . The addition of oxygen raised the  $T_{50}$  by  $\sim 100\ ^\circ\text{C}$ , for the most active catalyst with 1 wt% Ir. The difference in activity was attributed to the ability of each metal to adsorb oxygen. In catalytic tests in both the presence and absence of  $\text{O}_2$ , Pt/ $\text{Al}_2\text{O}_3$  was less active, while Ir- and Pd-based catalysts were less affected. The authors attributed the overall poor Pt performance to site blocking or competitive adsorption of  $\text{O}_2$  to the active, metallic Pt surface, and the better Ir and Pd performances to oxide phases that are less susceptible to oxygen poisoning. When comparing the crystallite size from XRD and TEM, larger crystallites of  $\text{IrO}_2$  (26.2 nm) were observed, as shown in Fig. 4B, which the authors suggested benefit the activity by easing oxygen desorption from defect-free surfaces, reducing oxygen-induced site blocking. Regardless of whether the high performance is from the active metal itself or properties derived from the support, oxygen desorption is essential to increase conversion due to competitive binding to active sites on the metal surface.

Parres-Esclapez *et al.* analyzed the activity of the Rh/ $\text{CeO}_2$  catalyst on  $\text{N}_2\text{O}$  decomposition and found that  $\text{CeO}_2$  had a higher rate of  $\text{N}_2\text{O}$  decomposition than  $\text{Al}_2\text{O}_3$  catalysts.<sup>27</sup> The authors related the difference in rate to different physicochemical properties of the catalysts. They noted that the apparent activation energy for Rh/ $\text{CeO}_2$  was  $\sim 25\ \text{kJ mol}^{-1}$  less than that of the Rh/ $\text{Al}_2\text{O}_3$ , possibly indicating different mechanisms for decomposition on  $\text{CeO}_2$  versus  $\text{Al}_2\text{O}_3$ . To elucidate the potential mechanisms over the catalysts, pulse decomposition experiments were conducted with  $^{15}\text{N}_2^{18}\text{O}$ . The study showed that the  $\gamma\text{-Al}_2\text{O}_3$ -supported catalyst produced  $^{18}\text{O}_2$  as the primary product, which indicated that the majority of the oxygen produced was a result of oxygen atoms coming from  $\text{N}_2\text{O}$  via the Eley-Rideal mechanism. However, when conducting the same experiment with the Rh/ $\text{CeO}_2$  catalysts at  $350\ ^\circ\text{C}$ ,  $\sim 50\%$   $^{18}\text{O}^{16}\text{O}$  evolved from the system. This indicated a more substantial participation of the support oxygen in the overall reaction mechanism. Therefore, the group noted the important role that the  $\text{CeO}_2$  support plays in exchanging oxygen atoms from the surface of the support to produce molecular oxygen, which was not as prominent for the  $\gamma\text{-Al}_2\text{O}_3$ -supported catalysts to as great of an extent, as shown in Fig. 4C.<sup>27</sup>

Zhu *et al.* performed an *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiment with Rh/ $\text{CeO}_2$  catalysts.<sup>35</sup> The DRIFTS measurements showed  $\text{N}_2\text{O}$  adsorption peaks both on the Rh sites and  $\text{CeO}_2$  support, indicating that both the metal and support play a role in the reaction mechanism, as also observed by Parres-Esclapez *et al.*<sup>27,35</sup> Prior to  $\text{N}_2\text{O}$ -DRIFTS, the samples were reduced,



facilitating the formation of  $\text{Ce}^{3+}$  sites, or oxygen vacancies. The  $\text{N}_2\text{O}$ -DRIFTS data showed that the support can be oxidized under  $\text{N}_2\text{O}$ , from  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$ , providing insight into the redox abilities and role of supports in the  $\text{N}_2\text{O}$  decomposition mechanism.<sup>35</sup> However, the authors noted that  $\text{Ce}^{4+}$  was not reduced to  $\text{Ce}^{3+}$  in their experiments at room temperature, indicating  $\text{O}_2$  desorption as a rate-limiting step.

The role of supports on  $\text{N}_2\text{O}$  decomposition has been further studied by Yoshida *et al.*, where Pt and Pd catalysts on  $\text{SiO}_2\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{MgO}$  (listed from most acidic to least acidic) supports were investigated.<sup>76</sup> The study aimed to relate how the acidity of the support impacts the oxidation and reduction properties of the catalysts, which is of concern due to the oxidative nature of the reaction. The researchers found that more acidic supports can suppress oxidation of the metal at lower temperatures, which can promote the desorption of  $\text{O}_2$  and increase conversion. This suggests that the support can aid in resisting oxygen site blocking and further enhance the reaction conversion.

Similarly, Dacquin *et al.* studied a Pd-supported catalyst on  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{LaCoO}_3$ .<sup>34</sup> When comparing the  $\text{N}_2\text{O}$  conversion during a temperature programmed experiment using a mixed stream of dry 1000 ppm NO and 1000 ppm  $\text{N}_2\text{O}$  gases, it was found that the conversion increased from 15% on  $\text{Pd/Al}_2\text{O}_3$  to 32% on  $\text{Pd/LaCoO}_3$  at 460 °C, and the apparent activation energy decreased from  $\sim 93$  to  $\sim 55$   $\text{kJ mol}^{-1}$ . The authors concluded that the increase in conversion and lower barrier arises from an interaction between the Pd and the reducible  $\text{LaCoO}_3$  support that can create anionic oxygen vacancies and supplies labile oxygen species, as seen with the increased intrinsic activity ceria.<sup>27,34</sup>

The inclusion of promoters can have an equally impactful role as the support on  $\text{N}_2\text{O}$  decomposition. Haber *et al.* found that alkali-metal promoters further enhanced the  $\text{N}_2\text{O}$  decomposition reaction by increasing metallic dispersion (prior to reaction).<sup>36</sup> The study examined a series of  $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$  catalysts with various alkali promoters. The Cs promoted catalyst gave the overall lowest  $T_{50}$  number ( $T_{50}$  performance based on promoters ranked from lowest to highest: Cs, K, Li, Na). The Li and Na-promoted catalysts experienced a clear optimum weight loading at 0.078 mol% of alkali metal oxide, whereas the Cs and K-promoted catalysts did not exhibit such a sharp optimum. The improved activity for the catalysts with larger alkali metals was attributed to an increased Rh dispersion, resulting from an electron-donating effect from the promoters. X-ray photoelectron spectroscopy (XPS) confirmed that the alkali metals increased the electron-density/charge effect on support oxygen, which may hinder Rh diffusion and suppress particle growth. In addition, Pd has been found to have a promotional effect towards  $\text{Rh/ZrO}_2$  catalysts.<sup>37</sup> Zhang *et al.* found that not only did Pd enhance the catalytic activity and decrease the overall activation energy but also influenced the ability to reduce Rh species to their active state and promote the formation of oxygen vacancies. Though also inhibited by

$\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ , Pd promoted Rh catalysts still showed lower  $T_{50}$  values than the baseline  $\text{Rh/ZrO}_2$  catalyst.<sup>37</sup>

Novel catalysts will continue to be researched to drive innovation and progress towards zero-emission processes. Single-atom catalysts (SACs) dispersed on a support have also been explored due to their high atom efficiency and unique electronic properties.<sup>77</sup> Liu *et al.* synthesized a Pt SAC on a  $\text{MgAl}_{1.2}\text{Fe}_{0.8}\text{O}_4$  spinel. Subsequent testing of the catalysts for  $\text{N}_2\text{O}$  decomposition revealed that the Pt SAC (calcined at 800 °C) had the lowest  $T_{50}$ , while the incipient wetness impregnation (IWI) catalyst (calcined at 300 °C) had the highest  $T_{50}$ .<sup>78</sup> Sun *et al.* developed a single-atom Ru on  $\text{CeO}_2$  nanorods catalyst with an ultralow Ru loading of 0.48 wt% for the direct  $\text{N}_2\text{O}$  decomposition.<sup>30</sup> Using a combined experimental and computational approach, they found that the  $\text{Ru/CeO}_2$  SAC outperformed the  $\text{Ru/CeO}_2$  nanoparticles due to enhanced  $\text{O}_2$  desorption and showed high  $\text{O}_2$  resistance. On the contrary, by controlled synthesis and comparing Rh single atoms, nanoclusters (1.1 nm), and nanoparticles (2.1 nm) supported on defect-rich  $\text{CeO}_2$ , Bao *et al.* reported that Rh nanoclusters exhibited a superior activity for direct  $\text{N}_2\text{O}$  decomposition compared to SAC and nanoparticles.<sup>79</sup> The recombination and desorption of oxygen were facilitated by the adjacent Rh atoms in the Rh cluster and positively charged Rh species. In addition to SACs, metal-organic frameworks (MOFs), which are highly porous three-dimensional crystalline materials composed of metal ions or clusters coordinated to organic ligands, are emerging as versatile and effective catalysts owing to their high surface area, tunable porosity, and customizable chemical functionality.<sup>80</sup> Palladium-loaded, metal-organic framework (MOF)-derived catalysts were developed with controlled thermal treatment to improve Pd dispersion for synergistic  $\text{N}_2\text{O}$  decomposition and CO oxidation.<sup>81</sup> They found that the (2%Pd/MIL)-*T* catalyst is highly active and achieved full  $\text{N}_2\text{O}$  decomposition at 550 °C under a space velocity of 240 000  $\text{ml h}^{-1} \text{g}_{\text{cat}}^{-1}$ , which outperformed the commercial  $\text{Pd/Cr}_2\text{O}_3$  and previous MOF-based catalysts. Tang *et al.* utilized ZIF-67 frameworks as precursors for preparing  $\text{Co/CoO}_x$ @carbon catalysts for direct  $\text{N}_2\text{O}$  decomposition and achieved a low  $T_{50}$  value of 305 °C.<sup>82</sup> It was noted that the ZIF67-derived amorphous graphitic carbon frameworks are instrumental in transferring/storing active oxygen and regenerating cobalt active centers. A hollow porous  $\text{NiO@CeO}_2$  octahedron catalyst derived from cerium-based metal-organic frameworks was prepared by Zhao *et al.* and showed a high activity for the  $\text{N}_2\text{O}$  decomposition.<sup>83</sup> By employing various characterization techniques, this remarkable catalytic performance was attributed to the hollow porous structures, uniform Ni dispersion, and large amount of oxygen vacancies in the MOF-derived  $\text{Ni/CeO}_2$  catalyst.

## 2.2 Metal oxides

The scarcity and price of precious metals continuously drive research to find alternative catalysts that provide increased



conversion at a lower cost. Therefore, improving the desorption of oxygen and regeneration of active sites for transition metal oxides and mixed oxide catalysts, such as Co, Mn, Cu, and Ni oxides, is essential to identify precious metal alternative catalysts for N<sub>2</sub>O decomposition.<sup>31,42,43,45,48</sup> For metal oxides, the metal sites tend to exhibit various oxidation states, which can influence the complexity of the catalyst and reaction conversions.

Yamashita and Vannice analyzed the different oxidation states of Mn oxide catalysts to determine the most active oxidation state of Mn.<sup>42</sup> The study analyzed the performance of MnO, Mn<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub>, and MnO<sub>2</sub> and found that Mn<sub>2</sub>O<sub>3</sub> had the largest sustained N<sub>2</sub>O decomposition rate of  $1400 \times 10^{-4} \mu\text{mol s}^{-1} \text{g}_{\text{cat}}^{-1}$ , compared to MnO, which had a rate of  $6.3 \times 10^{-4} \mu\text{mol s}^{-1} \text{g}_{\text{cat}}^{-1}$ . When analyzing the decomposition products, the Mn<sub>2</sub>O<sub>3</sub> catalyst produced stoichiometric decomposition products compared to the MnO catalyst, which only produced N<sub>2</sub> as a product. The authors indicate that other Mn oxides were being oxidized to Mn<sub>3</sub>O<sub>4</sub>, thus hindering the overall catalytic performance,<sup>42</sup> where it is concluded that the Mn<sup>3+</sup> oxidation state is the active site for this reaction.

There have been additional studies conducted to elucidate the mechanism for N<sub>2</sub>O decomposition. Jing *et al.* conducted *operando* XAS studies to better understand the decomposition mechanism on a RhO<sub>x</sub>/ZrO<sub>2</sub> catalyst, which displayed high activity in an N<sub>2</sub>O environment as well as with other inhibitors, such as O<sub>2</sub> and H<sub>2</sub>O. In their study, the catalysts were first treated with a heating step.<sup>84</sup> In conducting *in situ* XANES, the researchers elucidated that the heating step allowed for an initial reduction of Rh, forming defect sites on the catalyst. Following this study, the group introduced 1% N<sub>2</sub>O to their sample and analyzed the effluent with a GC while analyzing the catalyst using XANES. When conducting their study, the group found that the XANES spectra shifted to higher energy. Simultaneously, they saw N<sub>2</sub> and O<sub>2</sub> in the effluent from their GC data. The authors suggested that this displayed how the N<sub>2</sub>O acted as an oxidizing agent to the Rh. Relating this to the *in situ* XANES that was conducted, the authors suggested that the defect sites formed during the high temperature treatment facilitated the decomposition of N<sub>2</sub>O, further displaying how this reaction proceeded *via* a redox mechanism. Another *operando* study conducted by Jing *et al.* elucidated the impact of adding Ag as a promoter to a RhO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>85</sup> From their study using *operando* diffuse reflectance UV-vis, they found that the silver promotes the reduction of the Rh species, which is necessary to form defect sites for the reaction to occur as they previously found.<sup>84,85</sup>

In addition to identifying catalyst active sites, the influence of common inhibitors is important in understanding the functionality of the catalyst. Wilczkowska *et al.* analyzed the possible activation and deactivation mechanisms due to the presence of O<sub>2</sub> or H<sub>2</sub>O in the feed stream for a Co oxide spinel catalyst.<sup>31</sup> They found that O<sub>2</sub> inhibited the reaction at lower temperatures (<800 °C), but

increased activity at higher temperatures compared to experiments when O<sub>2</sub> was not present in the feed. The authors noted that the initial reduced activity at lower temperatures in the presence of O<sub>2</sub> can be attributed to competitive adsorption of O<sub>2</sub> on the active sites, creating a saturated Co species. XRD analysis revealed that the addition of O<sub>2</sub> in the feed stabilized the active Co<sub>3</sub>O<sub>4</sub> state at higher temperatures, whereas in an anoxic environment, the catalyst was reduced to CoO. When H<sub>2</sub>O was present in the feed, the activity had decreased with XRD revealing the catalyst to be reduced, while H<sub>2</sub>O blocked active sites due to competitive adsorption. This result was further confirmed from XPS with an increase in the ratio of O<sub>ads</sub>/O<sub>latt</sub> (where O<sub>ads</sub> and O<sub>latt</sub> are the oxygen associated with hydroxyl groups and the lattice, respectively) when H<sub>2</sub>O was present in the feed.<sup>31</sup> This was attributed to the competitive adsorption on the surface of the cobalt oxide catalyst.

Many studies have aimed to identify dopants and promoters that will both enhance the reaction as well as regenerate the active centers. Zabilskiy *et al.* sought to understand the role of incorporating CuO supported on CeO<sub>2</sub> nanorods.<sup>43</sup> Through XPS, the addition of CeO<sub>2</sub> to the catalyst was found to facilitate the increase in anion defect sites (oxygen vacancies). High-angle annular dark-field scanning transmission electron microscopy showed that the surface of the catalysts was enriched with Ce<sup>3+</sup> while the bulk was enriched with Ce<sup>4+</sup>. The authors attributed this to the ability of Ce to generate labile oxygens to regenerate the active Cu<sup>+</sup> sites, which is portrayed in Fig. 5A.<sup>43</sup> In addition, an increased activity for CuO on CeO<sub>2</sub> was correlated to Ce<sup>3+</sup> ions, determined by *operando* ultraviolet-visible spectroscopy (UV-vis).<sup>43</sup> It was concluded that a [Cu–O–Cu]<sup>2+</sup> species is formed on the surface with labile oxygens from the CeO<sub>2</sub> support donating species to help promote the formation of the active copper complexes.<sup>43</sup>

Some studies have also been performed on the role of alkali and alkali earth promoters on metal oxide catalysts. Xue *et al.* studied the incorporation of alkali and alkali earth metals into a cobalt–cerium composite oxide catalyst.<sup>44</sup> The study determined that the alkali metal-promoted oxide had lower T<sub>50</sub> numbers, with Cs showing the best T<sub>50</sub> of ~225 °C (compared to the unpromoted oxide, T<sub>50</sub> of ~350 °C), as shown in Fig. 5B. The authors attributed this impact to an electronic effect on Co<sup>2+</sup>.<sup>44</sup> This was further evidenced with O<sub>2</sub>-temperature programmed desorption (TPD) and H<sub>2</sub>-TPR. The authors found that larger-element alkali-promoted catalysts facilitated O<sub>2</sub> desorption at lower temperatures due to having a lower overall desorption intensity, while there was an increase in reducibility to regenerate the Co<sup>2+</sup> site as evidenced with H<sub>2</sub>-TPR. This indicated that the alkali metals donate electrons to facilitate oxygen desorption and increase N<sub>2</sub>O conversion to regenerate the active site.<sup>44</sup>

Zhao *et al.* sought to understand the impact of utilizing Cs as a promoter on common oxides, such as Co<sub>3</sub>O<sub>4</sub>, CuO, NiO, and Mn<sub>2</sub>O<sub>3</sub>.<sup>45</sup> The study found that the addition of Cs, as the most basic alkali metal, had a positive impact on the



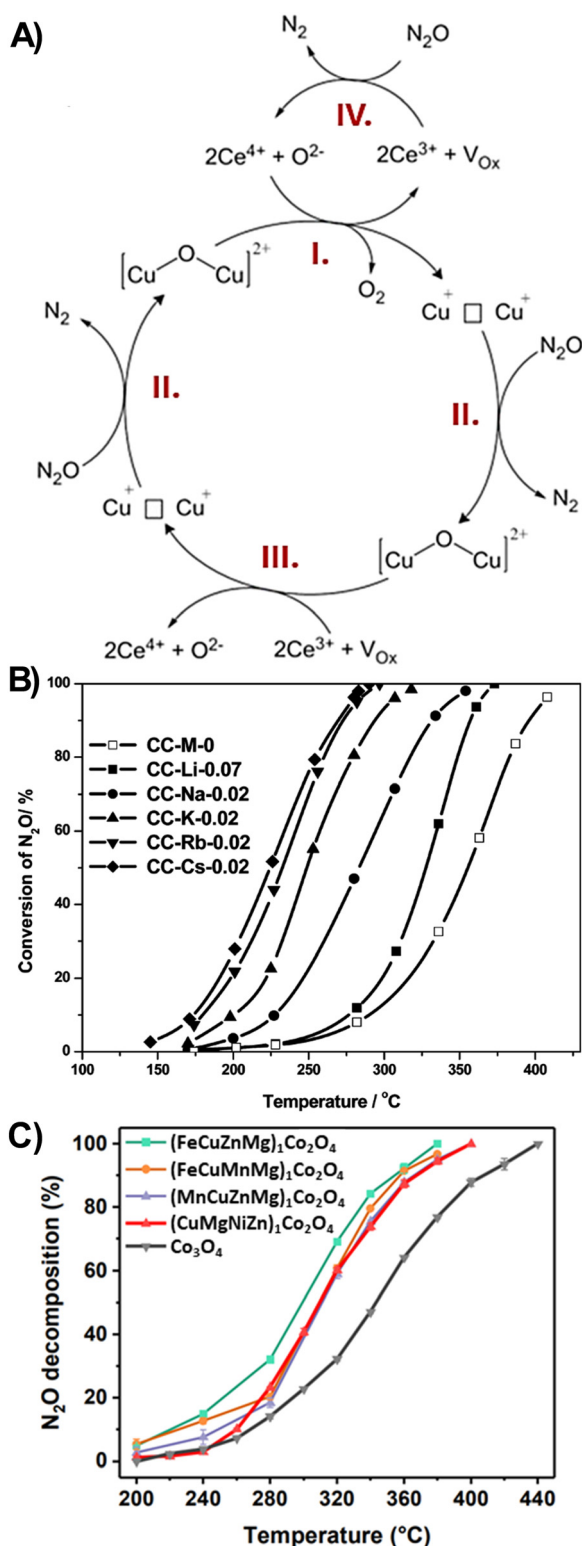


Fig. 5 (A) A proposed  $N_2O$  decomposition mechanism for a  $CuO/CeO_2$  oxide catalysts. Adapted from ref. 43 with permission from Elsevier. (B) Light-off curve plots of alkali metal promoted cobalt-cerium composite oxides. Reprinted from ref. 44 with permission from the American Chemical Society. (C) Light-off curve plots for spinel  $Co_3O_4$ -based HEOs. Adapted from ref. 57 with permission from the American Chemical Society.

