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# Modulated excitation DRIFTS and steady-state isotopic transient kinetic analysis (SSITKA) of NH<sub>3</sub>-SCR-DeNO<sub>x</sub> on Cu-containing zeolite Y

Magdalena Jabłońska,<sup>\*ab</sup> Rujito S. R. Suharbiansah,<sup>id ac</sup> Jie Yang,<sup>d</sup> Marek Rotko,<sup>e</sup> Pranjit Das,<sup>f</sup> Marko Bertmer,<sup>id f</sup> Jacek Grams,<sup>g</sup> Junjiang Zhu<sup>id d</sup> and Andreas Pöppel<sup>f</sup>

As-received commercial zeolite Y (in the forms of Na<sup>+</sup>, H<sup>+</sup>, and NH<sub>4</sub><sup>+</sup>) with an  $n(\text{Si})/n(\text{Al})$  ratio of about 2.6 modified with copper cations was investigated in the selective catalytic reduction of nitrogen oxide with ammonia (NH<sub>3</sub>-SCR-DeNO<sub>x</sub>). Operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) experiments using concentration modulation excitation (ME) coupled with phase-sensitive detection (PSD) analysis, together with steady-state isotopic transient kinetic analysis (SSITKA), were carried out to study key transient adsorbates on Cu-containing zeolite Y samples. We could observe different interactions between NO exposure to the NH<sub>3</sub> preadsorbed surface over the applied catalysts. For CuY\_CBV100, NO exposure to an NH<sub>3</sub>-preadsorbed surface leads to a decrease in NH<sub>3</sub> bound to Lewis acid sites (L-NH<sub>3</sub>) and the formation of new Brønsted acid sites (B-NH<sub>3</sub>). Part of the L-NH<sub>3</sub> migrates to these newly generated BAS. Based on the modulation excitation results, we could set the order of activity of the applied catalysts. For CuY\_CBV500, the situation differs. A strong B-NH<sub>3</sub> peak indicates a high concentration of Brønsted acid sites on the CuY\_CBV500 surface. NO can react with both L-NH<sub>3</sub> and B-NH<sub>3</sub>, and the presence of B-NH<sub>3</sub> contributes to the high N<sub>2</sub> selectivity observed. SSITKA revealed that CuY\_CBV100 exhibited a higher number of active centers on its surface, thus leading to higher NO conversion during NH<sub>3</sub>-SCR-DeNO<sub>x</sub>, but its reactivity is slightly lower than in the case of the other studied materials (especially CuY\_CBV500).

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## 1. Introduction

The selective catalytic reduction of NO with ammonia (NH<sub>3</sub>-SCR-DeNO<sub>x</sub>; 4 NH<sub>3</sub> + 4 NO + O<sub>2</sub> → 4 N<sub>2</sub> + 6 H<sub>2</sub>O) is an effective way of treating nitrogen oxide emissions to meet increasingly stringent international emission standards (e.g., ref. 1 and 2). The ability of Cu-containing zeolites to convert NO into N<sub>2</sub> in the presence of ammonia over Cu-Y was first discovered in

Japan in 1977. In this study, Seiyama *et al.*<sup>3</sup> already proposed a Langmuir-Hinshelwood type of reaction of NO and NH<sub>3</sub> coordinated to Cu(II) ions. According to the Langmuir-Hinshelwood (L-H) mechanism, the SCR reaction process occurs *via* adsorbed NH<sub>3</sub> species and adsorbed NO<sub>x</sub><sup>-</sup> species. Otherwise, in the Eley-Rideal (E-R) mechanism, the reaction occurs between adsorbed ammonia species (NH<sub>x</sub>;  $x < 3$ ) on redox sites and NO from the gas phase.<sup>1,4,5</sup> Furthermore, NH<sub>3</sub>-SCR-DeNO<sub>x</sub> over Cu-containing zeolites was approved to follow redox mechanisms, consisting of a reduction half-cycle and oxidation half-cycle. The reaction mechanism was investigated *via* numerous spectroscopic methods, such as *in situ* DR UV-vis or *in situ* FT-IR (e.g., ref. 6–8). Otherwise, transient techniques such as modulated excitation DRIFTS or steady-state isotopic transient kinetic analysis (SSITKA) are less frequently investigated. Operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments using concentration modulation excitation (ME) coupled with phase sensitive detection (PSD) analysis have been demonstrated to detect dynamic species that are directly involved in catalytic reactions (e.g., ref. 9–12). Vibrational signals of reactive species can be obtained by combining ME with *in situ* infrared (IR) spectroscopy. This approach

<sup>a</sup> Institute of Chemical Technology, Universität Leipzig, Linnéstr. 3, Leipzig 04103, Germany. E-mail: magdalena.jablonska@chemia.uni.lodz.pl

<sup>b</sup> University of Łódź, Faculty of Chemistry, Department of Inorganic and Analytical Chemistry, Tamka 12, Łódź 91-403, Poland

<sup>c</sup> Department of Sustainable Fuels and Green Chemistry, University of Chemistry and Technology, Technická 5, 166 28 Prague 6, Czech Republic

<sup>d</sup> Hubei Key Laboratory of Biomass Fibers and Eco-dyeing and Finishing, College of Chemistry and Chemical Engineering, Wuhan Textile University, Wuhan 430200, China

<sup>e</sup> Department of Chemical Technology, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq. 3, Lublin, 20-031, Poland

<sup>f</sup> Felix Bloch Institute for Solid State Physics, Universität Leipzig, Linnéstr. 5, Leipzig 04103, Germany