$Co_3O_4$  and  $CuO$  catalysts and an inhibiting impact for  $NiO$  and  $Mn_2O_3$  catalysts (an increased  $T_{50}$  number). For  $Co_3O_4$ , the  $T_{50}$  number decreased by  $\sim 150$  °C from the unpromoted catalyst and outperformed the worst-performing catalyst ( $Cs/Mn_2O_3$ ) by  $\sim 235$  °C. This change in activity was accompanied by a decrease in activation energy for the  $Co$  and  $Cu$  catalysts and an increase in activation energy for the  $Ni$  and  $Mn$  (inhibited) catalysts. For the  $Cs/Co_3O_4$  catalyst, XPS showed an increase in the  $Co^{3+}$  fraction (considered the active center of the catalyst) with increasing  $Cs$  concentration. In addition, the authors found that the  $O 1s$  peak of the  $Co$  was shifted to lower binding energies (529.8 eV to 529.4 eV) when promoted with  $Cs$ , indicating a potential electronic effect through the donation of electrons to the active center. Additionally,  $H_2$ -TPR showed that the first metal reduction peak of  $Cs$  promoted  $Co$ -based catalysts was shifted to lower temperatures. However, the second reduction peak for  $Co$ -based catalysts and all of the reduction peaks for the  $Cu$ -based catalysts were shifted to higher temperatures, indicating that  $Cs$  donated electrons to stabilize the active centers of these catalysts. When compared to  $Ni$  and  $Mn$  catalysts, which experienced poorer performance when doped with  $Cs$ , the TPR reduction peaks shifted slightly, indicating a lesser ability to be reduced, possibly explaining the decreased performance.<sup>45</sup>

Abu-Zied *et al.* chose to incorporate  $Rb$  into a  $Co_3O_4-CeO_2$  mixed oxide catalyst and analyzed the impact of changing the dopant concentration from 0.0125–0.2 ratio of  $Rb$  to  $Co$ .<sup>46</sup> Similarly to Zhao *et al.*, they found that the role of  $Rb$  was to enhance the ability of  $Co^{2+}$  to donate electrons to the  $N_2O$  to facilitate decomposition.<sup>45,46</sup> This was confirmed through XPS results as well as a decrease in the  $T_{50}$  number for the  $Rb$  fraction of 0.025 ( $T_{50}$  was  $\sim 350$  °C compared to the unpromoted cobalt oxide, which was about 450 °C).<sup>46</sup>

Despite numerous studies analyzing the impact of promoters, there have been few studies that sought to examine more “exotic” promoters, such as lanthanides. Lanthanides are known to have increased redox properties due to having an unfilled 4f orbital.<sup>47</sup> Liu *et al.* analyzed the impact of doping  $Co_3O_4$  catalysts with samarium ( $Sm$ ). Through *in situ* XPS experiment that exposed the catalyst to 5000 ppm of  $N_2O$  at various temperatures, the authors saw that there was no difference (or shift) in the  $Co 2p$  XPS spectrum under reaction conditions, indicating a stable  $Co$  active site. However, the  $Sm 3d$  spectra shifted to higher binding energies throughout the exposure to  $N_2O$  at different temperatures, indicating that the role of the samarium was to transfer electrons to cobalt to stabilize/regenerate the active site.<sup>47</sup> Similarly, Zhang *et al.* looked at the impact of doping  $NiO$  with praseodymium and found that praseodymium increased the overall surface area of the catalyst and improved the conversion to reach 100% at  $\sim 400$  °C (which is roughly the  $T_{50}$  of unpromoted  $NiO$ ).<sup>48</sup> In addition, they found that with the addition of  $Pr$ , there were little differences in activity when placed in a feed with oxygen, which is typically an inhibiting gas. From XPS, these



researchers observed that praseodymium helped weaken the nickel–oxygen bond, increasing the number of surface oxygens and promoting oxygen vacancies, as well as enhancing the reducibility of nickel. These factors are crucial for regenerating the active sites of the catalysts.<sup>48</sup> Other studies have found similar results when promoting  $\text{Co}_3\text{O}_4$  catalysts with other lanthanides. Sun *et al.* promoted a  $\text{Co}_3\text{O}_4$  catalyst with Ce and Pr.<sup>49</sup> They found that the Ce was imperative to aid in the formation of oxygen vacancies but overall restricted the formation of crystalline  $\text{Co}_3\text{O}_4$ . When Pr was doped into the catalyst, it added an electronic effect to further enhance the redox properties of the catalyst.<sup>49</sup> Dy has also been investigated as a promoter to  $\text{Co}_3\text{O}_4$  catalysts.<sup>50,51</sup> As previously described, alkali metals, such as K, have been discovered as beneficial towards increasing decomposition activity due to having strong electron donating properties. However, studies have noted that in the presence of inhibiting gases, such as  $\text{NO}_x$  and  $\text{CO}_2$ , the role of K becomes inhibited. To further aid in decreasing the Co–O bond and strengthen the redox capabilities of the active species, Dy has been found to be an effective promoter.<sup>50,51</sup>

In addition, there have been various studies discussing further elements that can improve the activity of  $\text{Co}_3\text{O}_4$  catalysts.<sup>52–55</sup> In short, Bi has been noted to create more active  $\text{Co}_3\text{O}_4$  catalysts by increasing surface area and exposing more active crystal planes.<sup>52</sup> Other non-metal atoms, such as F and N have also been used as dopants to  $\text{Co}_3\text{O}_4$  catalysts and are noted to promote the reaction by enhancing the surface basicity of the catalyst while creating more oxygen vacancies for the reactions to occur.<sup>53,54</sup>

High entropy oxides (HEOs) have been shown to exhibit unique properties beyond the sum of their constituent components and often outperform their mono- or bi-component counterparts. Recently, Li *et al.* explored a HEO spinel structure based on  $\text{Co}_3\text{O}_4$  for  $\text{N}_2\text{O}$  decomposition.<sup>57</sup> The  $(\text{CuMgNiZn})_1\text{Co}_2\text{O}_4$  HEO outperformed  $\text{Co}_3\text{O}_4$ , as well as each bimetallic  $\text{MCo}_2\text{O}_4$  ( $\text{M} = \text{Cu}, \text{Mg}, \text{Ni}, \text{Zn}$ ). The HEO had a lower  $T_{50}$  (313 °C) and activation energy (89.6  $\text{kJ mol}^{-1}$ ) than the base  $\text{Co}_3\text{O}_4$  (343 °C and 119.9  $\text{kJ mol}^{-1}$ , respectively) and demonstrated a higher thermal stability over 12 h (Fig. 5C). The enhanced performance was attributed to the abundance of surface oxygen vacancies, caused by the lattice distortion due to multiple cation sizes.  $\text{N}_2\text{O}$  decomposition was also studied on a  $\text{La}_{0.7}\text{Ba}_{0.3}\text{Mn}_{0.8}\text{In}_{0.2}\text{O}_3$  by Ishihara *et al.*<sup>58</sup> The base  $\text{LaMnO}_3$  perovskite structure was modified by partial replacement of La and Mn with Ba and In, respectively, leading to a lower  $T_{50}$  value of 443 °C. While not a true HEO by definition, this complex oxide material highlights property enhancement based on cation substitution.

### 2.3 Zeolites

Zeolites have been extensively studied for their role in the decomposition reaction of  $\text{N}_2\text{O}$ . Specifically, zeolites can boost  $\text{N}_2\text{O}$  decomposition due to various characteristics, such

as the increased surface area and structure giving rise to shape selectivity and control.<sup>26</sup> In addition, zeolites can support reactions due to their acidity.<sup>25,26</sup> Likewise, BEA and SSZ-13 have shown an additional benefit of hydrothermal stability, which is important for some processes that produce  $\text{N}_2\text{O}$  and contain water in the feed<sup>24</sup> (note: three-letter codes for zeolite structures are assigned by the International Zeolite Association<sup>86</sup>). Common zeolite structures for  $\text{N}_2\text{O}$  decomposition reactions are shown in Fig. 6A–D with labeled pore sizes.

Fe, Cu, and Co have been studied extensively for  $\text{N}_2\text{O}$  decomposition when exchanged into zeolites. Lin *et al.* analyzed Fe, Cu, and Co over a SSZ-13 zeolite and determined that the Fe-SSZ-13 catalyst had the largest decomposition rate when compared to the Co- and Cu-exchanged catalysts.<sup>28</sup>  $\text{H}_2$ -TPR and FTIR showed that the Fe-exchanged catalysts were found to have active dimeric  $[\text{Fe}-\text{O}-\text{Fe}]$  sites for decomposition, as well as Cu-exchanged catalysts having many dimeric  $\text{Cu}^{2+}$  sites to aid in the recombination of oxygen for the reaction mechanism.<sup>28</sup> The results indicate a dual site mechanism for both the Fe and Cu-based zeolites, compared to Co-exchanged zeolites, which displayed single  $\text{Co}^{2+}$  sites.<sup>28</sup> The authors related the apparent activity towards the trends in the activation energy, where the Fe-exchanged

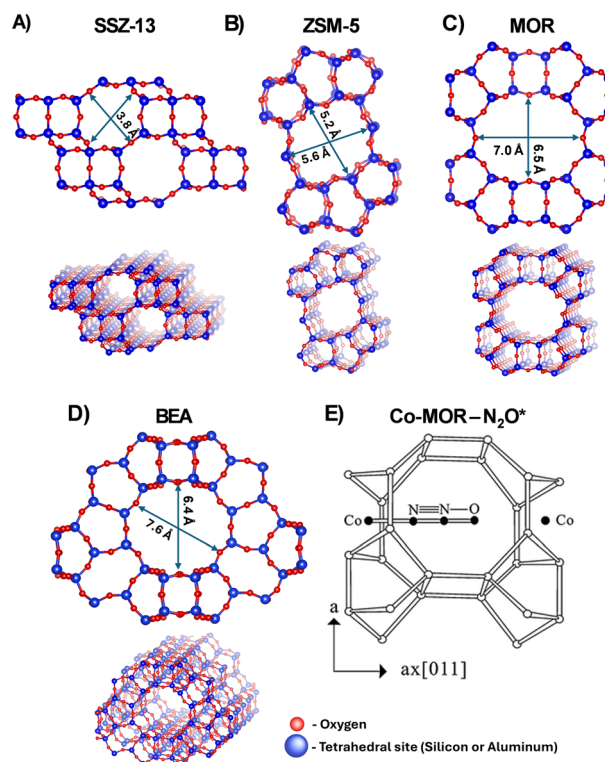


Fig. 6 (A–D) Structures for SSZ-13, ZSM-5, MOR, and BEA with associated pore sizes of commonly utilized zeolites for  $\text{N}_2\text{O}$  abatement reactions. Structural data from ref. 87–90, respectively. (E) Graphical representation of the interaction between  $\text{N}_2\text{O}$  and a  $\beta$ -type Co site of a Co-MOR zeolite. Reprinted from ref. 62 with permission from the Royal Society of Chemistry.



zeolites showed the lowest activation energy, corresponding to the highest reaction rate.

The formation of active sites depends on the interaction of metal ions with the zeolite framework. Zhang *et al.* analyzed how the structure of zeolites impacted the generation of Co active sites for N<sub>2</sub>O decomposition.<sup>62</sup> The study analyzed Co, exchanged into ZSM-5, BEA, MOR, and USY zeolites and found that the activity (based on lowest  $T_{50}$  value to highest  $T_{50}$  value) followed: MOR > BEA  $\approx$  ZSM-5 > USY, with a difference in  $T_{50}$  values of  $\sim$ 100 °C between the best and worst performing catalyst. The catalysts exhibited similar, yet slightly different, results when comparing activity in terms of turnover frequency (ZSM-5 > BEA > MOR > USY) but yielded a different result when comparing with Co loading (MOR > USY > BEA > ZSM-5). Not only could the differences be attributed to the type of zeolite, but the types of active sites as well as coordination to the framework were also found to be impactful. NO-FTIR (with NO used as a probe molecule), H<sub>2</sub>-TPR, and UV-vis DRS (diffuse reflectance spectra) revealed that the more active catalysts (Co-ZSM-5, Co-MOR, and Co-BEA) had larger amounts of Co<sup>2+</sup> sites compared to Co-USY, which had an increased amount of cobalt oxide.<sup>62</sup> It was found that an increase in Co concentration decreased the population of  $\alpha$ -type Co<sup>2+</sup> ions (Co<sup>2+</sup> coordinated to four framework oxygens in the straight channel) and increased the  $\beta$ -type Co<sup>2+</sup> ions (coordinated to more oxygens in the framework/cavity). This trend was evidenced more prominently in Co-BEA and Co-MOR when compared to Co-ZSM-5. The authors noted that the  $\alpha$ -type sites for the ZSM-5 catalysts enable an increased interaction between the reactants and ions, with a decreased interaction between the ion and the framework, which attributed towards increased interactions with the reactants to facilitate decomposition. Similarly, they found that weaker bonds were formed between the Co<sup>2+</sup> ion and the framework oxygens of the BEA zeolite in a  $\beta$ -type site, allowing the ions to coordinate with N<sub>2</sub>O for the reaction despite having more diffusional hinderances due to zeolite structure. On the other hand, the Co ions exchanged into MOR in a  $\beta$ -type site exhibited increased bonding of the ion to the framework, which decreased the affinity of the bonds to N<sub>2</sub>O. Though less accessible to bonding to the reactants, the authors noted that the structure within the MOR cavity locates Co<sup>2+</sup> ions in close proximity with one another leading to the formation of ion pairs that can facilitate N<sub>2</sub>O decomposition (Fig. 6E).<sup>62</sup>

Not only does the zeolite structure impact the reaction, but the ion exchange ratio and Si/Al ratio can impact the kinetics and mechanism of the reaction. Fanson *et al.* studied the Cu-ZSM-5 zeolite while analyzing the impact of the Si/Al ratio and Cu-exchange level on the kinetic rate oscillations for N<sub>2</sub>O decomposition to understand surface reaction intermediates.<sup>91</sup> They found that higher Si/Al ratios resulted in kinetic rate oscillations. The authors attributed these oscillations to the formation and coverage of a nitrate species intermediate that formed due to the interaction of N<sub>2</sub>O with the extra lattice oxygen in the zeolite. They concluded that

the mechanism involves the conversion of N<sub>2</sub>O to NO, which was shown to be rate determining step of this reaction on zeolites with a higher Si/Al ratio.<sup>91</sup>

Aside from the transition-metal exchanged zeolites, Sobalik *et al.* analyzed the impact of incorporating noble metals (Pt, Rh, and Ru) into Fe-FER zeolites.<sup>63</sup> It was found that when Fe and the noble metals were incorporated into the zeolite together, the  $T_{50}$  number decreased from  $\sim$ 420–450 °C for monometallic-FER zeolites to  $\sim$ 360–410 °C for bimetallic zeolites. In conducting isotopic experiments, the authors attributed this increased activity towards the ability of the noble metals to enhance recombination of the oxygen species that were bound to the surface and decreased the role of the oxygens from the framework of the zeolite.<sup>63</sup>

The role of the zeolite is also important in addition to the properties of the metals that allow for the reaction to occur. Guzmán-Vargas *et al.* synthesized Fe-exchange zeolites with BEA, FER, and ZSM-5 type zeolites.<sup>64</sup> Guzmán-Vargas *et al.* found the Fe-FER zeolite to be the most active with the lowest  $T_{50}$  ( $\sim$ 417–437 °C) compared to the least active, which was the Fe-ZSM-5 ( $T_{50}$ :  $\sim$ 497–507 °C). The authors related this difference in activity towards the ability of the host zeolite to yield “oxo-species”, where there is a cation in the species. They found through H<sub>2</sub>-TPR that the Fe-FER catalysts were able to generate these species, which is indicative of the active iron complex for the reaction.<sup>64</sup> Wang *et al.* also analyzed how the influence of the host zeolite impacted the formation of the active centers and related it to the apparent N<sub>2</sub>O decomposition activity.<sup>24</sup> In their study, they exchanged iron into both BEA and SSZ-13 zeolites. Based on UV-vis experiments, the authors found that the Fe-BEA zeolites had larger proportions of dimers and oligomeric iron-oxides as well as Fe<sub>2</sub>O<sub>3</sub> particles, which are inactive. This aligns with their catalytic activity tests.<sup>24</sup>

The porosity of the zeolite can also impact the reaction. Lim *et al.* looked at a variety of Fe-exchanged small pore zeolites, and they found that the smaller pore zeolites, such as the H-Fe-PST-7, outperformed the medium-pore zeolites, such as the Fe-ZSM-5.<sup>65</sup> Similarly, Rutkowska *et al.* sought to increase the surface area by decreasing the micropore volume of zeolites by incorporating BEA to SBA-15.<sup>26</sup> When analyzing N<sub>2</sub> adsorption–desorption tests, they found that they were able to increase the mesoporosity of the zeolite while decreasing the micropore volume. When exchanging Fe into the catalysts, they found that there was an increase in Fe<sup>3+</sup> centers when compared to the Fe-BEA catalysts, which had more Fe<sub>2</sub>O<sub>3</sub> structures in the extra framework. Though there was an increase in iron-oxides in the Fe-BEA, these catalysts still had similar activity to the micro/mesoporous structures. The authors did note, however, that these micro/mesoporous zeolites had a lower iron loading, as found through UV-vis, thus indicating that the introduction of mesoporosity can boost activity.<sup>26</sup> Wu *et al.* also examined the value of adding mesopores to zeolites through alkaline treatment.<sup>66</sup> They found that with the alkaline treatment, the overall ion-exchange percentage increased between the parent zeolite



and the modified zeolite, which correlated to a decrease in  $T_{50}$  (of between 50–100 °C) for all alkaline and parent zeolites.<sup>66</sup>

Furthermore, various *operando* studies have been conducted to elucidate the reaction mechanisms on Fe-zeolites. Cano-Blanco *et al.* performed a series of *operando* investigations on Fe-zeolites and discovered through *operando* diffuse reflectance UV-vis (DRUV) spectroscopy that  $N_2O$  decomposition on these materials is controlled by the reduction process in the redox mechanism, which was rate-limiting.<sup>92</sup> By coupling these findings with a series of other *operando* techniques, such as DRIFTS and electron paramagnetic resonance (EPR) spectroscopy, the researchers concluded that the Fe ions in the 6-membered rings playing a crucial role in the reaction mechanism. These Fe ions can complete the redox cycle necessary to regenerate active sites. *Operando* EPR studies further identified the  $Fe^{2+}$  species in the 6-membered ring of the zeolite as the active component for  $N_2O$  decomposition.<sup>92</sup>

#### 2.4 Impact of inhibiting gases

The above three subsections focus on the direct decomposition activity of three main catalyst types in more “idealized” gas feeds, which may not be the actual operating conditions these catalysts may face in industrial applications. Many industrial processes, such as denitrification,<sup>8</sup> treatment of byproducts from ammonia combustion,<sup>9</sup> adipic acid production and nitric acid production,<sup>12</sup> as well as byproducts from three-way catalytic converters produce other byproducts, such as  $NO_x$ ,  $O_2$ ,  $H_2O$ , and  $SO_2$ .<sup>11</sup> Many studies on direct decomposition catalysts show an inhibiting effect of  $NO$ ,  $O_2$ ,  $H_2O$ ,<sup>21</sup> and  $SO_2$ .<sup>43,46,93</sup> Specifically, it has been noted in literature that  $NO$ ,  $O_2$ , and  $H_2O$  have reversible inhibitory effects, indicating competitive adsorption/site blocking of the catalytic active sites.<sup>31,94</sup> Some literature has also suggested that  $NO$  decreases catalytic activity in that it has a competitive reaction pathway with labile oxygen in a  $CuO/CeO_2$  catalyst.<sup>21</sup>  $SO_2$  has also been found to negatively impact  $N_2O$  decomposition.<sup>40,93</sup> One study conducted a step change experiment in which various concentrations of  $SO_2$  were added or removed while running the experiment for 8 h. It was found that  $SO_2$  negatively impacted the performance with some irreversible deactivation in that the performance did not fully return to the initial activity once removing  $SO_2$ .<sup>93</sup> Studies suggest that the  $SO_2$  is responsible for creating Brønsted acid sites on  $Pd/Al_2O_3$  catalysts, which alters the oxidation state of the active material causing the irreversible deactivation.<sup>40</sup> For further catalytic improvement for such compounds, adding promoters or dopants can help facilitate the desorption and/or weaker binding of these inhibiting compounds, which creates a more robust catalyst under industrial conditions.<sup>37,45,49–55</sup> Yu *et al.* found that doping a  $Co_3O_4$  catalyst with K and Dy improved the catalyst's performance and stability in environments containing  $NO$ ,  $O_2$

and  $H_2O$ .<sup>51</sup> In addition, the choice of support or oxide is important as it could reduce the negative impacts water and  $O_2$  have on the  $N_2O$  decomposition.<sup>93,95,96</sup>

#### 2.5 Direct decomposition catalyst durability

In addition to catalytic activity, catalyst durability is a critical property for the industrial application of direct decomposition and SCR of  $N_2O$  processes, especially under actual plant operating conditions.

The catalyst durability in the direct decomposition of  $N_2O$  has been investigated in literature, with some studies using industry-relevant feed stream and reaction conditions. Porous  $Fe_2O_3-ZrO_2$  and  $NiO-ZrO_2$  nanocomposites were tested for direct  $N_2O$  decomposition and showed a stable  $N_2O$  conversion at 500 °C for 120 hours.<sup>97</sup> In this case, the robust catalytic performance was attributed to the presence of reducible M–O–Zr (M = metal) interactive species and crystalline tetragonal  $ZrO_2$  phase. Šádovská *et al.* studied the catalyst durability of Fe-FER, which is one of the highly active zeolite-based catalysts for  $N_2O$  decomposition.<sup>98</sup> The Fe-FER catalyst was exposed to a gas stream produced by  $NH_3$  oxidation over Pt wire at 800 °C, which is the real conditions in the secondary stage of  $N_2O$  abatement during  $HNO_3$  production, for 12 days. They found that the FER zeolite structure remained stable and the catalytic activity associated with Fe(II) cations for the  $N_2O$  decomposition was preserved after the catalyst aging under real process conditions. The excellent catalyst durability of Fe-FER compared to Fe-MFI under real conditions of nitric acid production plants was also discussed in other studies.<sup>99,100</sup> Melián-Cabrera *et al.* reported a stable  $N_2O$  conversion (~80%) for 50 hours at 427 °C with the presence of  $H_2O$  and  $O_2$  in the feed stream, which was attributed to the stabilization of iron species in the FER matrix.<sup>100</sup> Giecko *et al.* studied the  $N_2O$  decomposition on  $Fe_2O_3/Al_2O_3$  catalysts, which showed insignificant activity loss after 180 h time-on-stream in the pilot plant and 3300 h time-on-stream in the real nitric acid production plant.<sup>101</sup> In another study on the  $N_2O$  decomposition from adipic acid plant, Alini *et al.* found that  $CaMn_{0.6}Cu_{0.4}O_3$  perovskite catalyst has good stability when tested under real industrial conditions at the temperature of 700–750 °C for 1400 hours using off-gas stream that contains  $H_2O$ ,  $O_2$ ,  $CO_2$ , and  $N_2O$ .<sup>102</sup> Wang *et al.* also tested a  $Co_3O_4$  catalyst co-doped with Ni and Y and found it remained stable for 40 h with performance being attributed towards the promoters' role in enhancing  $O_2$  desorption, increasing electron donation abilities of the active ions, increasing the basicity of the catalyst, as well as promoting the reduction of  $Co^{3+}$  to  $Co^{2+}$ .<sup>55</sup>

### 3 Selective catalytic reduction of nitrous oxide

In addition to the direct catalytic decomposition of  $N_2O$ , the SCR of  $N_2O$  has gained significant attention from the



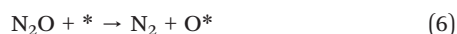
scientific community and industry alike.<sup>103</sup> The presence of reductants benefits the conversion of N<sub>2</sub>O over different heterogeneous catalysts, as it lowers the reaction temperature required for reducing N<sub>2</sub>O into inert nitrogen molecules. There are four main reductants that have been studied extensively in the literature for the SCR of N<sub>2</sub>O processes and will be discussed in the following sections: CO, hydrocarbons, NH<sub>3</sub>, and H<sub>2</sub>. The catalytic performance of SCR catalysts, indicated by T<sub>50</sub> values, under various reaction conditions are summarized in Table 2 and Fig. 2C. In general, it shows that iron-zeolites are the most studied catalysts for the SCR of N<sub>2</sub>O, especially when NH<sub>3</sub> is used as the reductant. The reaction mechanisms and the influence of common industry-relevant impurity gases, such as NO, O<sub>2</sub>, H<sub>2</sub>O, and SO<sub>2</sub>, on the SCR of N<sub>2</sub>O are discussed in this section.

### 3.1 Carbon monoxide (CO-SCR)

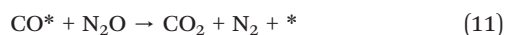
CO has been considered an efficient and selective reductant for the conversion of N<sub>2</sub>O. In general, CO can react with adsorbed oxygen and remove these atoms from the catalyst surface (also known as a scavenging effect), leading to a considerably decreased reaction temperature compared to the direct catalytic decomposition of N<sub>2</sub>O.<sup>69,70</sup> There are two main reaction mechanisms of N<sub>2</sub>O reduction by CO proposed in literature (*i.e.* the redox or associative routes) depending on the catalyst system.<sup>60</sup>

In the redox mechanism, N<sub>2</sub>O first adsorbs to the surface, releasing reduced N<sub>2</sub>, and leaving O adsorbed (eqn (6)). This is then followed by either the Langmuir–Hinshelwood mechanism (eqn (7) and (8)) or the Eley–Rideal mechanism (eqn (9)) to oxidize CO to CO<sub>2</sub>. In the associative mechanism, simultaneous oxidation and reduction occurs by adsorbed CO (eqn (10)) reacting with either gaseous N<sub>2</sub>O (eqn (11)) or adsorbed N<sub>2</sub>O (eqn (12) and (13)):

Redox mechanism:



Associative mechanism:



Delahay *et al.* studied a variety of reductants for the SCR of N<sub>2</sub>O over two Fe-BEA catalysts in the presence of oxygen.<sup>67</sup> It was found that CO is an effective reductant with an onset temperature of ~200 °C for N<sub>2</sub>O reduction, which is lower than other reductants like propene and ammonia. Based on the superimposed curves of N<sub>2</sub>O reduction by CO and N<sub>2</sub>O decomposition on the reduced Fe-BEA at below 330 °C, the reoxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> species by N<sub>2</sub>O was suggested to be the rate limiting step in the CO-SCR of N<sub>2</sub>O in the low temperature region. In a study of CO-SCR of N<sub>2</sub>O over Fe-ZSM-5 and Fe-silicalite, Pérez-Ramírez *et al.* reported that the reaction rate has a linear correlation with the CO/N<sub>2</sub>O feed ratio (up to 1:1) and depends strongly on the catalyst preparation method.<sup>69</sup> They found the preparation method affects the distribution of iron species on the catalyst surface as well as the interaction of CO with iron sites which in turn accelerate N<sub>2</sub>O removal. A site-dependent reaction mechanism was proposed by using *in situ* UV/vis and electron paramagnetic resonance (EPR) spectroscopy analyses. The authors concluded that while the reduction of N<sub>2</sub>O by coordinated CO on Fe<sup>3+</sup> ions can occur without changing oxidation states over isolated iron species, a redox Fe<sup>3+</sup>/Fe<sup>2+</sup> cycle with the formation of intermediate oxygen anion-radicals (O<sup>•-</sup>) happens over oligo-nuclear iron clusters. Wu *et al.* applied a multifaceted approach of experimental testing, catalyst characterization, and density functional theory (DFT)/*ab initio* molecular dynamics (AIMD) modeling to identify the catalytic role and transformation of different relevant iron species (mononuclear, binuclear, clusters, and Fe<sub>2</sub>O<sub>3</sub> particles, see Fig. 7A) in Fe-ZSM-5 catalysts upon exposure to CO in the SCR of N<sub>2</sub>O.<sup>111</sup> It was concluded that N<sub>2</sub>O is activated on isolated iron sites to generate adsorbed oxygen species that then react with CO following the Eley–Rideal mechanism, while CO interacts with Fe<sub>2</sub>O<sub>3</sub> particles to form oxygen vacancies that dissociate N<sub>2</sub>O following the Mars–van Krevelen mechanism (Fig. 7B). It is worth noting that the Mars–van Krevelen mechanism was also proposed in CO-SCR of N<sub>2</sub>O on phosphotungstic acid supported single-atom catalysts.<sup>112</sup> In this case, CO reductant is oxidized by the oxygen atom from the support to form an oxygen vacancy, which is replenished by N<sub>2</sub>O to release N<sub>2</sub> into gas phase. Recently, advanced *in situ/operando* spectroscopy approach was utilized to study the reduction and oxidation half cycles of CO-SCR of N<sub>2</sub>O over Fe-zeolites.<sup>113,114</sup> Qian *et al.* investigated the redox cycle of Fe-BEA catalyst during the CO-SCR of N<sub>2</sub>O in an excess oxygen environment by *operando/in situ* diffuse reflectance ultraviolet-visible (UV-vis) spectroscopy and *in situ* Fe K-edge X-ray absorption (XAS) spectroscopy.<sup>113</sup> Based on the *operando* UV-vis and XAS results, the redox cycle of Fe active sites was proposed in two steps: (i) Fe<sup>III</sup>-α-O species are reduced by CO to generate Fe<sup>II</sup> species and CO<sub>2</sub>; (ii) Fe<sup>II</sup> active sites reduce N<sub>2</sub>O to form N<sub>2</sub> and regenerate Fe<sup>III</sup>-α-O species. Quantitative spectro-kinetic analysis revealed a higher reactivity of Fe<sup>II</sup> sites with N<sub>2</sub>O compared to O<sub>2</sub>, enabling a selective CO + N<sub>2</sub>O reaction under excess O<sub>2</sub> conditions. Fischer *et al.* examined the redox



**Table 2** Summary of N<sub>2</sub>O SCR catalysts, grouped by reductant from top to bottom: CO, hydrocarbons, NH<sub>3</sub>, and H<sub>2</sub>. T<sub>50</sub> represents the temperature at which 50% conversion is reached, with flow conditions being defined by the gas hourly space velocity (GHSV), weight hourly space velocity (WHSV), or ratio of catalyst weight to volumetric gas flow rate (W/F). Note: GHSV, WHSV, and W/F were standardized based on feed conditions presented in the literature source for further comparison

Reductants	Other reactants <sup>a</sup>	Inhibitors <sup>b</sup>	Catalyst	Catalyst synthesis	Catalyst pretreatment	GHSV (h <sup>-1</sup> )	WHSV (h <sup>-1</sup> )	W/F (g s mL <sup>-1</sup> )	Feed composition	T <sub>50</sub> (°C)	Ref.
CO			Pt/Al <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub> -La <sub>2</sub> O <sub>3</sub>	Co-precipitation, impregnation	H <sub>2</sub> /He, 400 °C, 1 h followed by He, 400 °C, 1 h	10 000			0.1% N <sub>2</sub> O, 0.1% CO, He balance	239	38
CO		O <sub>2</sub>	Pt/Al <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub> -La <sub>2</sub> O <sub>3</sub>	Co-precipitation, impregnation	H <sub>2</sub> /He, 400 °C, 1 h followed by He, 400 °C, 1 h	10 000			0.1% N <sub>2</sub> O, 0.1% CO, 2% O <sub>2</sub> , He balance	427	38
CO			Al-Pd-Co-O mixed oxide	Co-precipitation of hydrotalcite-type precursors	Co-precipitation followed by He, 400 °C, 1 h	30 000			12 500 ppm N <sub>2</sub> O, 17 500 ppm CO, N <sub>2</sub> balance	133	61
CO			Al-Rh-Co-O mixed oxide	Co-precipitation of hydrotalcite-type precursors	Co-precipitation followed by He, 400 °C, 1 h	30 000			12 500 ppm N <sub>2</sub> O, 17 500 ppm CO, N <sub>2</sub> balance	160	61
CO			Co-Rh-Al-O mixed oxide	Co-precipitation of hydrotalcite-type precursors	N <sub>2</sub> , 500 °C, >3 h	30 000			12 500 ppm N <sub>2</sub> O, 17 500 ppm CO, N <sub>2</sub> balance	173	59
CO			Co-Pd-Al-O mixed oxide	Co-precipitation of hydrotalcite-type precursors	N <sub>2</sub> , 500 °C, >3 h	30 000			12 500 ppm N <sub>2</sub> O, 17 500 ppm CO, N <sub>2</sub> balance	174	59
CO		NO	Al-Pd-Co-O mixed oxide	Co-precipitation of hydrotalcite-type precursors	Co-precipitation followed by He, 400 °C, 1 h	30 000			12 500 ppm N <sub>2</sub> O, 17 500 ppm CO, 100 ppm NO, N <sub>2</sub> balance	256	61
CO			Co-Mn-Al-O mixed oxide	Co-precipitation of hydrotalcite-type precursors	He, 450 °C, 1 h		10.9		0.1 mol% N <sub>2</sub> O, 0.15 mol% CO, He balance	297	60
CO		O <sub>2</sub>	Co-Mn-Al-O mixed oxide	Co-precipitation of hydrotalcite-type precursors	He, 450 °C, 1 h		10.9		0.1 mol% N <sub>2</sub> O, 0.15 mol% CO, 20 mol% O <sub>2</sub> , He balance	447	60
CO		O <sub>2</sub>	Co-Pd-Al-O mixed oxide	Co-precipitation of hydrotalcite-type precursors	N <sub>2</sub> , 500 °C, >3 h	30 000			12 500 ppm N <sub>2</sub> O, 17 500 ppm CO, 10 500 ppm O <sub>2</sub> , N <sub>2</sub> balance	460	59
CO			Fe/ZSM-5	Sublimation	N <sub>2</sub> O/He, 450 °C, 1 h		10.9		N <sub>2</sub> O (1.5 mbar) and CO (0.3–1.5 mbar), He balance	298–458	69
CO			Fe-ZSM-5	Ion exchange	O <sub>2</sub> , 500 °C, 1 h		9.9		1000 ppm N <sub>2</sub> O, 1000 ppm CO, He balance	306–460	104
CO			Fe/silicalite	Isomorphous substitution, ion exchange, steam activation	N <sub>2</sub> O/CO/He, 450 °C, 1 h		11.3		N <sub>2</sub> O (1.5 mbar), CO (1 mbar), He balance	362	68
CO			Fe/ZSM-5	Isomorphous	He, 450 °C, 2 h	90 000			N <sub>2</sub> O (1.5 mbar),	362–507	70