<sup>g</sup> Institute of General and Ecological Chemistry, Faculty of Chemistry, Łódź University of Technology, Zeromskiego 116, Łódź, 90-924, Poland



effectively removes the signals from unreactive species that do not vary at the same frequency as the ME on, isolating only the dynamic components relevant to the reaction. Through phase-sensitive detection (PSD) analysis, time-resolved spectra are transformed into phase-resolved spectra that capture signals exclusively from species responding to the modulation sequence. As a result, signals from unresponsive or static species are effectively removed, while those from active and perturbed species are highlighted. Modulation excitation diffuse reflectance infrared Fourier transform spectroscopy (ME DRIFTS) has previously been employed to investigate the reaction mechanisms of  $\text{NH}_3$ -SCR-DeNO<sub>x</sub> over  $\text{V}_2\text{O}_5/\text{TiO}_2$  and  $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ ,<sup>13,14</sup> Cu-SSZ-13,<sup>15</sup> as well as  $\text{CeO}_2$  and  $\text{WO}_3/\text{CeO}_2$ .<sup>9</sup>

SSITKA, developed largely through the work of Biloen,<sup>16</sup> Bennett,<sup>17</sup> Happel,<sup>18</sup> and Bell,<sup>19</sup> is a technique used in heterogeneous catalysis to gain insight into the reaction pathways of surface-catalyzed processes. The SSITKA method is a widely recognized technique that allows for the determination of key kinetic parameters under actual reaction conditions. SSITKA provides information on the homogeneity or heterogeneity of the catalyst surface, offering valuable insight into possible reaction mechanisms. The simplest approach involves analyzing the shape of the curves that depict changes in product concentration over time following a switch between reactants with different isotopic compositions.<sup>20</sup> SSITKA was already applied to study the reaction mechanism over zeolites Cu-Y (ref. 21) and Cu-SSZ-13,<sup>7,22</sup> and revealed kinetic parameters, such as average-surface lifetime, surface concentration and intrinsic activity over the applied catalysts.

Both SSITKA and modulated studies offered direct spectroscopic evidence of key transient intermediates and their kinetic parameters. Thus, in the present study, a series of commercially available zeolite Y samples were modified with copper cations, fully characterized in terms of their physicochemical properties, and further evaluated for the  $\text{NH}_3$ -SCR-DeNO<sub>x</sub> activity and  $\text{N}_2$  selectivity. The reaction mechanism was evaluated *via* steady-state isotopic transient kinetic analysis (SSITKA), and modulated studies were supported *via* temperature-programmed methods. Thus, this work is a continuation of our previous work<sup>21</sup> on commercial zeolite Y applied in  $\text{NH}_3$ -SCR-DeNO<sub>x</sub>. However, in the present study, our approach was dictated by economic considerations, *i.e.*, commercially available zeolites in various forms ( $\text{Na}^+$ ,  $\text{NH}_4^+$ , and  $\text{H}^+$ ) were used without any other modification.

## 2. Experimental

### 2.1. Catalyst preparation

Table 1 shows the commercially available zeolite Y samples purchased from Zeolyst that were applied in this study. As-received samples (*i.e.*, without any pretreatment) were ion-exchanged using a 0.05 M aqueous solution of copper(II) acetate ( $\geq 98$  wt%, Alfa Aesar) at room temperature (*ca.* 25 °C)

**Table 1** The data for commercially available zeolites used in this study were provided by the manufacturer. The  $n(\text{Si})/n(\text{Al})$  ratios are as specified by the manufacturer<sup>23</sup>

Sample	Form	$n(\text{Si})/n(\text{Al})$	Treatment <sup>24</sup>
CBV100	$\text{Na}^+$	2.55	Parent zeolite
CBV300	$\text{NH}_4^+$	2.55	Ion-exchanged
CBV400	$\text{H}^+$	2.55	Ion-exchanged
CBV500	$\text{NH}_4^+$	2.6	Ion-exchanged, mildly steamed

for 24 h (1 g of zeolite per 100 ml of copper precursor solution). Finally, the samples were filtered and thoroughly washed until pH 7 was reached, dried, and calcined at 550 °C for 4 h in static air (with a heating rate of 1 °C min<sup>-1</sup>).

### 2.2. Catalyst characterization and catalytic experiments

The zeolite Y samples and their Cu-containing forms (CuY) were characterized using X-ray diffraction (XRD),  $\text{N}_2$  sorption, scanning electron microscopy analysis (SEM), time-of-flight secondary ion mass spectrometry (ToF-SIMS), solid-state nuclear magnetic resonance (NMR), inductively coupled plasma optical emission spectroscopy (ICP-OES), diffuse reflectance UV-vis spectroscopy (DR UV-vis), and temperature-programmed reduction (TPR-H<sub>2</sub>). All Cu-containing Y samples were examined for their catalytic activity and  $\text{N}_2$  selectivity in  $\text{NH}_3$ -SCR-DeNO<sub>x</sub>. The reaction mechanism was thoroughly evaluated *via* transient techniques (steady-state transient isotopic analysis, SSITKA) and modulated excitation DRIFTS, supported *via* temperature-programmed studies. The details of the experimental procedure can be found in the SI.