Table 2 (continued)

Reductants	Other reactants <sup>a</sup>	Inhibitors <sup>b</sup>	Catalyst	Catalyst synthesis	Catalyst pretreatment	GHSV (h <sup>-1</sup> )	WHSV (h <sup>-1</sup> )	W/F (g s mL <sup>-1</sup> )	Feed composition	T <sub>50</sub> (°C)	Ref.
CO	O <sub>2</sub>		Fe-BEA	substitution, ion exchange, steam activation Ion exchange	3% H <sub>2</sub> /Ar, 13 mL min <sup>-1</sup> , ramp from 80–700 °C at 10 °C min <sup>-1</sup> He, 600 °C, 1 h	35 000			CO (0.2–3.0 mbar), He balance 0.2% N <sub>2</sub> O, 0.2% CO, 3% O <sub>2</sub> , He balance	369–377	67
CO			Fe-USY	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 5000 ppm CO, He balance	372	72
CO	O <sub>2</sub>		Fe-USY	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 5000 ppm CO, 50 000 ppm O <sub>2</sub> , He balance	372	72
CO			Fe/ZSM-5	Isomorphous substitution, ion exchange, steam activation	He, 450 °C, 2 h	90 000			N <sub>2</sub> O (1.5 mbar), CO (0.2–1.5 mbar), He balance	381–509	71
CO			Fe/ZSM-5	Isomorphous substitution, steam activation	N <sub>2</sub> O/He, 450 °C, 1 h	10.9			N <sub>2</sub> O (1.5 mbar) and CO (0.3–1.5 mbar), He balance	385–495	69
CO			Fe/ZSM-5	Isomorphous substitution, ion exchange, steam activation	N <sub>2</sub> O/CO/He, 450 °C, 1 h	11.3			N <sub>2</sub> O (1.5 mbar), CO (1 mbar), He balance	408	68
CO	NO		Fe/ZSM-5	Isomorphous substitution, ion exchange, steam activation	He, 450 °C, 2 h	90 000			N <sub>2</sub> O (1.5 mbar), CO (1.5 mbar), NO (1.5 mbar), He balance	413	70
CH <sub>4</sub>			Pd/Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He, 100 mL min <sup>-1</sup> , 600 °C, 1 h	35 000			0.12% N <sub>2</sub> O, 0.5% CH <sub>4</sub> , He balance	258	40
C <sub>3</sub> H <sub>6</sub>			Rh/Al <sub>2</sub> O <sub>3</sub>	Dry impregnation				0.12	500 ppm N <sub>2</sub> O, 1000 ppm C <sub>3</sub> H <sub>6</sub> , He balance	292	39
C <sub>3</sub> H <sub>6</sub>			Pt/Al <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub> -La <sub>2</sub> O <sub>3</sub>	Co-precipitation, impregnation	H <sub>2</sub> /He, 400 °C, 1 h followed by He, 400 °C, 1 h	10 000			0.1% N <sub>2</sub> O, 0.1% C <sub>3</sub> H <sub>6</sub> , He balance	317	38
CH <sub>4</sub>	O <sub>2</sub>		Pd/Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He, 100 mL min <sup>-1</sup> , 600 °C, 1 h	35 000			0.12% N <sub>2</sub> O, 0.5% CH <sub>4</sub> , 5% O <sub>2</sub> , He balance	331	40
CH <sub>4</sub>	SO <sub>2</sub>		Pd/Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He, 100 mL min <sup>-1</sup> , 600 °C, 1 h	35 000			0.12% N <sub>2</sub> O, 0.5% CH <sub>4</sub> , 300 ppm SO <sub>2</sub> , He balance	355–462	40
CH <sub>4</sub>	H <sub>2</sub> O		Pd/Al <sub>2</sub> O <sub>3</sub>	Dry impregnation	He, 100 mL min <sup>-1</sup> , 600 °C, 1 h	35 000			0.12% N <sub>2</sub> O, 0.5% CH <sub>4</sub> , 3% H <sub>2</sub> O, He balance	376–414	40
C <sub>3</sub> H <sub>6</sub>	O <sub>2</sub>		Rh/Al <sub>2</sub> O <sub>3</sub>	Dry impregnation				0.12	500 ppm N <sub>2</sub> O, 1000 ppm C <sub>3</sub> H <sub>6</sub> , 5% O <sub>2</sub> , He balance	392	39
C <sub>3</sub> H <sub>6</sub>	O <sub>2</sub>		Rh/Al <sub>2</sub> O <sub>3</sub>	Dry impregnation				0.12	500 ppm N <sub>2</sub> O, 1000 ppm C <sub>3</sub> H <sub>6</sub> , 5% O <sub>2</sub> , 50 ppm SO <sub>2</sub> , He balance	403	39
C <sub>3</sub> H <sub>6</sub>	O <sub>2</sub>		Ru/Al <sub>2</sub> O <sub>3</sub>	Dry impregnation				0.12	500 ppm N <sub>2</sub> O, 1000 ppm C <sub>3</sub> H <sub>6</sub> , 5% O <sub>2</sub> , He balance	413	39
C <sub>3</sub> H <sub>6</sub>	O <sub>2</sub>	H <sub>2</sub> O	Rh/Al <sub>2</sub> O <sub>3</sub>	Dry impregnation				0.12	500 ppm N <sub>2</sub> O, 1000 ppm C <sub>3</sub> H <sub>6</sub> , 5% O <sub>2</sub> , 10% H <sub>2</sub> O, He balance	419	39
C <sub>3</sub> H <sub>6</sub>	O <sub>2</sub>	SO <sub>2</sub>	Ru/Al <sub>2</sub> O <sub>3</sub>	Dry impregnation				0.12	500 ppm N <sub>2</sub> O, 1000 ppm C <sub>3</sub> H <sub>6</sub> , 5% O <sub>2</sub> , 50 ppm SO <sub>2</sub> , He balance	420	39



Table 2 (continued)

Reductants	Other reactants <sup>a</sup>	Inhibitors <sup>b</sup>	Catalyst	Catalyst synthesis	Catalyst pretreatment	GHSV (h <sup>-1</sup> )	WHSV (h <sup>-1</sup> )	W/F (g s mL <sup>-1</sup> )	Feed composition	T <sub>50</sub> (°C)	Ref.
C <sub>3</sub> H <sub>6</sub>	O <sub>2</sub>	H <sub>2</sub> O	Ru/Al <sub>2</sub> O <sub>3</sub>	Dry impregnation				0.12	500 ppm N <sub>2</sub> O, 1000 ppm C <sub>3</sub> H <sub>6</sub> , 5% O <sub>2</sub> , 10% H <sub>2</sub> O, He balance	450	39
C <sub>3</sub> H <sub>6</sub>		O <sub>2</sub>	Pt/Al <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub> -La <sub>2</sub> O <sub>3</sub>	Co-precipitation, impregnation	H <sub>2</sub> /He, 400 °C, 1 h followed by He, 400 °C, 1 h	10 000			0.1% N <sub>2</sub> O, 0.1% C <sub>3</sub> H <sub>6</sub> , 2% O <sub>2</sub> , He balance	454	38
C <sub>3</sub> H <sub>6</sub>			Ru/Al <sub>2</sub> O <sub>3</sub>	Dry impregnation				0.12	500 ppm N <sub>2</sub> O, 1000 ppm C <sub>3</sub> H <sub>6</sub> , He balance	485	39
C <sub>3</sub> H <sub>8</sub>	O <sub>2</sub>		Fe/ZSM-5	Solid state ion exchange	He, 500 °C	7500			1000 ppm N <sub>2</sub> O, 1000 ppm C <sub>3</sub> H <sub>8</sub> , 4% O <sub>2</sub> , He balance	279	105
CH <sub>4</sub>			Fe-ZSM-5	Ion exchange	O <sub>2</sub> , 500 °C, 1 h		9.9		950 ppm N <sub>2</sub> O, 500 ppm CH <sub>4</sub> , He balance	290–395	104
C <sub>3</sub> H <sub>8</sub>		O <sub>2</sub> , H <sub>2</sub> O	Pd-Fe/ZSM-5	Ion exchange, incipient wetness impregnation	N <sub>2</sub> , 175 °C, 2 h	20 000			1900 ppm C <sub>3</sub> H <sub>8</sub> , 1500 ppm N <sub>2</sub> O, 100 ppm NO, 100 ppm NO <sub>2</sub> , 0.5% H <sub>2</sub> O, 2.5% O <sub>2</sub> , N <sub>2</sub> balance	304	106
C <sub>3</sub> H <sub>8</sub>	O <sub>2</sub>		Fe/silicalite	Isomorphous substitution, ion exchange, steam activation	N <sub>2</sub> O/C <sub>3</sub> H <sub>8</sub> /O <sub>2</sub> /He, 450 °C, 1 h		11.3		N <sub>2</sub> O (1.5 mbar), C <sub>3</sub> H <sub>8</sub> (1.5 mbar), He balance	330	68
C <sub>2</sub> H <sub>6</sub>	O <sub>2</sub>		Fe/ZSM-5	Isomorphous substitution, ion exchange, steam activation	O <sub>2</sub> /He, 450 °C, 1 h	60 000			N <sub>2</sub> O (1.5 mbar), C <sub>2</sub> H <sub>6</sub> (0.44 mbar), O <sub>2</sub> (20 mbar), He balance	332	107
C <sub>3</sub> H <sub>8</sub>	O <sub>2</sub>	H <sub>2</sub> O	Fe/ZSM-5	Solid state ion exchange	He, 500 °C	7500			1000 ppm N <sub>2</sub> O, 1000 ppm C <sub>3</sub> H <sub>8</sub> , 7% H <sub>2</sub> O, 4% O <sub>2</sub> , He balance	332	105
CH <sub>4</sub>	O <sub>2</sub>		Fe/ZSM-5	Isomorphous substitution, ion exchange, steam activation	O <sub>2</sub> /He, 450 °C, 1 h	60 000			N <sub>2</sub> O (1.5 mbar), CH <sub>4</sub> (0.93 mbar), O <sub>2</sub> (20 mbar), He balance	337	107
CH <sub>4</sub>	O <sub>2</sub>		Fe-ZSM-5	Ion exchange	O <sub>2</sub> , 500 °C, 1 h		9.9		950 ppm N <sub>2</sub> O, 500 ppm CH <sub>4</sub> , 10% O <sub>2</sub> , He balance	338–470	104
CH <sub>4</sub>			Fe-USY	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 2000 ppm CH <sub>4</sub> , He balance	344	72
<i>n</i> -C <sub>10</sub> H <sub>22</sub>	O <sub>2</sub>		Fe-BEA	Ion exchange	3% H <sub>2</sub> /Ar, 13 mL min <sup>-1</sup> , ramp from 80–700 °C at 10 °C min <sup>-1</sup>	35 000			0.2% N <sub>2</sub> O, 0.03% <i>n</i> -C <sub>10</sub> H <sub>22</sub> , 3% O <sub>2</sub> , He balance	346–377	67
C <sub>2</sub> H <sub>6</sub>	O <sub>2</sub>	NO	Fe/ZSM-5	Isomorphous substitution, ion exchange, steam activation	O <sub>2</sub> /He, 450 °C, 1 h	60 000			N <sub>2</sub> O (1.5 mbar), C <sub>2</sub> H <sub>6</sub> (0.44 mbar), NO (0.13 mbar), O <sub>2</sub> (20 mbar), He balance	347	107
CH <sub>4</sub>		O <sub>2</sub> , H <sub>2</sub> O	Pd-Fe/ZSM-5	Ion exchange, incipient wetness impregnation	N <sub>2</sub> , 175 °C, 2 h	20 000			4500 ppm CH <sub>4</sub> , 1500 ppm N <sub>2</sub> O, 100 ppm NO, 100 ppm NO <sub>2</sub> , 0.5% H <sub>2</sub> O, 2.5% O <sub>2</sub> , N <sub>2</sub> balance	351	106
CH <sub>4</sub>		O <sub>2</sub>	Fe-USY	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 2000 ppm CH <sub>4</sub> , 50 000 ppm O <sub>2</sub> , He balance	352	72
C <sub>3</sub> H <sub>8</sub>	O <sub>2</sub>		Fe/ZSM-5	Isomorphous substitution, ion exchange, steam activation	N <sub>2</sub> O/C <sub>3</sub> H <sub>8</sub> /O <sub>2</sub> /He, 450 °C, 1 h		11.3		N <sub>2</sub> O (1.5 mbar), C <sub>3</sub> H <sub>8</sub> (1.5 mbar), He balance	357	68



Table 2 (continued)

Reductants	Other reactants <sup>a</sup>	Inhibitors <sup>b</sup>	Catalyst	Catalyst synthesis	Catalyst pretreatment	GHSV (h <sup>-1</sup> )	WHSV (h <sup>-1</sup> )	W/F (g s mL <sup>-1</sup> )	Feed composition	T <sub>50</sub> (°C)	Ref.
C <sub>3</sub> H <sub>8</sub>	O <sub>2</sub>	NO	Fe/ZSM-5	Solid state ion exchange	He, 500 °C	7500			1000 ppm N <sub>2</sub> O, 1000 ppm C <sub>3</sub> H <sub>8</sub> , 1000 ppm NO, 4% O <sub>2</sub> , He balance	357	105
C <sub>3</sub> H <sub>8</sub>	O <sub>2</sub>		Fe/ZSM-5	Isomorphous substitution, ion exchange, steam activation	N <sub>2</sub> O/C <sub>3</sub> H <sub>8</sub> /O <sub>2</sub> /He, 450 °C, 1 h	60 000			N <sub>2</sub> O (1.5 mbar), O <sub>2</sub> (50 mbar), C <sub>3</sub> H <sub>8</sub> (1.5 mbar), He balance	357	108
C <sub>3</sub> H <sub>6</sub>	O <sub>2</sub>		Fe-BEA	Ion exchange	3% H <sub>2</sub> /Ar, 13 mL min <sup>-1</sup> , ramp from 80–700 °C at 10 °C	35 000			0.2% N <sub>2</sub> O, 0.1% C <sub>3</sub> H <sub>6</sub> , 3% O <sub>2</sub> , He balance	369–392	67
C <sub>3</sub> H <sub>8</sub>	O <sub>2</sub>	NO	Fe/ZSM-5	Isomorphous substitution, ion exchange, steam activation	N <sub>2</sub> O/C <sub>3</sub> H <sub>8</sub> /O <sub>2</sub> /NO/He, 450 °C, 1 h	60 000			N <sub>2</sub> O (1.5 mbar), O <sub>2</sub> (50 mbar), C <sub>3</sub> H <sub>8</sub> (1.5 mbar), NO (4.5 mbar), He balance	384	108
CH <sub>4</sub>		H <sub>2</sub> O	Fe-USY	Ion exchange	He, 600 °C, 1 h	30 000			GHSV = 30 000 h <sup>-1</sup> , 5000 ppm N <sub>2</sub> O, 2000 ppm CH <sub>4</sub> , 700 ppm NO, He balance	385	72
C <sub>2</sub> H <sub>6</sub>	O <sub>2</sub>	NH <sub>3</sub>	Fe/ZSM-5	Isomorphous substitution, ion exchange, steam activation	O <sub>2</sub> /He, 450 °C, 1 h	60 000			N <sub>2</sub> O (1.5 mbar), C <sub>2</sub> H <sub>6</sub> (0.44 mbar), NH <sub>3</sub> (1.1 mbar of NH <sub>3</sub> ), O <sub>2</sub> (20 mbar), He balance	388	107
CH <sub>4</sub>		NO	Fe-USY	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 2000 ppm CH <sub>4</sub> , 700 ppm NO, He balance	396	72
CH <sub>4</sub>	O <sub>2</sub>	NH <sub>3</sub>	Fe/ZSM-5	Isomorphous substitution, ion exchange, steam activation	O <sub>2</sub> /He, 450 °C, 1 h	60 000			N <sub>2</sub> O (1.5 mbar), CH <sub>4</sub> (0.93 mbar), NH <sub>3</sub> (1.1 mbar of NH <sub>3</sub> ), O <sub>2</sub> (20 mbar), He balance	397	107
CH <sub>4</sub>	O <sub>2</sub>	NO	Fe/ZSM-5	Isomorphous substitution, ion exchange, steam activation	O <sub>2</sub> /He, 450 °C, 1 h	60 000			N <sub>2</sub> O (1.5 mbar), CH <sub>4</sub> (0.93 mbar), NO (0.13 mbar), O <sub>2</sub> (20 mbar), He balance	421	107
NH <sub>3</sub>			RuO <sub>2</sub>	Bulk oxide	He, 400 °C, 1 h		5.5		N <sub>2</sub> O (1.5 mbar), NH <sub>3</sub> (1.5 mbar), He balance	256	56
NH <sub>3</sub>	O <sub>2</sub>		RuO <sub>2</sub>	Bulk oxide	He, 400 °C, 1 h		5.5		N <sub>2</sub> O (1.5 mbar), NH <sub>3</sub> (1.5 mbar), O <sub>2</sub> (1.5 mbar), He balance	345	56
NH <sub>3</sub>			Rh-FAU	Wet impregnation	Air, 500 °C	30 000			He balance	272	75
NH <sub>3</sub>	O <sub>2</sub>		Fe-BEA	Ion exchange	Air, 50 mL min <sup>-1</sup> , 550 °C, 2 h	50 000			0.2% N <sub>2</sub> O, 0.2% NH <sub>3</sub> , He balance	295	109
NH <sub>3</sub>	O <sub>2</sub>		Fe-ZSM-5	Ion exchange	He, 600 °C, 1 h	50 000			1000 ppm N <sub>2</sub> O, 1500 ppm NH <sub>3</sub> , 8% O <sub>2</sub> , Ar balance	310	109
NH <sub>3</sub>	O <sub>2</sub> , NO		Fe-FER	Ion exchange	Air, 50 mL min <sup>-1</sup> , 550 °C, 2 h	200			1000 ppm N <sub>2</sub> O, 1500 ppm NH <sub>3</sub> , 8% O <sub>2</sub> , Ar balance	327	64
NH <sub>3</sub>			Fe-MOR	Ion exchange	He, 600 °C, 1 h	30 000			0.1/0.15/3/0/0.25/96.5	367	73
NH <sub>3</sub>	O <sub>2</sub>		Fe-MOR	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 4000 ppm NH <sub>3</sub> , He balance	367	73
NH <sub>3</sub>	O <sub>2</sub>		Fe-MOR	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 4000 ppm NH <sub>3</sub> , 50 000 ppm O <sub>2</sub> , He balance	367	73
NH <sub>3</sub>	O <sub>2</sub>		Fe-MOR	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 4000 ppm NH <sub>3</sub> , 50 000 ppm O <sub>2</sub> , He balance	367	74
NH <sub>3</sub>	O <sub>2</sub>		Fe-FAU	Ion exchange	He, 600 °C, 1 h	50 000			1000 ppm N <sub>2</sub> O, 1500 ppm NH <sub>3</sub> , He balance	370	109



Table 2 (continued)

Reductants	Other reactants <sup>a</sup>	Inhibitors <sup>b</sup>	Catalyst	Catalyst synthesis	Catalyst pretreatment	GHSV (h <sup>-1</sup> )	WHSV (h <sup>-1</sup> )	W/F (g s mL <sup>-1</sup> )	Feed composition	T <sub>50</sub> (°C)	Ref.
NH <sub>3</sub>			Fe-MOR	Ion exchange	He, 600 °C, 1 h	30 000			8% O <sub>2</sub> , Ar balance		
NH <sub>3</sub>	O <sub>2</sub>		Fe-BEA	Ion exchange	3% H <sub>2</sub> /Ar, 13 mL min <sup>-1</sup> , ramp from 80–700 °C at 10 °C min <sup>-1</sup>	35 000			5000 ppm N <sub>2</sub> O, 4000 ppm NH <sub>3</sub> , He balance	374	74
NH <sub>3</sub>	H <sub>2</sub> O		Fe-BEA	Ion exchange	O <sub>2</sub> /N <sub>2</sub> , 500 °C, 1 h	200 000			540 ppm N <sub>2</sub> O, 360 ppm NH <sub>3</sub> , 2.5% H <sub>2</sub> O, N <sub>2</sub> balance	389	24
NH <sub>3</sub>			Fe-BEA	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 4000 ppm NH <sub>3</sub> , He balance	397	73
NH <sub>3</sub>	O <sub>2</sub>		Fe-ZSM-5	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 4000 ppm NH <sub>3</sub> , 50 000 ppm O <sub>2</sub> , He balance	397	73
NH <sub>3</sub>	O <sub>2</sub>		Fe-ZSM-35	Ion exchange		50 000			1000 ppm N <sub>2</sub> O, 1500 ppm NH <sub>3</sub> , 8% O <sub>2</sub> , Ar balance	400	109
NH <sub>3</sub>			Fe-USY	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 4000 ppm NH <sub>3</sub> , He balance	402	72
NH <sub>3</sub>			Fe-USY	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 4000 ppm NH <sub>3</sub> , He balance	407	73
NH <sub>3</sub>	O <sub>2</sub>		Fe-BEA	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 4000 ppm NH <sub>3</sub> , 50 000 ppm O <sub>2</sub> , He balance	407	73
NH <sub>3</sub>			Fe-ZSM-5	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 4000 ppm NH <sub>3</sub> , He balance	417	73
NH <sub>3</sub>	O <sub>2</sub>		Fe-FER	Ion exchange	Air, 50 mL min <sup>-1</sup> , 550 °C, 2 h	35 000			N <sub>2</sub> O/O <sub>2</sub> /NH <sub>3</sub> /He = 0.2/3.0/0.2/96.6	417	64
NH <sub>3</sub>	H <sub>2</sub> O	O <sub>2</sub>	Fe-BEA	Ion exchange	O <sub>2</sub> /N <sub>2</sub> , 500 °C, 1 h	200 000			540 ppm N <sub>2</sub> O, 360 ppm NH <sub>3</sub> , 2.5% H <sub>2</sub> O, 14% O <sub>2</sub> , N <sub>2</sub> balance	426	24
NH <sub>3</sub>	H <sub>2</sub> O		Fe-SSZ-13	Ion exchange	O <sub>2</sub> /N <sub>2</sub> , 500 °C, 1 h	200 000			540 ppm N <sub>2</sub> O, 360 ppm NH <sub>3</sub> , 2.5% H <sub>2</sub> O, N <sub>2</sub> balance	429	24
NH <sub>3</sub>		O <sub>2</sub>	Fe-USY	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 4000 ppm NH <sub>3</sub> , 50 000 ppm O <sub>2</sub> , He balance	430	72
NH <sub>3</sub>	O <sub>2</sub>		Fe-MCM-22	Ion exchange		50 000			1000 ppm N <sub>2</sub> O, 1500 ppm NH <sub>3</sub> , 8% O <sub>2</sub> , Ar balance	435	109
NH <sub>3</sub>	O <sub>2</sub>		Fe-USY	Ion exchange	He, 600 °C, 1 h	30 000			5000 ppm N <sub>2</sub> O, 4000 ppm NH <sub>3</sub> , 50 000 ppm O <sub>2</sub> , He balance	437	73
NH <sub>3</sub>	O <sub>2</sub>		Fe-SSZ-13	Ion exchange		50 000			1000 ppm N <sub>2</sub> O, 1500 ppm NH <sub>3</sub> , 8% O <sub>2</sub> , Ar balance	450	109
NH <sub>3</sub>	H <sub>2</sub> O	O <sub>2</sub>	Fe-SSZ-13	Ion exchange	O <sub>2</sub> /N <sub>2</sub> , 500 °C, 1 h	200 000			540 ppm N <sub>2</sub> O, 360 ppm NH <sub>3</sub> , 2.5% H <sub>2</sub> O, 14% O <sub>2</sub> , N <sub>2</sub> balance	455	24
NH <sub>3</sub>		O <sub>2</sub>	Rh-FAU	Wet impregnation	Air, 500 °C	30 000			0.2% N <sub>2</sub> O, 0.2% NH <sub>3</sub> , 3% O <sub>2</sub> , He balance	487	75
H <sub>2</sub>			Ni-Pt/SiO <sub>2</sub>	Incipient wetness impregnation	H <sub>2</sub> , 400 °C, 1 h	25 000			1250 ppm N <sub>2</sub> O, 1250 ppm H <sub>2</sub> , He balance	27–62	41
H <sub>2</sub>			Pt/SiO <sub>2</sub>	Incipient wetness impregnation	H <sub>2</sub> , 400 °C, 1 h	25 000			1250 ppm N <sub>2</sub> O, 1250 ppm H <sub>2</sub> , He balance	122	41
H <sub>2</sub>			Ni/SiO <sub>2</sub>	Incipient wetness impregnation	H <sub>2</sub> , 400 °C, 1 h	25 000			1250 ppm N <sub>2</sub> O, 1250 ppm H <sub>2</sub> , He balance	527	41



Table 2 (continued)

Reductants	Other reactants <sup>a</sup>	Inhibitors <sup>b</sup>	Catalyst	Catalyst synthesis	Catalyst pretreatment	GHSV (h <sup>-1</sup> )	WHSV (h <sup>-1</sup> )	W/F (g s mL <sup>-1</sup> )	Feed composition	T <sub>50</sub> (°C)	Ref.
H <sub>2</sub>			Ti <sub>0.99</sub> Pd <sub>0.01</sub> O <sub>2-δ</sub>	Solution combustion		43 000			N <sub>2</sub> O:H <sub>2</sub> = 1:3 vol%, He balance	52	110
H <sub>2</sub>			Ti <sub>0.99</sub> Rh <sub>0.01</sub> O <sub>2-δ</sub>	Solution combustion		43 000			N <sub>2</sub> O:H <sub>2</sub> = 1:3 vol%, He balance	93	110
H <sub>2</sub>			Ti <sub>0.99</sub> Pt <sub>0.01</sub> O <sub>2-δ</sub>	Solution combustion		43 000			N <sub>2</sub> O:H <sub>2</sub> = 1:3 vol%, He balance	107	110
H <sub>2</sub>			Ti <sub>0.99</sub> Ru <sub>0.01</sub> O <sub>2-δ</sub>	Solution combustion		43 000			N <sub>2</sub> O:H <sub>2</sub> = 1:3 vol%, He balance	129	110
H <sub>2</sub>			RuO <sub>2</sub>	Bulk oxide	He, 400 °C, 1 h		5.5		N <sub>2</sub> O (1.5 mbar), H <sub>2</sub> (1.5 mbar), He balance	216	56
H <sub>2</sub>			RuO <sub>2</sub>	Bulk oxide	H <sub>2</sub> /He, 400 °C, 1 h		5.5		N <sub>2</sub> O (1.5 mbar), H <sub>2</sub> (1.5 mbar), He balance	305	56
H <sub>2</sub>	O <sub>2</sub>		RuO <sub>2</sub>	Bulk oxide	He, 400 °C, 1 h		5.5		N <sub>2</sub> O (1.5 mbar), H <sub>2</sub> (1.5 mbar), O <sub>2</sub> (1.5 mbar), He balance	345	56
H <sub>2</sub>	O <sub>2</sub>		Fe-BEA	Ion exchange	3% H <sub>2</sub> /Ar, 13 mL min <sup>-1</sup> , ramp from 80–700 °C at 10 °C min <sup>-1</sup>	35 000			0.2% N <sub>2</sub> O, 0.2% H <sub>2</sub> , 3% O <sub>2</sub>	497–504	67

<sup>a</sup> Other reactants – present in the feed but do not inhibit N<sub>2</sub>O conversion. <sup>b</sup> Inhibitors – present in the feed and inhibit N<sub>2</sub>O conversion.

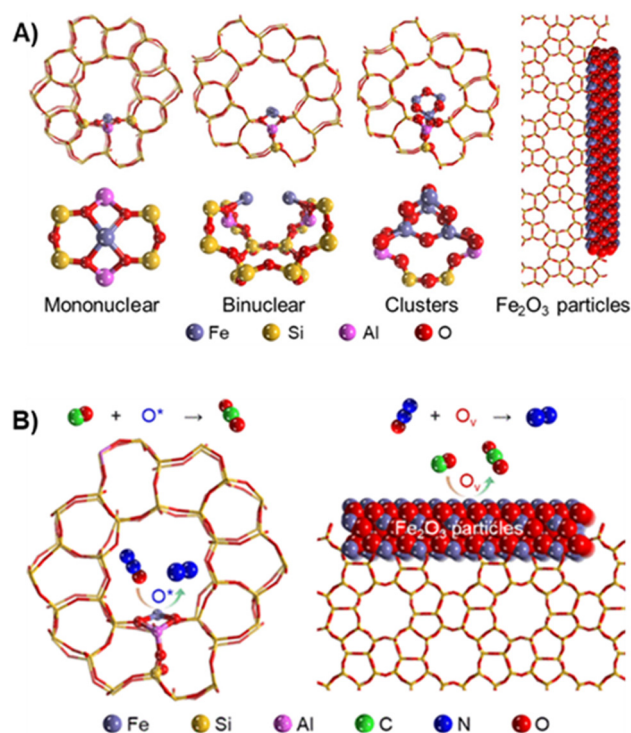


Fig. 7 (A) Schematic illustration of the different iron species in Fe/ZSM-5. (B) Proposed mechanisms of the SCR of N<sub>2</sub>O by CO on isolated iron sites and Fe<sub>2</sub>O<sub>3</sub> particles. Reprinted from ref. 111 with permission from the American Chemical Society.

kinetics in the CO-SCR of N<sub>2</sub>O over Fe-FER by combining modulation excitation with *operando* electron paramagnetic resonance (EPR) spectroscopy.<sup>114</sup> They found that isolated Fe<sup>II</sup> species in β-cationic positions are the only active sites during the reaction by enabling reversible Fe<sup>II</sup>/Fe<sup>III</sup> cycles, while isolated Fe<sup>II</sup> sites in γ-cationic positions and oligomeric Fe species are spectator species.

Single atom catalysts have attracted increasing attention in recent years due to their superior catalytic performance and efficient atomic utilization. Khan *et al.* examined the reduction of N<sub>2</sub>O in the presence of CO over metal-free Si-coordinated phthalocyanine catalyst by DFT calculations.<sup>115</sup> They found that the Si atom is energetically stabilized on the phthalocyanine support and can act as the active site for the N<sub>2</sub>O dissociation. In another study, Ragab *et al.* employed DFT method to investigate aluminum-decorated C<sub>24</sub>N<sub>24</sub> fullerene catalyst for the N<sub>2</sub>O reduction in the presence of CO and O<sub>2</sub>.<sup>116</sup> This single-atom catalyst exhibited a relatively low energy barrier and strong N<sub>2</sub>O binding, minimizing the potential inhibition by CO and O<sub>2</sub> due to the competitive adsorption.

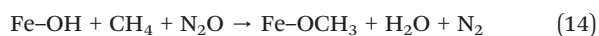
The presence of other gas molecules in the feed such as NO, oxygen, and water, which are commonly found in the nitric acid production tail gas, can affect the CO-SCR of N<sub>2</sub>O over Fe-zeolites. This is clearly shown by the shift of T<sub>50</sub> values with adding impurity gases to the feed stream on the same catalyst system (Table 2). N<sub>2</sub>O decomposition can be assisted by addition of NO to facilitate oxygen desorption *via*

adsorbed  $\text{NO}_2^-$  intermediates over oligo-nuclear iron species, however, CO-SCR of  $\text{N}_2\text{O}$  was inhibited by strong adsorption of NO on isolated iron sites in Fe-ZSM-5, especially at the low temperature regime.<sup>70</sup> This inhibitory effect of NO on CO-SCR of  $\text{N}_2\text{O}$  becomes less significant at high temperatures due to weaker adsorption of NO on iron active sites. Conversely, Wu *et al.* found that the addition of oxygen in the reactant feed showed an inhibitory effect on CO-SCR of  $\text{N}_2\text{O}$  over Fe-ZSM-5, which is attributed to the reaction between CO and  $\text{O}_2$ .<sup>111</sup> The presence of water exhibited a more negative effect than oxygen for this system.

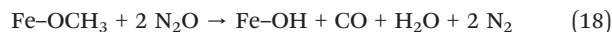
While iron supported on zeolites are the most common catalysts for CO-SCR of  $\text{N}_2\text{O}$ , a few studies were conducted on noble metals (*i.e.*, Pt/ $\text{Al}_2\text{O}_3$ , Pd/ $\text{Al}_2\text{O}_3$ , or Rh/ $\text{Al}_2\text{O}_3$ ) and mixed oxides (*i.e.*, Co-Rh-Al-O, Co-Pd-Al-O, or Co-Pd-Ce-Al-O).<sup>60,61,117–119</sup> Konsolakis *et al.* investigated rare earth oxide-modified Pt/ $\text{Al}_2\text{O}_3$ - $\text{CeO}_2$  and Pt/ $\text{Al}_2\text{O}_3$ - $\text{CeO}_2$ - $\text{La}_2\text{O}_3$  structured catalysts (*i.e.* coated on ceramic honeycomb monoliths) in the absence and presence of excess oxygen and water.<sup>117</sup> Like the Fe-zeolites, reducing agents such as CO significantly improve  $\text{N}_2\text{O}$  conversion by aiding in the removal of strongly adsorbed oxygen species. In addition, oxygen and water have a detrimental effect on  $\text{N}_2\text{O}$  conversion, which were attributed to competitive adsorption and irreversible changes in platinum oxidation state. In another study on the role of rare-earth oxides promoters, Holles *et al.* found that ceria improves CO-SCR of  $\text{N}_2\text{O}$  on Pd/ $\text{Al}_2\text{O}_3$  and Rh/ $\text{Al}_2\text{O}_3$  due to additional storage sites for dissociated oxygen atoms and high reducibility, while  $\text{La}_2\text{O}_3$  hinders the reaction due to lower metal dispersion.<sup>119</sup> The positive effect of adding CO as a reductant on the conversion of  $\text{N}_2\text{O}$  was reported for reactions over metal oxides (Co-Rh-Al, Co-Pd-Al, Co-Pd-Ce-Al) prepared by co-precipitation of hydrotalcite-type precursors.<sup>59–61</sup> They found that the presence of oxygen inhibits  $\text{N}_2\text{O}$  conversion over metal oxides, and NO showed an insignificant influence.