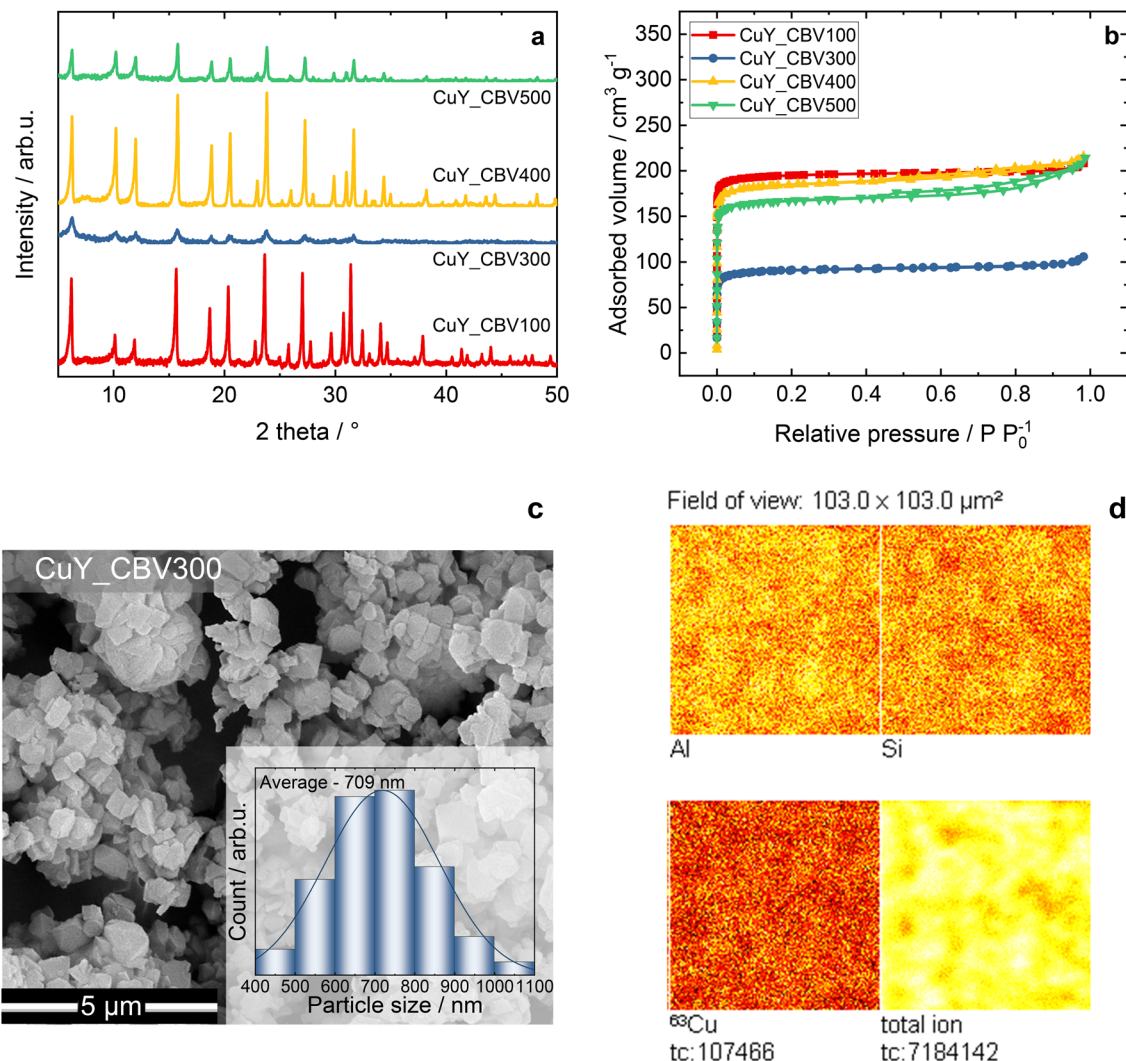
## 3. Results and discussion

### 3.1. Structural and textural/redox properties

Fig. 1a and S1a show the XRD patterns of the pristine Y and Cu-modified zeolite Y. The ion exchange process did not alter the primary peaks in the XRD pattern of the Y-type zeolite. Fig. 1b and S1b–d present the  $\text{N}_2$  adsorption–desorption isotherms measured at -196 °C. According to the IUPAC classification,<sup>25</sup> all samples possess mixed type I and type IV characteristics with a dominant micropore volume (Table S1). The textural properties of the pristine zeolite Y samples decrease after modification with copper, indicating partial blockage of the zeolite pores. The copper content varied in the range of 3.8–8.3 wt% along with an  $n(\text{Cu})/n(\text{Al})$  ratio of 0.17–0.42 (Table 2).

The morphology of the copper-containing CuY\_CBV300 sample is shown in Fig. 1c, while the SEM micrographs of the remaining Cu-containing zeolite Y samples are presented in Fig. S2. All materials exhibited the typical morphology of faujasite-type zeolites, consisting of agglomerated cubic crystals with well-defined edges and smooth surfaces.<sup>26</sup> The particles displayed relatively uniform shapes without any noticeable structural collapse or fragmentation after copper ion exchange and subsequent calcination at 550 °C. Interestingly, although the CuY\_CBV300 sample showed





**Fig. 1** a) XRD patterns and b) N<sub>2</sub> sorption isotherms of the Cu-containing zeolite Y samples and c) SEM images of CuY\_CBV300. The particle size distribution was obtained by measuring 100 particles from SEM images and d) ToF-SIMS images collected from the surface of CuY\_CBV300 (tc - total counts).

**Table 2** Elemental composition ( $\omega_i$ : mass fractions),  $n(\text{Si})/n(\text{Al})$  and  $n(\text{Cu})/n(\text{Al})$  ratios of the calcined zeolite Y samples and their Cu-containing forms

Sample	$\omega_{\text{Al}}/\text{wt}\%$	$\omega_{\text{Si}}/\text{wt}\%$	$\omega_{\text{Na}}/\text{wt}\%$	$\omega_{\text{Cu}}/\text{wt}\%$	$n(\text{Si})/n(\text{Al})$	$n(\text{Cu})/n(\text{Al})$
CBV100	9.9	25.7	8.9	—	2.49	—
CuY_CBV100	8.3	28.2	2.6	8.2	3.26	0.42
CBV300	11.1	28.2	1.9	—	2.45	—
CuY_CBV300	9.9	29.2	0.4	6.1	2.87	0.26
CBV400	11.3	28.0	1.9	—	2.38	—
CuY_CBV400	8.8	27.6	0.2	4.8	3.01	0.23
CBV500	10.8	30.0	0.1	—	2.67	—
CuY_CBV500	8.8	30.1	0.1	3.6	3.29	0.17

more distinct changes in its textural properties according to N<sub>2</sub> sorption analysis (*e.g.*, specific surface area and pore volume), the SEM images did not reveal any pronounced morphological differences compared to the other CuY\_CBV samples. The average particle size distributions, determined using ImageJ software, were in the range of 678–851 nm. This slight increase in size can be attributed to the partial

aggregation of crystallites during the copper ion-exchange and calcination steps. Overall, SEM analysis confirms that copper introduction did not alter the primary morphology of the zeolite Y crystals, and the structural properties of the faujasite framework were well preserved.