### 3.2 Hydrocarbons (HC-SCR)

The presence of hydrocarbons in the SCR of  $\text{N}_2\text{O}$  over iron zeolites has been studied extensively in literature and applied in commercial  $\text{NO}_x$ - $\text{N}_2\text{O}$  abatement processes.<sup>107</sup> Hydrocarbons are selective reductants and effective for the reduction of  $\text{N}_2\text{O}$  over Fe-BEA catalysts.<sup>67</sup> The reaction mechanism of  $\text{N}_2\text{O}$  reduction by  $\text{C}_3\text{H}_6$  over noble metals supported on alumina and by  $\text{C}_3\text{H}_8$  over Fe-zeolites was proposed to be related to the removal of adsorbed atomic oxygen species by these hydrocarbons to form CO and  $\text{CO}_2$ .<sup>39,108</sup> Deeper investigations on  $\text{CH}_4$ -SCR reaction mechanism combining infrared spectroscopy and catalytic reaction tests over Fe-ZSM-5 and Fe-BEA indicated an interaction of methane and  $\text{N}_2\text{O}$  molecules on iron hydroxyl groups with the sequential oxidation to methoxy and formate intermediate species (eqn (14)–(17)).<sup>72,120,121</sup>



A minor amount of CO detected in product streams may indicate the presence of an additional pathway with incomplete oxidation of  $\text{CH}_4$  (eqn (14), (18) and (19)).<sup>72,120,121</sup>



Hevia *et al.* studied light hydrocarbons ( $\text{C}_1$ - $\text{C}_3$ ) with different degrees of unsaturation and proposed a set of criteria to optimally select hydrocarbons for SCR of  $\text{N}_2\text{O}$  over Fe-ZSM-5 zeolites, including  $\text{N}_2\text{O}$  reduction activity and operation temperature, hydrocarbon utilization or the selectivity to react with  $\text{N}_2\text{O}$  in  $\text{O}_2$  excess, CO and  $\text{CO}_2$  formation, sensitivity to NO and  $\text{NH}_3$ , and cost.<sup>107</sup> It was found that ethane and methane are the most effective reductants, while alkenes and alkynes require a higher temperature to consume  $\text{O}^*$  and are less effective due to undesired non-selective reaction with oxygen. Nobukawa *et al.* similarly investigated the SCR of  $\text{N}_2\text{O}$  on Fe-ZSM-5 and found that methane is a more efficient reductant compared to higher alkanes (ethane and propane), hydrogen, and CO.<sup>104</sup>  $\text{H}_2$ -TPR and extended X-ray absorption fine structure analyses were performed to show that the high  $\text{N}_2\text{O}$  reduction activity at high Fe/Al ratio in Fe-ZSM-5 catalysts is likely due to the presence of binuclear iron species. In addition, the redox cycle of these active iron sites is promoted by the formation of methoxy species, which originated from the interaction of methane with  $\text{N}_2\text{O}$ -derived adsorbed oxygen. Conversely, Van den Brink *et al.* reported that propane is more active than methane in the SCR of  $\text{N}_2\text{O}$  over palladium-promoted Fe-ZSM-5 in the same temperature range of 200–500 °C.<sup>106</sup> The presence of water in the feed stream was found to be detrimental to the catalytic performance of  $\text{N}_2\text{O}$  reduction by propane over Fe-ZSM-5 catalysts.<sup>105,106</sup> A more significant inhibitory effect of NO on the reduction of  $\text{N}_2\text{O}$  by hydrocarbons was observed over different iron zeolite frameworks (Fe-ZSM-5, Fe-BEA, Fe-USY), which was ascribed to the competitive adsorption for iron active sites.<sup>72,105,108</sup> In addition to water and NO, oxygen also exhibited an adverse effect on the HC-SCR of  $\text{N}_2\text{O}$ , which was mainly attributed to competitive adsorption and non-selective oxidation of hydrocarbon intermediates to form CO.<sup>72</sup> As a result, they proposed that  $\text{N}_2\text{O}$  conversion in a mixed  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , NO stream can be a combination of three pathways:  $\text{CH}_4$ -SCR, CO-SCR, and NO-assisted direct decomposition.

Regarding the catalytic iron species, Pérez-Ramírez *et al.* proposed that isolated extra-framework iron sites play an important role in the reduction of  $\text{N}_2\text{O}$  by propane,<sup>108</sup> which was further verified by comparing steam-activated



samples of Fe-silicalite and Fe-ZSM-5.<sup>68</sup> By employing UV-vis diffuse reflectance spectroscopy (DRS), it was revealed that isolated iron species dominate, steam-activated Fe/silicalite gave higher activity over the steam-activated Fe/ZSM-5 containing iron clustered species. However, the presence of iron clusters may be beneficial for the direct N<sub>2</sub>O decomposition, as oxygen recombination is the rate limiting step. In addition, this comparison of Fe-silicalite and Fe-ZSM-5 implies a minor role of acid sites in the hydrocarbon-assisted reduction of N<sub>2</sub>O. Another study by Debbagh *et al.* reported that the reduction of N<sub>2</sub>O by methane and CO over Fe-ZSM-5 follows different reaction mechanisms over different iron sites.<sup>71</sup> Specifically, while CO is active over isolated iron species, the reduction of N<sub>2</sub>O by hydrocarbons such as CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> happens more favorably over oligo-nuclear iron-oxo clusters.

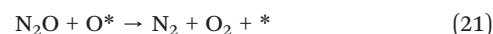
Recently, *in situ* characterization and *operando* studies have provided insights into the active sites and reaction mechanism of the CH<sub>4</sub>-SCR of N<sub>2</sub>O over zeolite-based catalysts.<sup>122–125</sup> Campa *et al.* investigated N<sub>2</sub>O reduction with CH<sub>4</sub> on metal-free H-NaMOR catalysts in the absence and presence of oxygen using *in situ* and *operando* FTIR methods.<sup>122</sup> It was suggested that N<sub>2</sub>O and CH<sub>4</sub> are synergistically activated on dehydrated Si–OH–Al pairs as main active sites. In addition, formaldehyde-like species are possible reaction intermediates during the CH<sub>4</sub>-SCR of N<sub>2</sub>O. This observation is consistent with the other studies on Fe-MOR, Fe-FER, Co-MOR, and Ni-MOR catalysts that employed *in situ* UV-vis DRS and *operando* FTIR experiments.<sup>123,125</sup> The catalytic performance of Fe-MOR and Fe-FER catalysts were attributed to the stabilization of Fe<sup>II</sup> species and bifunctional active sites, which consist of Fe<sup>III</sup>-oxo species and nearby reactive OH species, in these zeolite frameworks.<sup>123</sup> In another study on CH<sub>4</sub>-SCR of N<sub>2</sub>O on Fe-BEA with *operando* IR and *in situ* XAFS-DRIFTS, Liu *et al.* found that both NO and NH<sub>3</sub> inhibit the reduction of N<sub>2</sub>O due to their strong adsorption on Fe<sup>II</sup> active sites and rapid reaction with Fe<sup>III</sup>-OH and  $\alpha$ -oxygens.<sup>124</sup>

In addition to Fe-zeolites, Rh/Al<sub>2</sub>O<sub>3</sub>, Ru/Al<sub>2</sub>O<sub>3</sub>, and Pd/Al<sub>2</sub>O<sub>3</sub> have been studied for the HC-SCR of N<sub>2</sub>O.<sup>39,40</sup> Christoforou *et al.* investigated Rh, Ru, Pd, Co, Cu, Fe, and In with various catalyst supports (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, calcined hydrotalcite MgAl<sub>2</sub>(OH)<sub>8</sub>·H<sub>2</sub>O) and found that Rh/Al<sub>2</sub>O<sub>3</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> are the most active catalysts for HC-SCR of N<sub>2</sub>O in the presence of excess O<sub>2</sub>.<sup>39</sup> However, propene was found to facilitate N<sub>2</sub>O reduction over Rh/Al<sub>2</sub>O<sub>3</sub> by scavenging N<sub>2</sub>O-derived O, helping maintain catalytically available Rh sites. Propene was found to potentially alter the redox state of active metal sites, lowering and inhibiting catalytic performance on Ru/Al<sub>2</sub>O<sub>3</sub> as it reduces Ru<sup>3+</sup>/Ru<sup>4+</sup> sites that are active for N<sub>2</sub>O decomposition. The presence of oxygen in the feed stream also hinders N<sub>2</sub>O reduction over Rh/Al<sub>2</sub>O<sub>3</sub> but alleviates the inhibition of propene over Ru/Al<sub>2</sub>O<sub>3</sub>, as O<sub>2</sub> oxidizes propene into CO and CO<sub>2</sub>. Water was suggested to inhibit C<sub>3</sub>H<sub>6</sub>-SCR of N<sub>2</sub>O in the presence of O<sub>2</sub> by competitive adsorption with N<sub>2</sub>O and potentially the

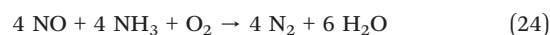
formation of Ru oxyhydroxides that alter electronic structure of active RuO<sub>2</sub> active sites. On the contrary, the presence of SO<sub>2</sub> impedes N<sub>2</sub>O reduction by the formation of sulfate species, consistent with the findings of Konsolakis *et al.* for CH<sub>4</sub>-SCR of N<sub>2</sub>O over Pd/Al<sub>2</sub>O<sub>3</sub>.<sup>40</sup> It was noted that water effects were reversible, whereas SO<sub>2</sub> deactivation was irreversible.

### 3.3 Ammonia (NH<sub>3</sub>-SCR)

Ammonia is another potential reductant for the SCR of N<sub>2</sub>O over different catalysts such as metal-zeolites and metal oxides.<sup>56,67,126–128</sup> Mauvezin *et al.* evaluated the decomposition and reduction of N<sub>2</sub>O by ammonia over several metals supported on FAU zeolite, including Rh, Ru, Pd, Co, Cu, Ni, and Fe.<sup>75</sup> It appeared that Fe-FAU was the most efficient catalyst for NH<sub>3</sub>-SCR of N<sub>2</sub>O in the presence of oxygen. In terms of reaction mechanism of NH<sub>3</sub>-SCR of N<sub>2</sub>O over Fe-zeolites, it was suggested that the addition of ammonia assists the decomposition of N<sub>2</sub>O by removing the surface oxygen species (eqn (23) of eqn (20)–(23)).<sup>64</sup>



Zhang *et al.* proposed a more detailed reaction pathway and mechanism of NH<sub>3</sub>-SCR of N<sub>2</sub>O over Fe-MOR and Fe-BEA catalysts related to the redox cycle of Fe<sup>3+</sup>-OH/Fe<sup>2+</sup>-OH sites through –NH<sub>2</sub> and NO intermediates.<sup>74</sup> Multiple temperature programmed experimental techniques and FT-IR of N<sub>2</sub>O/NH<sub>3</sub> interaction were employed. It was found that the rate-limiting step over Fe-MOR is reduction of Fe<sup>3+</sup>-OH by ammonia into Fe<sup>2+</sup>-OH and N≡N bond breaking was the main N<sub>2</sub>O splitting mechanism. Similarly, N<sub>2</sub>O oxidation of Fe<sup>2+</sup>-OH was the rate-determining step for Fe-BEA with N–O bond breaking being the main N<sub>2</sub>O splitting mechanism. The next reaction steps of nitric oxide in the presence of oxygen follow the typical SCR mechanism to form nitrogen and water (eqn (24)).



The high activity of Fe-MOR was ascribed to the pore structure of MOR zeolites and the high iron loading, which enable the genesis of proximal Fe<sup>3+</sup> ions or Fe<sup>3+</sup>···Fe<sup>3+</sup> pairs as the active sites for the N≡NO splitting.

The zeolite structure strongly influences the distribution of iron species, which plays an important role in catalytic activity of Fe-zeolites for the N<sub>2</sub>O decomposition and reduction by ammonia.<sup>64</sup> Wang *et al.* studied the nature of iron species by UV-vis, Mössbauer, and EPR spectroscopies, as well as H<sub>2</sub>-TPR, and kinetic measurements.<sup>24</sup> It was found



that isolated and binuclear Fe sites are present in Fe/SSZ-13, whereas Fe/BEA contains mostly oligomeric  $\text{Fe}_x\text{O}_y$  species and exhibited a higher  $\text{NH}_3$ -SCR activity compared to Fe/SSZ-13. This indicates that larger site ensembles, such as oligo-nuclear iron-oxo clusters, are the main active sites of the  $\text{NH}_3$ -SCR of  $\text{N}_2\text{O}$  instead of isolated iron species. A similar finding about the catalytic effect of zeolite structure on Fe-zeolites has been reported by Du *et al.*<sup>109</sup> The  $\text{NH}_3$ -SCR of  $\text{N}_2\text{O}$  activity followed the order: Fe-BEA > Fe-ZSM-5 > Fe-FAU > Fe-ZSM-35 > Fe-MCM-22 > Fe-SSZ-13. UV-vis DRS, XPS, and  $\text{H}_2$ -TPR analyses verified that  $\text{Fe}^{3+}$  sites are more favorably located inside straight-channel zeolite pores compared to cage-type zeolites, leading to the high activity observed in Fe-BEA and Fe-ZSM-5. In addition, Fe-zeolites with larger pore sizes facilitate the internal diffusion of  $\text{N}_2\text{O}$  inside zeolite channels, thereby improving the catalytic reduction of  $\text{N}_2\text{O}$  by ammonia. Zhang *et al.* performed  $\text{H}_2$ -TPR, UV-vis DRS, and  $\text{NH}_3/\text{O}_2$ -TPD to analyze the nature and distribution of iron species, including isolated  $\text{Fe}^{3+}$ , oligo-nuclear  $\text{Fe}_x^{3+}\text{O}_y$  clusters, and  $\text{Fe}_2\text{O}_3$  nanoparticles on external surface.<sup>73</sup> It was also determined that larger zeolite channels contain more exchanged Fe ions, which explains higher Fe loadings in Fe-MOR and Fe-USY compared to Fe-BEA and Fe-ZSM-5. Interestingly, it was suggested that isolated  $\text{Fe}^{3+}$  ions are active species for the reduction of  $\text{N}_2\text{O}$ , while the  $\text{Fe}_x^{3+}\text{O}_y$  clusters are less active due to strong ammonia adsorption on Brønsted acid sites formed on the bridge oxide ions in binuclear iron species. On the other hand, *operando* electron paramagnetic resonance measurements were performed by Fischer *et al.* to elucidate the active sites and kinetically relevant reaction steps during  $\text{N}_2\text{O}$  decomposition and reduction over Fe-SSZ-13 with different reductants, including  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2$ .<sup>129</sup> They found that isolated  $\text{Fe}^{2+}$  species in axial coordination are the main active sites for direct  $\text{N}_2\text{O}$  decomposition, while  $\text{Fe}_x\text{O}_y$  clusters and  $\text{Fe}^{2+}$  sites in distorted geometries are responsible for  $\text{N}_2\text{O}$  reduction in the presence of reductants.

Regarding the effect of other gases in the feed, it was reported that oxygen showed an inhibitory effect on  $\text{NH}_3$ -SCR of  $\text{N}_2\text{O}$  over Fe-MFI, Fe-FAU, Fe-BEA, and Fe-SSZ-13, likely due to the non-selective oxidation of ammonia.<sup>24,75,127</sup> However, the presence of oxygen had no significant influence on  $\text{N}_2\text{O}$  conversion over Fe-MOR whereas  $\text{NH}_3$ -SCR of  $\text{N}_2\text{O}$  outperformed ammonia oxidation.<sup>73,74</sup> While the influence of NO on  $\text{N}_2\text{O}$  reduction by  $\text{NH}_3$  over Fe-MOR was negligible,<sup>73</sup> the reduction of  $\text{N}_2\text{O}$  by  $\text{NH}_3$  over Fe-FER and Fe-BEA was promoted by NO, due to the fast surface reaction between adsorbed  $\text{O}^*$  and  $\text{NO}^*$  species.<sup>64</sup> On the contrary, Zhuang *et al.* found that a small fraction of NO (100 ppm) in the feed stream can inhibit the  $\text{NH}_3$ -SCR of  $\text{N}_2\text{O}$  over Pd/ $\text{Al}_2\text{O}_3$  catalyst.<sup>130</sup> Interestingly, by modifying the  $\text{Al}_2\text{O}_3$  support to create oxygen vacancies containing free electrons, the Pd-based catalyst exhibited superior performance in the low temperature regime below 300 °C, along with desirable NO inhibition resistance. Baek *et al.* studied the effect of water on the  $\text{NH}_3$ -SCR of  $\text{N}_2\text{O}$  over Fe-BEA using DRIFTS and self-consistent-charge density-

functional-tight-binding calculations.<sup>131</sup> It was found that the presence of water vapor increases hydroxyl groups on the Fe-BEA surface. Instead of the conventional explanation, where the presence of water vapor leads to competitive adsorption, the authors attributed decreased  $\text{N}_2\text{O}$  conversion to surface hydroxyl groups that induce stronger adsorption of  $\text{N}_2\text{O}$ .

### 3.4 Hydrogen ( $\text{H}_2$ -SCR)

The research on  $\text{N}_2\text{O}$  reduction by hydrogen is limited (mainly reported with noble metal catalysts).<sup>41,110</sup> Hydrogen is not a selective reductant in the SCR of  $\text{N}_2\text{O}$  over Fe-BEA and  $\text{RuO}_2$  catalysts, as it favorably reacts with oxygen present in the reactant feed.<sup>56,67</sup> Santiago *et al.* employed a combination of steady-state reaction tests at ambient pressure, transient reaction studies in the temporal analysis of products (TAP) reactor (see section 4.1), and DFT simulations to unravel the mechanism of decomposition and reduction of  $\text{N}_2\text{O}$  by hydrogen or ammonia on  $\text{RuO}_2$ .<sup>56</sup> It was found that hydrogen facilitates the reduction of the catalyst surface to form highly active oxygen vacancies, and it appears to be a more effective reductant compared to ammonia in this catalytic system, as ammonia-derived intermediates strongly adsorb on  $\text{RuO}_2$  surface and block active sites for  $\text{N}_2\text{O}$  conversion. Arenas-Alatorre *et al.* studied  $\text{N}_2\text{O}$  decomposition and reduction by  $\text{H}_2$  over Pt/ $\text{SiO}_2$ , Ni/ $\text{SiO}_2$ , and NiPt/ $\text{SiO}_2$  catalysts, which showed much lower  $T_{50}$  values compared to other catalyst systems (Table 2).<sup>41</sup> It was found that the addition of  $\text{H}_2$  improves  $\text{N}_2\text{O}$  conversion over studied monometallic and bimetallic catalysts. Bimetallic (6–8 nm NiPt) catalysts exhibited a higher activity compared to Pt/ $\text{SiO}_2$  and Ni/ $\text{SiO}_2$  catalysts in the  $\text{H}_2$ -SCR of  $\text{N}_2\text{O}$ , which was ascribed to the geometric and electronic effects of alloying. Another study of  $\text{N}_2\text{O}$  reduction by  $\text{H}_2$  on noble metal substituted  $\text{TiO}_2$  catalysts ( $\text{Ti}_{0.99}\text{M}_{0.01}\text{O}_{2-\delta}$ , where M = Ru, Rh, Pd, Pt) also reported significantly low  $T_{50}$  values (Table 2), notably for Pd-substituted  $\text{TiO}_2$ . The authors attributed the high activity to a bi-functional pathway:  $\text{N}_2\text{O}$  dissociation at oxide-ion vacancies and rapid  $\text{H}_2$  activation on substituted metal ions that scavenge  $\text{O}^*$  to produce  $\text{H}_2\text{O}$ ; this mechanism was supported by  $\text{H}_2$ -TPR/uptake trends and kinetic modeling.<sup>110</sup> The reduction of  $\text{N}_2\text{O}$  by  $\text{H}_2$  was also studied on various polyoxometalate-supported single-atom catalysts  $\text{M}_1/\text{PTA}$  (M = Fe, Co, Mn, Ru, Rh, Os, Ir, and Pt; PTA =  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ) by DFT.<sup>132</sup>  $\text{Os}_1/\text{PTA}$  SAC exhibited high activity with a low rate-limiting energy barrier, which was attributed to a strong charge-transfer cooperative effect of metal and support along the favorable reaction pathways. The Os atom and PTA support acts as electron reservoirs, effectively modulating the adsorption/desorption and bond-breaking steps.