Fig. 1d, S3 and S4 show the spatial distribution of selected ions (Al<sup>+</sup>, Si<sup>+</sup>, Cu<sup>+</sup>, and total ion<sup>+</sup>) on the surfaces



of the analyzed samples, collected over areas of approximately  $100 \times 100 \mu\text{m}$ , while Tables S2 and S3 summarize the intensity ratios of selected ions calculated from the acquired spectra. The obtained results indicate that the distribution of the analyzed ions on the surface of the tested materials is generally homogeneous, and the morphology of their surface is rather responsible for certain inhomogeneities observed in the images. On the other hand, notable variations in the intensity of signals originating from the main components of the analyzed samples were noted. The lowest values of the  $\text{Al}^+/\text{Si}^+$  intensity ratio were found for CBV300 and CuY\_CBV300 (0.75 and 1.14, respectively), suggesting the lowest aluminum concentrations. For the remaining samples, the  $\text{Al}^+/\text{Si}^+$  intensity ratio varied between 2.99 and 4.69 for zeolites, and 1.31 and 3.51 for Cu-containing materials. A different trend was observed for the  $\text{Cu}^+/\text{Al}^+$  intensity ratio, which reached its highest value for the CuY\_CBV100 sample (0.66). This catalyst also exhibited the highest value of  $\text{Cu}^+/\text{total ion}^+$  (0.019). In contrast, variations in the  $\text{Cu}^+/\text{Si}^+$

ratio were less pronounced, ranging from 0.62 for CuY\_CVB300 to 0.93 in the case of CuY\_CVB400.

Fig. 2a shows the DR UV-vis spectra of Cu-containing zeolite Y samples (calcined at  $550 \text{ }^\circ\text{C}$  for 4 h in static air). For all samples, well-defined and distinct peaks were observed. According to the literature, the absorption bands in the 200–260 nm range can be attributed to oxygen-to-metal charge-transfer transitions associated with  $\text{Cu}^+$  or  $\text{Cu}^{2+}$  cations stabilized within the zeolite framework.<sup>27,28</sup> The bands observed between 260 and 550 nm indicate the presence of  $\text{Cu}_x\text{O}_y$  species and  $[\text{Cu}-\text{O}-\text{Cu}]^{2+}$  species.<sup>29,30</sup> However, in our previous study,<sup>21</sup> we excluded the presence of  $[\text{Cu}-\text{O}-\text{Cu}]^{2+}$  species in the Cu-containing zeolite Y samples. Absorption in the 550–900 nm region is assigned to the d-d transitions of  $\text{Cu}^{2+}$  ions in pseudo-octahedral coordination, such as  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ .<sup>27,28</sup> Fig. 2b and S5 show the solid-state  $^{29}\text{Si}$  and  $^{27}\text{Al}$  NMR spectra of the Cu-containing zeolite Y samples, while Tables S4 and S5 present the deconvolution of  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR spectra. The  $^{29}\text{Si}$  Al MAS-NMR spectra of all Cu-ion-exchanged zeolites

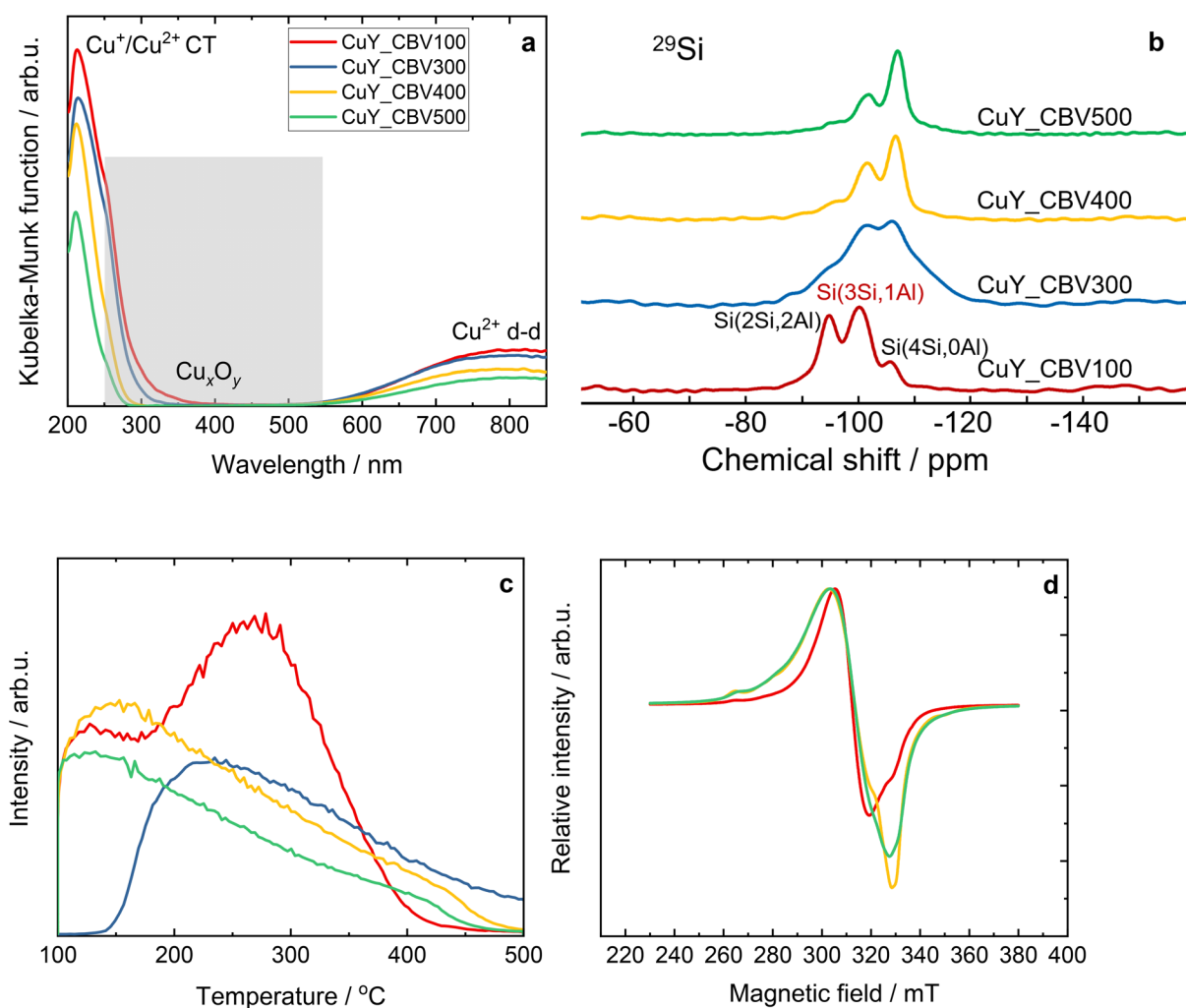


Fig. 2 a) DR UV-vis spectra, b)  $^{29}\text{Si}$  MAS spectra and c)  $\text{NH}_3$ -TPD spectra of Cu-containing zeolite Y samples and d) CW-EPR spectra of the activated samples recorded at  $-196 \text{ }^\circ\text{C}$ ; a-d) the sample names are the same.



showed that the contribution of Si sites significantly varied among samples. In all spectra, contributions from Si(0Al), Si(1Al), and Si(2Al) are present. In general, an increase of Si(0Al) is observed from CuY\_CBV100 to CuY\_CBV500. CuY\_CBV300 shows broader signals, indicating a large distribution of shifts due to a more disordered arrangement of silicon sites. The  $^{27}\text{Al}$  spectra are dominated by the signal at *ca.* 61 ppm, indicating four-coordinated aluminum as expected.<sup>31,32</sup> CuY\_CBV100 shows an ordered signal, while the other samples are best described by a distribution of chemical shifts leading to broader signals. Additionally, the amount of five- and especially six-coordinated aluminum increases from CuY\_CBV300 to CuY\_CBV500. Six-coordinated aluminum is typically assigned to extra-framework aluminum, while five-coordinated aluminum hints at some defects in the structure.

Fig. 2c presents the  $\text{NH}_3$ -TPD spectra of Cu-containing zeolite Y samples. According to the literature indications, the peak below 200 °C is derived from weakly adsorbed ammonia molecules *via* hydrogen bonding, while the peaks above 200 °C are attributed to strong Brønsted acid sites.<sup>33,34</sup> The tetrahedral framework of these aluminosilicates introduces a negative charge within the zeolite structure. When this charge is balanced by a proton, oxygen becomes bonded to the Si–O–Al bridge, forming hydroxyl groups that serve as strong Brønsted acid sites. The interaction between aluminum and oxygen atoms weakens the O–H bond, thereby enhancing the acidity of the protons in the [–Al(OH)–Si–] groups.<sup>35</sup> However, as the number of aluminum atoms increases, the framework becomes less unbalanced, resulting in a decrease in the strength of the acid sites. All samples possess a similar  $n(\text{Si})/n(\text{Al})$  ratio; however, there are significant differences in Si species. CuY\_CBV100 revealed a significant contribution of both Si(2Si, 2Al) and Si(3Si, 1Al), while for other samples, there is an increasing contribution of Si(4Si, 0Al) species. For CuY\_CBV100,  $\text{Na}^+$  cations are inherently weak Lewis acid sites and contribute to the adsorbed ammonia below 200 °C.

Fig. S6 and 2d show the CW-EPR spectra of the activated samples recorded at –196 °C. The weights of the samples are measured beforehand to get a weight-normalized EPR spectrum for each of the samples afterwards. The samples are measured using X-band continuous wave EPR spectroscopy for the hydrated state (as-made) at –196 °C (Fig. S6). It is evident from the spectrum that the  $\text{Cu}^{2+}$  species is present in all the samples, and they exhibit different spectral behaviour. Double integration of the EPR spectra indicates the intensity of  $\text{Cu}^{2+}$  species present in the samples. It is normalized to the  $\text{Cu}^{2+}$  intensity in CuY\_CBV500 and listed in Table S6. After this, all the samples are activated using a vacuum of  $1 \times 10^{-2}$  mbar at a temperature of 250 °C for 2 h and then cooled down gradually back to room temperature. Then, the EPR spectra are recorded to see the changes caused by the activation procedure. Upon simulation using EasySpin 6.0.6,<sup>36</sup> the presence of two species is revealed with an axially

symmetric species, species *C* and an isotropic species, species *D*. The spin Hamiltonian parameters used for species *C* are  $g_{xx} = g_{yy} = 2.08$  (1),  $g_{zz} = 2.33$  (1) and  $A_{xx} = A_{yy} = 60$  (8) MHz,  $A_{zz} = 520$  (5) MHz; whereas for species *B*,  $g_{\text{iso}} = 2.16$  (1). The Gaussian line shape is used for both the species, with 2.5 mT broadening for species *C* and 20 mT broadening for species *D*. In this case, nonzero *g* strain is used and is listed in Table S7. Fig. S7 shows the weighted average experimental spectra and the simulated spectra for all the activated samples. The species *C* arises from the  $\text{Cu}^{2+}$  ions present in the hexagonal prism of the zeolite, bound to six zeolitic oxygens.<sup>37</sup> The species *D* arises from a high local concentration of  $\text{Cu}^{2+}$  that could potentially be from the higher local concentration of species *C*.<sup>37</sup> The weight of the individual species is given in Table S8 (uncertainty 5%). Based on this analysis, we have isolated magnetically diluted  $\text{Cu}^{2+}$  species as hexaaqua water complexes exist in the fresh material and as  $\text{Cu}^{2+}$  in the hexagonal prisms bound to six framework oxygens. But the majority of the  $\text{Cu}^{2+}$  appears as non-magnetically diluted  $\text{Cu}^{2+}$ , in either hexaaquawater complexes or presumably also hexagonal prisms. The amount of the latter seems to increase after activation, especially in the CuY\_CBV100 sample. Indeed,  $\text{Cu}^{2+}$  species serve as active centers for low temperature during  $\text{NH}_3$ -SCR-DeNO<sub>x</sub>.<sup>21</sup>