The comparison of different reductants for the SCR of  $\text{N}_2\text{O}$  is summarized in Table 3. The usage of CO and  $\text{NH}_3$  can be cost-effective when available as a byproduct gas in industrial plants or when coupled with existing SCR systems.



**Table 3** Comparison of different reductants for the SCR of N<sub>2</sub>O

Reductants	Common catalysts	Estimated cost (catalyst, reductant)	By-products	Potential application
CO	Fe-zeolites	Low	CO <sub>2</sub>	Power plant flue gas
CH <sub>4</sub>	Fe-zeolites	Low	CO, CO <sub>2</sub> , H <sub>2</sub> O	Nitric acid production tail gas
NH <sub>3</sub>	Fe-zeolites	Low	NO, N <sub>2</sub> , H <sub>2</sub> O	Ammonia-fueled engine exhaust
H <sub>2</sub>	Noble metals	High	H <sub>2</sub> O	Low-temperature constraints

Methane is a low-value hydrocarbon and the major component of the natural gas stream, enabling economical use in the SCR of N<sub>2</sub>O. On the other hand, the industrial application of hydrogen is still limited due to the high costs associated with hydrogen production, transportation, and storage.

### 3.5 Catalyst durability and exotic reductants for SCR

The research on the catalyst durability in the selective catalytic reduction of N<sub>2</sub>O remains limited. Zhang *et al.* reported that the catalytic activity of Fe-MOR for NH<sub>3</sub>-SCR of N<sub>2</sub>O remains almost unchanged for more than 100 hours under simulated nitric acid plant conditions at 427 °C with the presence of oxygen and water vapor in the feed stream.<sup>133</sup> It is worth noting that Fe-zeolites, which are the most common catalyst for the SCR of nitrous oxide, have also been studied extensively for the NH<sub>3</sub>-SCR of nitric oxide, particularly in relation to treatment processes of exhaust gases from diesel engines, coal-fired plants, and industrial boilers.<sup>134</sup> The catalyst durability of Fe-zeolites in the NH<sub>3</sub>-SCR of NO is significantly affected by sulfur and phosphorus poisoning, as well as their hydrothermal stability at elevated temperatures, which constrains their practical applications.<sup>135</sup>

In SCR reactors, other more exotic reductants may also play a key role in future N<sub>2</sub>O abatement technologies. In addition to the CO, hydrocarbons, NH<sub>3</sub>, and H<sub>2</sub> methods discussed previously, other reducing agents can be considered and new technologies envisioned. Expanding on carbonaceous reductants like CO and hydrocarbons, solid carbon species like coke, charcoal, and biochar could also be used. Wang *et al.* investigated the reduction of N<sub>2</sub>O by biomass char with the presence of CO and O<sub>2</sub> in a fixed bed reactor system.<sup>136</sup> While biomass char and CO facilitated the reduction of N<sub>2</sub>O by lowering both the onset temperature and the apparent activation energy, an inhibitory effect was observed with O<sub>2</sub>. The solid carbon materials could also play a role as a catalytic surface as was observed by Xie *et al.*, who studied activated coke catalysts for SCR of NO.<sup>137</sup> Similarly, Wang *et al.* looked at the effect of cost effective and high surface area activated carbon at 200–300 °C in a 1000 ppm NO in N<sub>2</sub> gas stream.<sup>138</sup> They saw detection of CO and reduced NO after the reactor, indicating the carbon had reduced NO to N<sub>2</sub>. As noted previously, the produced CO can further reduce other NO<sub>x</sub> species. While neither group tested N<sub>2</sub>O abatement, their results suggest a need for further study.

While ammonia is the most common reductant for SCR, other nitrogen species could also serve as reductants for N<sub>2</sub>O. Urea is used in diesel exhaust fluid to mitigate NO<sub>x</sub>, which thermally decomposes releasing ammonia for the standard NH<sub>3</sub>-SCR mechanism.<sup>139</sup> While nitrogen in the –3 oxidation state (*e.g.* ammonia and urea) has the most electrons to contribute to N<sub>2</sub>O reduction, nitrogen species in the –2 (*e.g.* hydrazine) and –1 oxidation states (*e.g.* hydroxylamine) could also be used. In one instance, Zheng *et al.* developed a kinetic model for NO removal by hydrazine, that could be similarly applied to N<sub>2</sub>O.<sup>140</sup>

SO<sub>x</sub> and NO<sub>x</sub> are often emitted together from industrial processes but are typically removed individually using flue gas desulfurization followed by SCR.<sup>141</sup> Merging these processes has been explored through simultaneous catalytic desulfurization and denitrification (SCDD). Hydrogen sulfide has been used as a reductant in SCDD. Developing this technology, Lü *et al.* were able to achieve conversion rates of 75% for SO<sub>2</sub> and 90% for NO in the same reactor at 280 °C.<sup>142</sup> Separately, Yang *et al.* found that a sulfide-driven autotrophic denitrification step reduced N<sub>2</sub>O emissions during a wastewater treatment system known as sulfate reduction-autotrophic denitrification–nitrification integrated process.<sup>143</sup> This process combined elements of the sulfur- and nitrogen-cycles, reducing nitrate ions in solution to nitrogen gas while oxidizing sulfide ions to sulfate/sulfite ions and elemental sulfur. The N<sub>2</sub>O reduction rate scaled linearly with sulfide concentration at pH 7. While quite dissimilar to gas phase SCR, it highlights the principles of incorporating sulfide as a reductant for N<sub>2</sub>O abatement.

## 4 Mechanistic investigation of nitrous oxide abatement

### 4.1 Temporal analysis of products (TAP) experiments

Fundamental understanding of reaction mechanisms and the nature of active sites are important to advance catalyst development for efficient chemical processing. Most of the experimental approaches on studying direct decomposition and SCR of N<sub>2</sub>O are based on light-off curve measurements (*i.e.* tracking reactant conversion as a function of temperature). Transient kinetic studies of heterogeneous-catalyzed gas phase reactions in TAP reactors can be effectively utilized to obtain kinetic parameters (*e.g.*, rate constants of simple reaction steps, lifetime of reactive surface species, *etc.*) based on the time-dependent interactions between gas molecules and the catalyst surface, and offer deeper mechanistic insights into simple reaction steps

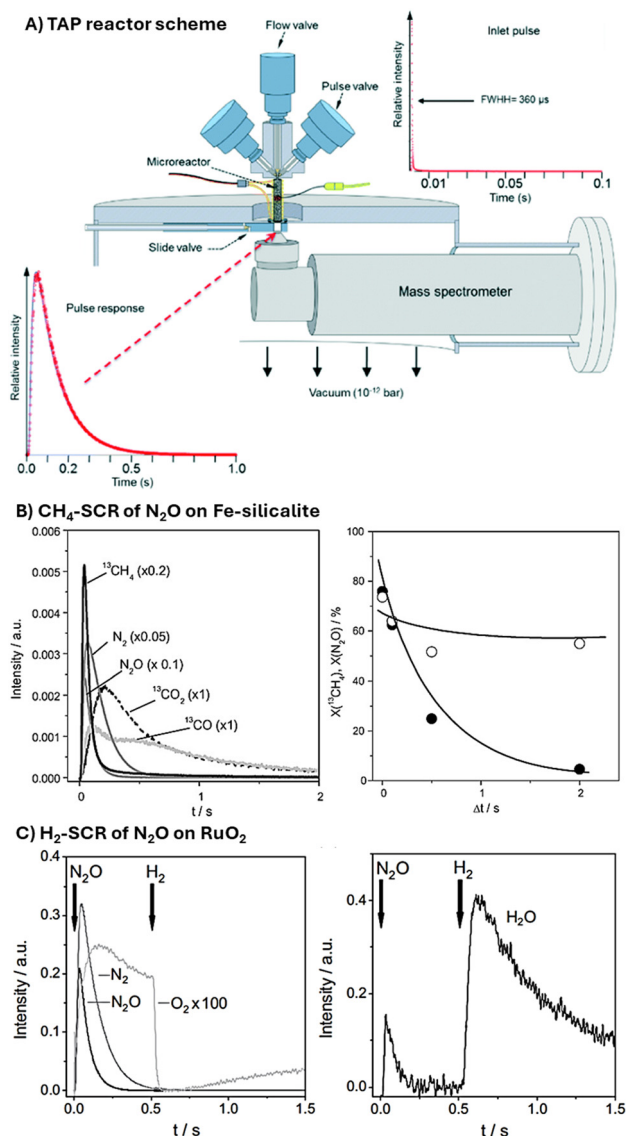


(Fig. 8A). A more detailed description of the TAP reactor and experiments were reported elsewhere.<sup>144–147</sup>

As mentioned in section 2 and 3, the reaction mechanism of direct decomposition and SCR of  $\text{N}_2\text{O}$  depend on the nature and distribution of active sites, leading to distinct catalyst performance. These correlations have been investigated on common  $\text{N}_2\text{O}$  abatement catalyst systems, including noble metals, metal oxides, and zeolites, in TAP reactors. Several studies have performed pulse response experiments to understand the mechanism and kinetics of

$\text{N}_2\text{O}$  abatement reactions with Fe-based catalysts.<sup>71,147</sup> Kondratenko and Pérez-Ramírez studied direct decomposition of  $\text{N}_2\text{O}$  in a TAP reactor and found that the direct decomposition of  $\text{N}_2\text{O}$  over steam-activated Fe-silicalite occurs on free, isolated iron species and iron sites associated with adsorbed mono-atomic oxygen species ( $^*\text{O}$ ) at 500–575 °C.<sup>149</sup> They found that  $\text{O}_2$  forms *via* decomposition of a bi-atomic oxygen species ( $^*\text{O}_2$ ) adsorbed over the iron site. This species is derived from  $\text{O}^*\text{O}$ , which is formed *via* interaction of  $\text{N}_2\text{O}$  with the iron site associated with ( $^*\text{O}$ ). The recombination of  $^*\text{O}$  species or direct formation  $\text{N}_2\text{O}$  and  $^*\text{O}$  (Eley-Rideal) mechanisms were excluded. This  $\text{N}_2\text{O}$  decomposition pathway over Fe-silicalite was also applicable to Fe-ZSM-5, which has markedly different iron speciation including both isolated and oligomeric iron-oxo species, as well as small  $\text{Fe}_2\text{O}_3$  nanoparticles, indicating the generality of the reaction mechanism.<sup>150</sup> In addition, the kinetic parameters of  $\text{N}_2\text{O}$  decomposition, such as turnover frequency of  $\text{N}_2$  formation, rate constant and activation energy of elementary steps, were calculated from a TAP-derived kinetic model for the comparison between Fe-ZSM-5 and Fe-silicalite. The relative activities of these catalysts in the TAP experiment were found to be consistent with the steady-state performance. On the other hand, it was suggested that the oxygen is formed directly *via* the reaction of gas-phase  $\text{N}_2\text{O}$  with adsorbed mono-atomic oxygen species originating from the decomposition of adsorbed  $\text{N}_2\text{O}$  on Rh-ZSM-5 catalyst.<sup>151</sup> The higher catalytic activity of Rh-ZSM-5 compared to Fe-ZSM-5 was attributed to the stronger  $\text{N}_2\text{O}$  adsorption and faster oxygen formation to regenerate free active sites over rhodium sites.

The  $\text{N}_2\text{O}$  decomposition reaction mechanism at high temperature regime (550–700 °C) over  $\text{BaFeAl}_{11}\text{O}_{19}$  hexaaluminate was investigated in the TAP reactor and compared with lower temperature regime (400–500 °C) over Fe-ZSM-5 zeolites.<sup>56,152</sup> Regardless of the catalyst support (hexaaluminate or ZSM-5), it was indicated that  $\text{N}_2\text{O}$  decomposition activity is more favorable over clustered iron species ( $\text{Fe-O}_x$ ) than isolated iron sites. Large iron oxide particles were detrimental to activity, thus there is an optimum in clustering of iron species. Regardless of the catalyst support optimum in clustering. The NO-promoted  $\text{N}_2\text{O}$  decomposition over Fe-zeolites was investigated by multitrack experiments in a TAP-reactor-like high-vacuum reactor system.<sup>153</sup> The addition of nitric oxide benefits  $\text{N}_2\text{O}$  decomposition by removal of adsorbed oxygen atoms and facilitating migration and recombination of these atomic oxygen species on catalyst surface. Mechanistic studies of  $\text{N}_2\text{O}$  decomposition by transient kinetic methods were also performed over other materials such as Na-doped CaO, Pt gauze, and Pt-Rh gauze.<sup>154–156</sup> It is noted that the formation of gas-phase oxygen by recombination of two adsorbed oxygen atoms on surface Pt sites was less favorable under transient vacuum conditions as compared to ambient pressure steady-state conditions, which was ascribed to a low surface coverage of these atomic oxygen species in high-



**Fig. 8** (A) Schematic of a TAP reactor. Reprinted from ref. 147 under CC BY 3.0 license. (B) Transient responses of  $\text{N}_2\text{O}$ ,  $^{13}\text{CH}_4$ ,  $\text{N}_2$ ,  $^{13}\text{CO}$ , and  $^{13}\text{CO}_2$  upon simultaneous pulsing of  $\text{N}_2\text{O}$  and  $^{13}\text{CH}_4$  and conversion of  $^{13}\text{CH}_4$  (●) and  $\text{N}_2\text{O}$  (○) as a function of the time delay ( $\Delta t$ ) between the pulses of  $\text{N}_2\text{O}$  and  $^{13}\text{CH}_4$  over Fe-silicalite at 450 °C (723 K). Reprinted from ref. 148 with permission from Elsevier. (C) Transient responses of  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$  in pump-probe experiments of  $\text{N}_2\text{O}:\text{Ar} = 1:1$  and  $\text{H}_2:\text{Xe} = 1:1$  at 250 °C (523 K) with a time delay of 0.5 s between the pulsed mixtures. Reprinted from ref. 56 with permission from Elsevier.



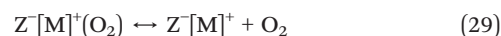
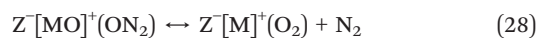
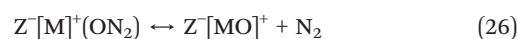
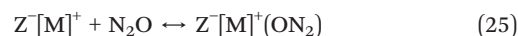
vacuum TAP reactor.<sup>157</sup> This observation further underscores the impact of surface coverage under relevant reaction conditions on the underlying mechanisms, which is of critical importance when extrapolating TAP-derived models to steady-state experiments. The reduction of N<sub>2</sub>O over Fe-zeolites using CO, methane, and propane as reductants, was investigated by pump/probe pulse response experiments the TAP reactor (Fig. 8B).<sup>56,148,156,158,159</sup> Varying the time delay,  $\Delta t$ , between the N<sub>2</sub>O and hydrocarbon pulse on Fe-silicalite shows that the reactive oxygen generated from N<sub>2</sub>O on extra-framework Fe sites has a short lifetime, as evidenced by the decline in hydrocarbon conversion with increasing time delay.<sup>156</sup> The finding on the short lifetime of highly reactive oxygen species formed upon interaction of N<sub>2</sub>O on extra-framework iron sites was consistent for both methane and propane, with the latter being a more effective reductant for N<sub>2</sub>O reduction under both high vacuum TAP conditions and ambient pressure flow experiments.<sup>148,159</sup> Santiago *et al.* also used the pump/probe format pulsing N<sub>2</sub>O followed by ammonia and hydrogen reductants over a RuO<sub>2</sub> catalyst. The time delay was fixed at 0.5 s, and as shown in Fig. 8C, the H<sub>2</sub> pulse suppresses the O<sub>2</sub> response from N<sub>2</sub>O and increases yield of H<sub>2</sub>O, indicating that N<sub>2</sub>O-derived surface oxygen remains reactive over the 0.5 s window and is readily scavenged by H<sub>2</sub>.<sup>56</sup> In addition, the promotion effect of H<sub>2</sub> and NH<sub>3</sub> on the N<sub>2</sub>O reduction is diminished in the presence of oxygen due to non-selective oxidation reactions of these reductants.

#### 4.2 Density functional theory (DFT) modeling

DFT enables atomic-level insight into catalytic mechanisms and electronic structure information, enabling it to be used both as an explanatory tool for the performance of a catalyst, and as a screening tool for catalyst discovery. The energy at each elementary reaction step, the activation energy between steps, and the energies of proposed catalytic intermediaries can be directly calculated. From these energetics, the active site(s), rate limiting step, and energetically favorable pathway can be determined. Additionally, DFT provides electronic structure information, notably the d-band center, Bader (partial) charge, charge density, and electronic density of states to rationalize catalytic performance. A more extensive treatment of DFT for catalysis and the background of methods can be found in literature.<sup>160–162</sup> It has been utilized for studies of supported metal, mixed oxide, and zeolite catalysts in both the direct decomposition and the SCR of N<sub>2</sub>O.