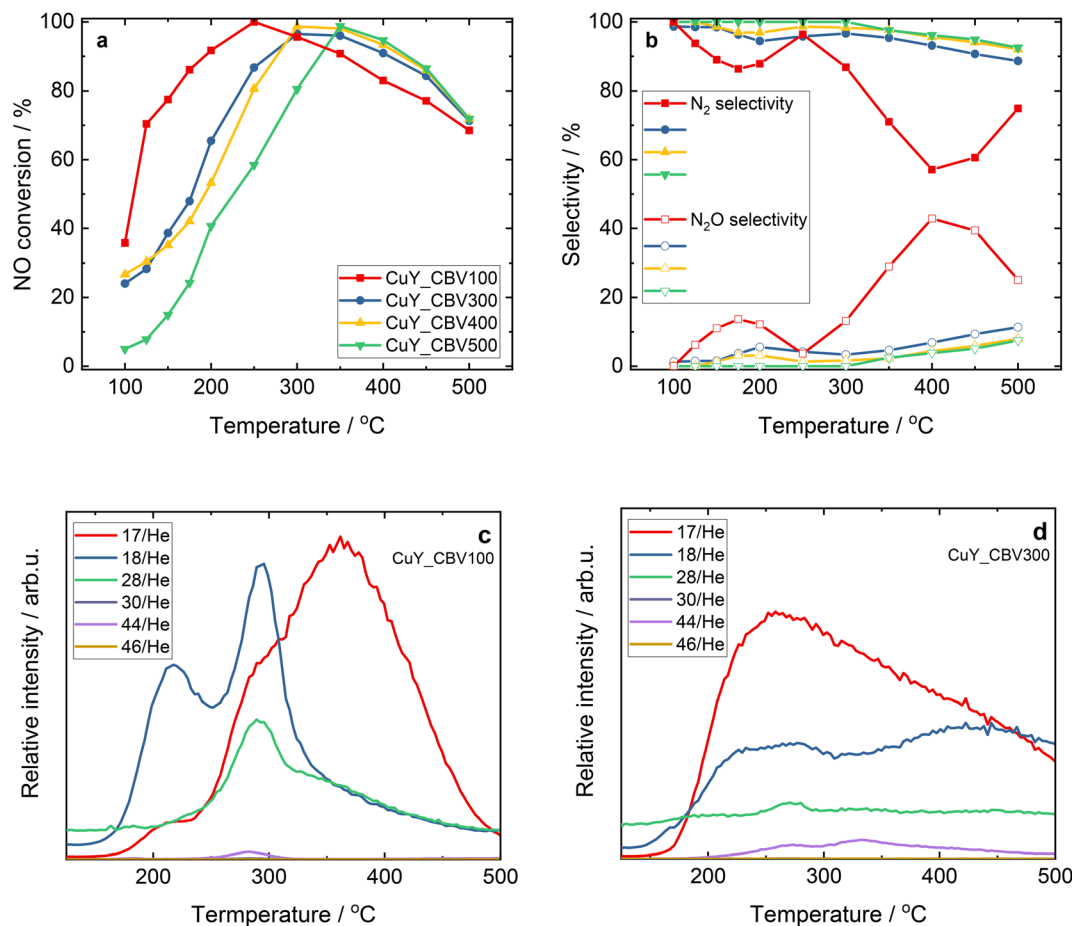
### 3.2. Catalytic studies and sample-specific insights into $\text{NH}_3$ -SCR-DeNO<sub>x</sub>

Fig. 3 shows the NO conversion and selectivity of Cu-containing zeolites during  $\text{NH}_3$ -SCR-DeNO<sub>x</sub>. Similar to our previous studies,<sup>21</sup> CuY\_CBV100 approved the highest activity together with the highest formation of  $\text{N}_2\text{O}$ . Similarly, CuY\_CBV500 shows NO conversion below 80% below 300 °C, with  $\text{N}_2$  selectivity above 85%. Interestingly, we did not observe any differences in the catalytic data for the samples prepared from as-received zeolites compared to calcined zeolites (before ion exchange with a copper precursor).

Both CuY\_CBV300 and CuY\_CBV400 possess similar activity and  $\text{N}_2$  selectivity in  $\text{NH}_3$ -SCR-DeNO<sub>x</sub>, as in fact it is the same support zeolite Y (starting form of CBV300 is in  $\text{NH}_4^+$ , while for CBV400 it is  $\text{H}^+$ ). Dynamic changes of Cu-containing zeolite Y samples (Fig. S8) were investigated in six consecutive reactions of heating up (75–500 °C) and cooling down (500–75 °C). The catalysts revealed stable NO conversion and  $\text{N}_2$  selectivity.

Furthermore, we conducted stop flow studies for all catalysts at 125 °C (Fig. 3c and d and S9). Thus,  $\text{NH}_3$ -SCR-DeNO<sub>x</sub> was conducted at 125 °C for 2 h, followed by purging in He for 3 h and finally, temperature-programmed studies from 125 °C up to 500 °C. In addition to  $\text{NH}_3$  (mass-to-charge ratio (*m/z*) 17) and/or NO (*m/z* 30) desorption, the detection of reaction products such as  $\text{N}_2$  (*m/z* 28),  $\text{N}_2\text{O}$  (*m/z* 44),  $\text{NO}_2$  (*m/z* 46), and  $\text{H}_2\text{O}$  (*m/z* 18) was also conducted. The stop flow analysis revealed that the adsorbed ammonia was the main difference between CuY\_CBV100 and CuY\_CBV300 (300/500), and thus, their





**Fig. 3** a) NO conversion and b)  $N_2$  and  $N_2O$  selectivity during  $NH_3$ -SCR-De $NO_x$  over Cu-containing Y samples; a) and b) the sample names are the same. c) and d) Stop-flow experiments over Cu-containing Y samples. Reaction conditions:  $m_K = 0.1$  g,  $c(NO) = 0.1$  vol%,  $c(NH_3) = 0.1$  vol%,  $c(O_2) = 5$  vol%, He balance,  $F_{TOT} = 120$  ml  $min^{-1}$ , GHSV = 30 000  $h^{-1}$ .

accessibility for NO molecules from the gas phase during the  $NH_3$ -SCR-De $NO_x$  and  $NH_3$  oxidation above 350 °C. Also, the shape of the  $NH_3$  adsorbed during stop-flow analysis is similar to the one detected during  $NH_3$ -TPD profiles (Fig. 3c and d vs. 2c). Additionally, we carried out modulation excitation diffuse reflectance infrared Fourier transform spectroscopy (ME DRIFTS). From Fig. 4a, only  $NH_3$  adsorbed on Lewis acid sites (L- $NH_3$ ) is observed on CuY\_CBV100. When the  $NH_3$  adsorbed surface of CuY\_CBV100 is exposed to NO, the L- $NH_3$  decreases, and a peak at ca. 1440  $cm^{-1}$  and a band between 3000 and 2000  $cm^{-1}$  rise. It indicates that L- $NH_3$  is consumed by NO, and the  $H_2O$  product is formed, which does not leave the surface and adsorbs to induce these peaks due to the relatively low temperature. One possibility that cannot be ruled out is that the  $H_2O$  product induces the formation of Brønsted acid sites,<sup>38,39</sup> then some L- $NH_3$  moves to the BAS and induces the peaks of 1440  $cm^{-1}$ . For CuY\_CBV300, CuY\_CBV400, and CuY\_CBV500, L- $NH_3$  and B- $NH_3$  are detected, and the amount of B- $NH_3$  is ranked as CuY\_CBV300 < CuY\_CBV400 < CuY\_CBV500. This means that there are more BAS on CuY\_CBV500. When the  $NH_3$

adsorbed surface of CuY\_CBV500 is exposed to NO, L- $NH_3$  and B- $NH_3$  both decrease, which means that they are consumed by NO.

For CuY\_CBV100, peaks at 1650, 1614 and 1440  $cm^{-1}$  show an obvious response to the NO pulse in  $NH_3 + O_2$ , and the peak at 1614 shows opposite dynamic change compared to the peak at 1650  $cm^{-1}$ , similar to that at 1440  $cm^{-1}$ . This means that the consumption of L- $NH_3$  induces the formation of species attributed to 1650 and 1440  $cm^{-1}$ . Furthermore, the peak at 1440  $cm^{-1}$  shows a slight delay compared to 1650  $cm^{-1}$ , which might be due to the reason that the species at 1650  $cm^{-1}$  induces the formation of species at 1440  $cm^{-1}$ . For CuY\_CBV300, CuY\_CBV400, and CuY\_CBV500, the intensity of response to the NO pulse is obviously lower than that of CuY\_CBV100, and they are ranked as CuY\_CBV300 > CuY\_CBV400 > CuY\_CBV500.

In addition, the peak at 1620  $cm^{-1}$  shows opposite dynamic change compared to the peak at 1450  $cm^{-1}$ . It seems that LAS domains trigger this reaction (Fig. 5 and S10).

Recently, Kubota *et al.*<sup>9</sup> published molecular aspects of the mechanism of  $NH_3$ -SCR-De $NO_x$  on tungsten-loaded ceria from modulated excitation DRIFTS. This mechanism seems