Mechanistic studies with DFT for direct decomposition of N<sub>2</sub>O have helped determine active sites, activation barriers, the role of promoters, and provided an electronic structure explanation. Kim *et al.* computationally studied the decomposition of N<sub>2</sub>O on Pd<sub>x</sub>Cu<sub>y</sub> compositions.<sup>163</sup> It was found that Pd adsorbs N<sub>2</sub>O onto the metal surface stronger than Cu, while Cu more easily dissociates N<sub>2</sub>O than Pd. Intermediate Pd<sub>x</sub>Cu<sub>y</sub> compositions were found to have a

balance of these traits leading to improved activity. The PdCu catalyst had only a slight reduction in N<sub>2</sub>O adsorption strength *vs.* pure Pd (−38.58 *vs.* −42.45 kJ mol<sup>−1</sup>), and a lower N<sub>2</sub>O dissociation activation energy (8.70 *vs.* 24.14 kJ mol<sup>−1</sup>). Electronic structure analysis found that the PdCu alloy had a higher d-band center position (−1.64 eV) *vs.* pure Pd (−1.67 eV) or Cu (−2.29 eV), which may enable higher catalytic activity. The Pd<sub>3</sub>Cu alloy had the weakest O adsorption and highest predicted decomposition activity, which matches the experimental observations reported in literature.<sup>32</sup> Sun *et al.* conducted DFT calculations for alkaline-earth-modified metal oxide catalysts (A<sub>0.5</sub>Co<sub>2.5</sub>O<sub>4</sub> with A = Mg, Ca, Sr, Ba) in tandem with experiments for direct N<sub>2</sub>O decomposition.<sup>164</sup> Ba was found to significantly lower the oxygen vacancy formation energy *vs.* the unmodified Co<sub>3</sub>O<sub>4</sub> oxide (261.46 *vs.* 172.71 kJ mol<sup>−1</sup>) for the near O site. The lower oxygen vacancy formation energy of Ba<sub>0.5</sub>Co<sub>2.5</sub>O<sub>4</sub> was attributed to the lower valency of Ba compared to Co. The oxygen vacancies in the oxide allowed the catalyst to chemisorb more O, which enables the reduction of N<sub>2</sub>O, resulting in a 73 °C reduction in the T<sub>90</sub> temperature for Ba<sub>0.5</sub>Co<sub>2.5</sub>O<sub>4</sub> *vs.* Co<sub>3</sub>O<sub>4</sub>. Wang *et al.* utilized DFT to investigate both the oxygen vacancy formation energy and the N<sub>2</sub>O decomposition activation energy over oxygen vacancies and metal sites in CeO<sub>2</sub> and Co-doped CeO<sub>2</sub>.<sup>165</sup> The doping of Co at a Co/Ce ratio of 1 was found to reduce the oxygen vacancy formation energy from 219.99 to −29.91 kJ mol<sup>−1</sup>. Additionally, the activation energy over both the metal sites (224.81 *versus* 311.65 kJ mol<sup>−1</sup>) and oxygen vacancies (111.92 *versus* 284.63 kJ mol<sup>−1</sup>) were lower for the Co-doped CeO<sub>2</sub>, indicating the oxygen vacancies serve as active sites for the direct decomposition of N<sub>2</sub>O. Heyden *et al.* performed a comprehensive DFT study of the energetics and kinetics of direct N<sub>2</sub>O decomposition on the hydrated and dehydrated mononuclear Fe sites in a Fe-ZSM-5 zeolite catalysts to determine the active sites, method of low concentration H<sub>2</sub>O deactivation, and rate constants.<sup>166</sup> The decomposition was modeled following the E–R-like mechanism shown in eqn (25)–(29) (M = Fe mononuclear site, Z = zeolite site):



The Z<sup>−</sup>[Fe]<sup>+</sup> and Z<sup>−</sup>[FeO]<sup>+</sup> had exothermic enthalpies of adsorption for N<sub>2</sub>O; however, the oxidation of bare Z<sup>−</sup>[Fe]<sup>+</sup> by N<sub>2</sub>O is very exothermic (−259.5 kJ mol<sup>−1</sup> or −2.69 eV), making the reverse reaction unlikely to occur during N<sub>2</sub>O decomposition, making Z<sup>−</sup>[FeO]<sup>+</sup> the active site. After determining Z<sup>−</sup>[FeO]<sup>+</sup> was the active site, H<sub>2</sub>O adsorption and



potential catalyst deactivation were evaluated.  $\text{H}_2\text{O}$  absorbs without barriers to  $\text{Z}^-\text{[FeO]}^+$ , forming  $\text{Z}^-\text{[Fe(OH)}_2]^+$ , which has a higher activation energy for  $\text{N}_2\text{O}$  decomposition. The formation of  $\text{Z}^-\text{[Fe(OH)}_2]^+$  sites resulted in a more than doubling of the activation energy from (106.7–229.3  $\text{kJ mol}^{-1}$ ) as water content increased from 0 to 100 ppb.

SCR of  $\text{N}_2\text{O}$  with a variety of reductant agents has also been studied using DFT.<sup>111,167</sup> The reaction pathways on isolated iron sites and  $\text{Fe}_2\text{O}_3$  particles on a Fe/ZSM-5 catalyst for CO-SCR previously discussed in section 3.1 and superior performance of the CO-SCR *versus* direct decomposition were supported by DFT calculations.<sup>111</sup> DFT simulations showed the pristine  $\text{Fe}_2\text{O}_3$  is unable to adsorb  $\text{N}_2\text{O}$  initially and required an oxygen vacancy for  $\text{N}_2\text{O}$  adsorption to occur. With the oxygen vacancy being formed by CO oxidation the CO-SCR follows the MvK mechanism. On the isolate iron sites CO was unable to adsorb, causing initial  $\text{N}_2\text{O}$  adsorption and release of  $\text{N}_2$ , followed by CO bonding with  $\text{O}^*$  forming  $\text{CO}_2$  for subsequent desorption, thus following the E–R reaction mechanism. For both the isolated Fe site and the on  $\text{Fe}_2\text{O}_3$  the desorption of  $\text{CO}_2$ , a product of CO-SCR, had a far lower activation energy than that of  $\text{O}_2$ , a product of direct  $\text{N}_2\text{O}$  decomposition, explaining the improved low temperature regime (300–250 °C) conversion efficiency of CO-SCR. When NO is used as a reductant, it can activate the catalytically inactive  $\text{Z}^-\text{[Fe(OH)}_2]^+$  sites, by absorbing and subsequently forming  $\text{HNO}_2$ , which is easily desorbed leaving catalytically active  $\text{Z}^-\text{[FeOH]}^+$  sites, resulting in improved decomposition performance below 427 °C (700 K).<sup>167</sup> Further studies involving more complex alloy compositions may be a critical step in developing next generation catalysts.

## 5 Outlook

### 5.1 High-throughput experimentation and machine learning for catalyst discovery

High-throughput (HT) synthesis and screening coupled with computationally guided design are essential as the exploratory compositional space continues to grow for novel catalytic discovery. Limited throughput of single-channel reactors hinders the ability to achieve rapid materials discovery.<sup>168</sup> HT reactor testing is beneficial for rapid materials discovery due to the ability to test multiple catalysts simultaneously, which greatly decreases the time needed to test a large number of catalysts within a compositional design space.<sup>169–171</sup> In general, HT experimentation has been implemented to test up to 48 different catalysts at a single time.<sup>172–174</sup> The ability to collect large amounts of data from HT experimentation allows for the development of machine learning (ML) models to probe the complex design space and determine which features are important for specific reactions.<sup>175</sup>

Currently, only a limited number of studies utilize HT experimentation to develop  $\text{N}_2\text{O}$  abatement catalysts. In one study, Li *et al.* utilized HT experimentation to analyze a variety of  $\text{N}_2\text{O}$  decomposition catalysts under the same

reaction conditions. A reactor capable of testing 48 catalysts simultaneously was used. The activity across many catalysts was related back to the characteristics of the catalyst, such as the impact of the support and pretreatment conditions.<sup>21</sup> Another study by Hendershot *et al.* investigated the optimization of a  $\text{NO}_x$  storage and reduction catalyst by using a statistical design of experiments model coupled with HT experimentation.<sup>176</sup> The HT setup quantified the production of  $\text{N}_2\text{O}$  from the catalysts as one of the factors analyzed. This work demonstrates the ability to analyze  $\text{N}_2\text{O}$  in an HT setup, which highlights the potential for further applications in future  $\text{N}_2\text{O}$  abatement technologies.

Recent studies have also applied ML to predict the  $\text{N}_2\text{O}$  emissions from wastewater treatment and agricultural crop production, two of the largest sources to global  $\text{N}_2\text{O}$  emissions (see Fig. 1).<sup>177,178</sup> Additionally, ML has been employed to predict the adsorption of  $\text{N}_2\text{O}$  on activated carbon and carbon molecular sieves.<sup>179</sup> A major development in computational studies that can be leveraged for catalytic  $\text{N}_2\text{O}$  abatement is machine-learned interatomic potentials (MLIPs). MLIPs, such as M3GNet, are trained on large databases of DFT data with neural networks to learn the underlying features to property relationships and use this to form universal interatomic potentials.<sup>180</sup> MLIPs provide DFT level accuracy for the energetics of elementary reaction steps at a fraction of the computational cost (~4–7 orders of magnitude faster). Furthermore, MLIPs enable the inclusion of time and temperature effects to capture the modelling of realistic catalyst dynamics.<sup>181</sup> Coupled, these provide a very powerful tool for catalyst discover. However, to date, MLIPs have not been utilized in the literature for catalytic  $\text{N}_2\text{O}$  abatement and have only been used to study ternary oxides for syngas conversion and a  $\text{NO} + \text{CO}$  reaction.<sup>182,183</sup> Leveraging MLIPs for  $\text{N}_2\text{O}$  abatement studies would enable both more accurate activity predictions by incorporating the catalyst evolution and would also facilitate the exploration of exponentially larger compositional space of the catalysts.

Coupling experimentation and computational data with ML model development can allow researchers to take advantage of active learning (AL) to predict optimal catalysts while using HT experimentation to test large amounts of data. This approach has been utilized for  $\text{NH}_3$  synthesis catalysts. A feature space of descriptors to characterize a promoted Ru catalyst for  $\text{NH}_3$  synthesis was subdivided into reaction conditions, metal–support interactions, promoter–support interactions, metal–promoter interactions, catalyst preparation, and catalyst pretreatment, for a total of 536 features, which was reduced to 160 after feature selection. For AL to find the best performing promoters, the feature space was reduced again from 160 to 53 to limit it to only features that vary with the promoter. The AL predicted top performing promoter was synthesized and tested with HT experimentation, and the data added for the subsequent prediction.<sup>170</sup> Another ML approach was developed by Wang *et al.* that divided the feature space into catalyst composition, preparation conditions, and reaction conditions for the  $\text{NH}_3$



for  $\text{NO}_x$ . The advantage of this feature space is it allows the catalyst composition to be optimized.<sup>184</sup> Though not explicitly studying  $\text{N}_2\text{O}$  abatement catalysts, these previous studies highlight the features and methodologies that have been proven effective and can be applied to these reactions.

Future studies coupling high-throughput experimentation with machine learning are imperative for catalytic discovery and optimization of novel catalysts for  $\text{N}_2\text{O}$  abatement reactions. This methodology will allow for rapid material screening to facilitate novel catalytic discovery at a more rapid pace while elucidating trends with ML.

## 5.2 Industrial outlook for catalytic design

In many industrial plants, such as nitric acid and adipic acid,  $\text{N}_2\text{O}$  is not a “pure” byproduct but is rather produced in an effluent with other gases that may be inhibiting. With this comes an opportunity to develop novel catalysts that are tailored towards being resistant to other inhibiting gases. Many industrial pollutants, such as water and  $\text{SO}_2$ , are emitted in addition to  $\text{N}_2\text{O}$ . As previously discussed in section 2.4 and 3.5, these other additional gases in the feed stream inhibit catalytic activity and can result in irreversible deactivation of the catalyst. These considerations motivate the need for the discovery of resilient catalysts through the altering of the support or the addition of promoters to influence the binding of reactants and inhibitors. Many studies have begun to analyze catalyst compositions to improve their toxicity resistance. In short, other research groups have found that the addition of  $\text{CeO}_2$  to a catalyst can increase water resistance with the synthesis of the catalysts also having an impact on the performance in the presence of catalytic toxins.<sup>13,21,35</sup> In addition, a different review article summarized that the toxicity resistance can be further improved upon through the synthesis of varied structure materials, such as core-shell type catalysts or through doping the catalyst with other elements, such as Ti, Zn, or K as these dopants can further weaken the binding of these catalytic toxins to the active sites.<sup>13,185–187</sup> Though there have been studies first analyzing how to improve the toxicity resistance of abatement catalysts, there is still a drive to further develop catalysts that can be resistant to industrial pollutants while achieving high activity, increased longevity, and decreased cost. In addition, with the development of novel catalysts, it is imperative to assess the longevity of the catalysts in realistic industrial conditions as increasing the catalysts lifetime will help save industrial operating costs. Other considerations for novel catalyst design should include catalyst cost, increasing activity at lower temperatures, as well as minimizing the environmental footprint for the large-scale synthesis and utilization of these catalysts. High performing catalysts, as seen with the direct decomposition section, include noble metals with the incorporation of other elements as promoters or supports, such as rare earth metals. This combination of materials may be active, but it may also come with tradeoffs in terms of cost deeming large-scale

implementation challenging. Through larger studies, novel active materials and combinations of metals, supports, and promoters can be found while reducing expensive component weight loadings to decrease costs. With these additional considerations in mind, ML and HT experiments can be utilized to more rapidly achieve industrial  $\text{N}_2\text{O}$  abatement goals.

In conjunction with the opportunities for catalytic design for these industrial applications, there also comes additional challenges with the integration of these systems into large-scale industrial units. One challenge that will be faced involves the reactor design to allow for effective conversion of  $\text{N}_2\text{O}$ . This can be done by designing packed bed reactors with monoliths or with the use of membrane reactors to further enhance catalytic activity. In addition, new reactor designs come with the consideration of pressure drop through the catalytic bed. With a pressure drop in the system, it will become more costly for operations not only in energy requirements but because it can alter the thermodynamics of the reaction and negatively impact catalytic activity. This problem can be further mitigated by developing pelletized catalysts or through the synthesis of monoliths. In addition, there is further work needed to be done to assess how these catalysts perform in conjunction with other catalytic systems, such as de- $\text{NO}_x$ , to ensure selectivity and decomposition of all harmful products. As these new industrial reactor designs are studied, chosen catalytic systems should be subjected to longevity tests to ensure sufficient catalytic activity in the industrial gas streams.

Following catalytic design considerations, further work is also needed in the work of technoeconomic analysis and life cycle analysis. A technoeconomic analysis would be able to help researchers and industry determine if an effective catalytic design is economically viable for large-scale applications. As mentioned, some catalysts may show higher activity but are hindered for further usage due to high cost of materials. However, there may be tradeoffs with choosing cheaper materials that may not have as high of activity but will meet  $\text{N}_2\text{O}$  abatement requirements. In addition, lifecycle analysis should be performed to analyze the environmental impact of the catalysts used from their creation to their disposal. This can aid in helping companies choose materials for their catalytic reactor systems that are less environmentally harmful to better align with industrial goals of reducing their carbon footprint.

## 6 Conclusions

Various catalytic designs for  $\text{N}_2\text{O}$  abatement were reviewed, with a specific focus on direct decomposition and selective catalytic reduction (SCR) pathways. Mechanistic insights for different catalytic systems, supported by transient kinetic studies and density functional theory calculations were also discussed. The review emphasizes viable operating conditions and mechanisms, highlighting three main catalyst-based



designs of supported metal, metal oxide, and zeolite catalysts.

Previous studies have identified Rh as one of the most active metals for direct decomposition, with the choice of support playing a crucial role in regenerating catalytic active sites. Metal oxide catalysts, such as  $\text{Co}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{NiO}$ , as well as Fe-, Co-, and Cu-exchanged zeolites, have also emerged as promising, cost-effective alternatives to noble metal-based catalysts. Additionally, the incorporation of alkali metals and lanthanides as promoters has been shown to increase the catalytic activity by improving redox properties and promoting oxygen desorption from catalyst surfaces, thereby offering an opportunity to further lower respective  $T_{50}$  values.

The addition of reductants for SCR shifts the  $\text{N}_2\text{O}$  conversion towards lower  $T_{50}$  values, as shown across various catalyst systems (e.g., Fe-zeolites, Rh-FAU,  $\text{RuO}_2$ , and metal oxides). Reductants (i.e., CO, hydrocarbons,  $\text{NH}_3$ , and  $\text{H}_2$ ) effectively aid in  $\text{N}_2\text{O}$  abatement by promoting the removal of the adsorbed oxygen species and reducing the temperature required for  $\text{N}_2\text{O}$  conversion.  $\text{H}_2$  achieves the lowest  $T_{50}$  median temperature (129 °C) for the SCR catalysts, whereas hydrocarbons exhibited the highest at temperature (413 °C for  $\text{C}_3\text{H}_6$ ). However, it should be noted that comparing the efficiency of reductants is not trivial, as the performance depends on the catalyst active sites-reductant interaction, as well as reaction conditions.

Fe-zeolites (e.g., Fe-MFI, Fe-MOR, Fe-BEA, and Fe-SSZ-13) are extensively studied for their high  $\text{N}_2\text{O}$ -SCR activity, low cost, and low toxicity, which makes them suitable for industrial applications. Moreover, the SCR catalysts reported a lower median  $T_{50}$  (374 °C) than direct decomposition (432 °C). Among the catalyst classes (supported metals, metal oxides, and zeolites), the metal oxide catalysts achieved the lowest  $T_{50}$  values (350 °C and 216 °C for direct decomposition and SCR, respectively).

Future catalytic design must be tailored to be robust against common impurity gases found in industrial sources, such as  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}$ , and  $\text{SO}_2$ . The literature suggests that  $\text{O}_2$  desorption is a rate-limiting step in the direct decomposition of  $\text{N}_2\text{O}$  and also inhibits the SCR of  $\text{N}_2\text{O}$ . Overall, the presence of  $\text{O}_2$  and  $\text{H}_2\text{O}$  typically hinders both abatement processes through competitive adsorption, non-selective oxidation of reductants, and alteration of the surface redox state of the catalyst. Coupling machine learning (ML) with high throughput (HT) experiments offers a promising approach to rapidly screen catalytic materials and gaseous reaction feeds for enhanced catalytic activity while tailoring different considerations towards industrial concerns and applications.

## Author contributions

Conceptualization: DDR. Data curation: HC, SS. Funding acquisition: DDR, MC. Investigation: HC, SS, MNG, MM. Project administration: DDR, JL, RF, DA, MC. Supervision: DDR, JL, RF, DA, MC. Visualization: HC, SS, MNG, MM.

Writing – original draft: HC, SS, MNG, MM. Writing – review & editing: HC, SS, MNG, MM, DDR.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results, software or code have been included, and no new data were generated or analysed as part of this review.

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