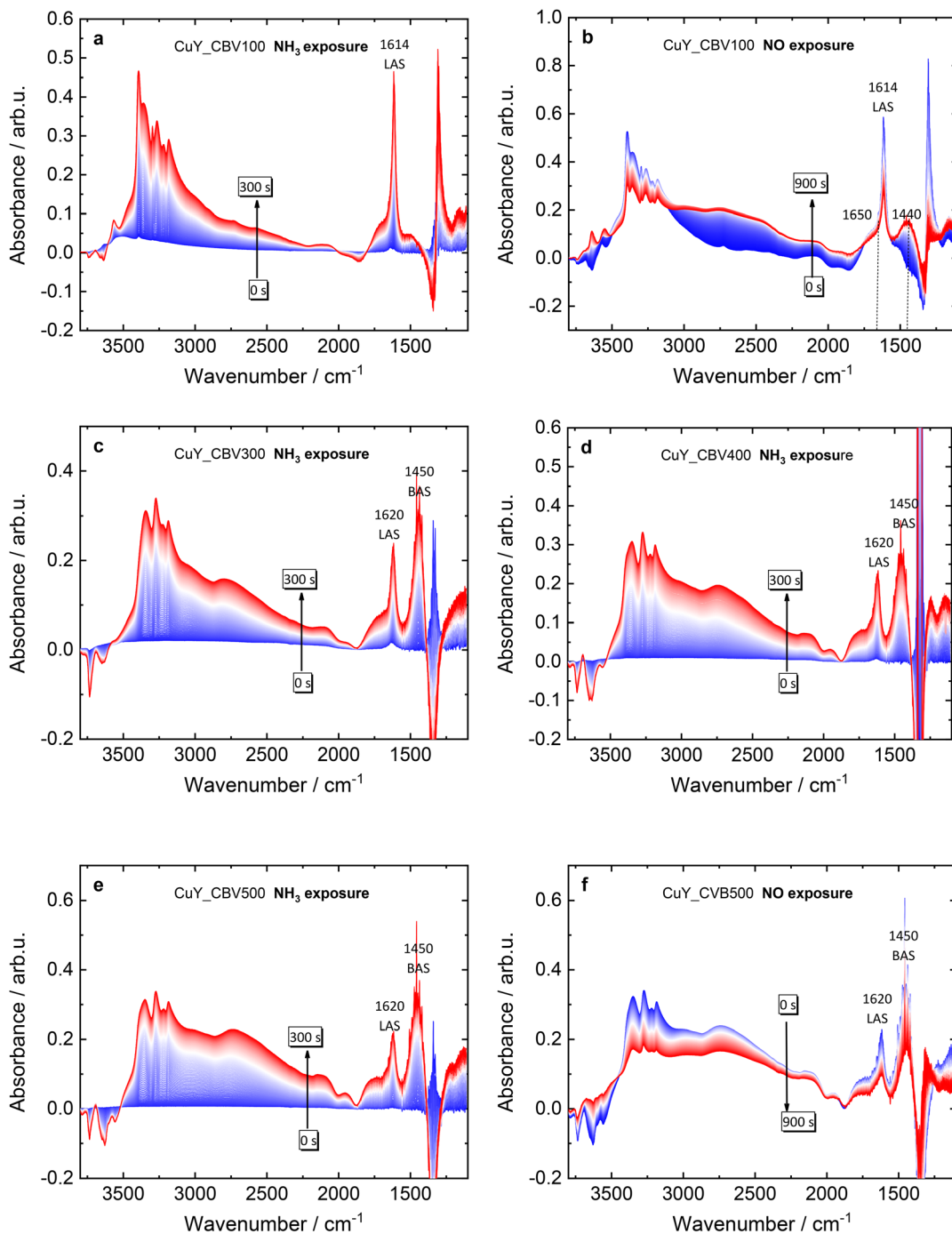


Fig. 4 Time-resolved *in situ* IR spectra of  $\text{NH}_3$  adsorption (a) and NO exposure (b) on CuY\_CBV100, time-resolved *in situ* IR spectra of  $\text{NH}_3$  adsorption on CuY\_CBV300 (c) and CuY\_CBV400 (d), and time-resolved *in situ* IR spectra of  $\text{NH}_3$  adsorption (e) and NO exposure (f) on CuY\_CBV500.

to be valid also, in our case. Thus, we could assume that during the  $\text{NH}_3$ -SCR-DeNO<sub>x</sub> process,  $\text{NH}_3$  adsorbed on  $\text{Cu}^{2+}$  Lewis acid sites reacts with NO to produce  $\text{Cu}^+$  sites,  $\text{N}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{H}^+$  associated with Brønsted acid sites. The protons from the initially adsorbed Lewis acid sites desorb and are subsequently re-adsorbed onto the newly formed Brønsted acid sites, while  $\text{Cu}^{2+}$  is regenerated through oxidation facilitated by  $\text{O}_2$  and  $\text{H}^+$ .

Fig. 6 presents the results of the SSITKA analysis between 100 and 150 °C for the Cu-containing zeolite Y. Under steady-state conditions, switching between unlabeled and labeled reaction mixtures was performed without perturbation. Consequently, the total rate of formation of any product (*i.e.*, the chemical composition of the surface) does not change due to the abrupt replacement of one reactant by its isotope. In this way, kinetic parameters such as the average surface



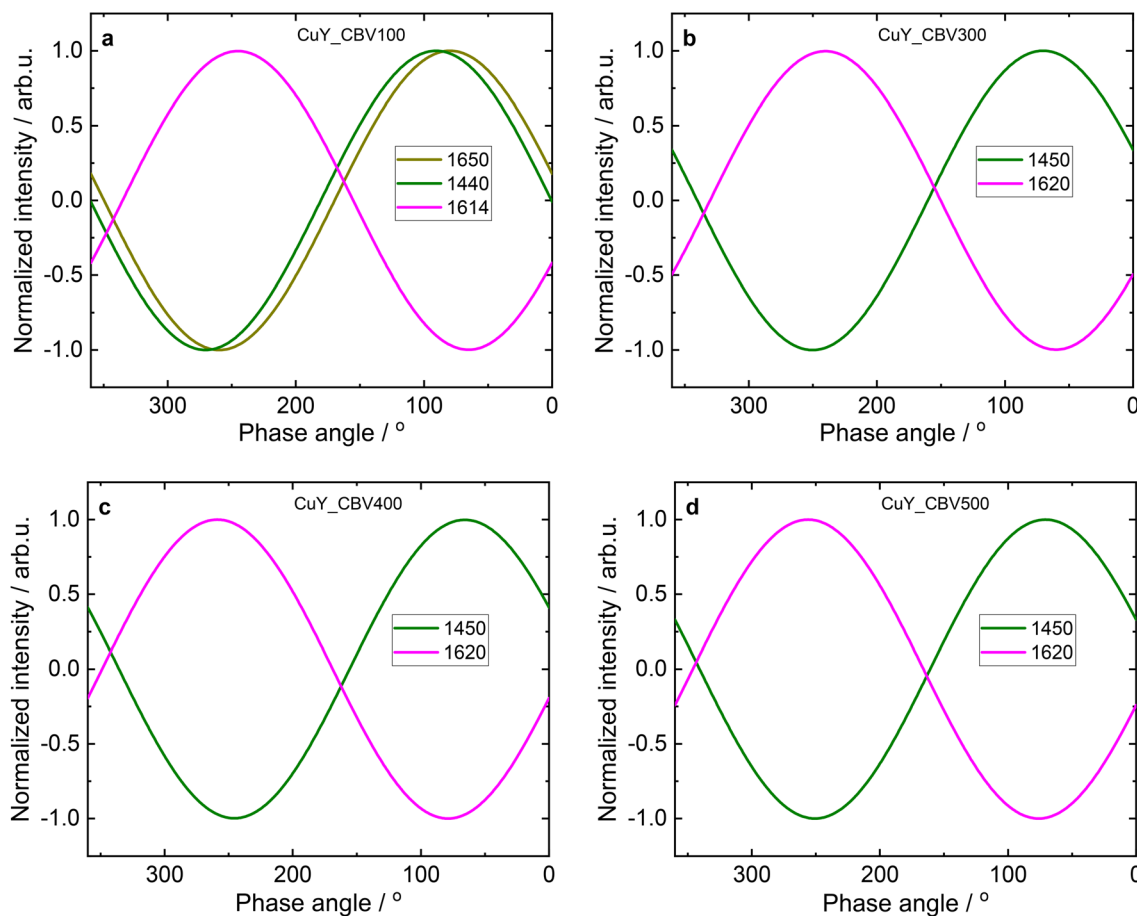


Fig. 5 Phase angle dependence of the IR signal intensity of selected peaks on CuY\_CBV100 (a) and CuY\_CBV300 (b) and the phase angle dependence of the IR signal intensity of selected peaks on CuY\_CBV400 (c) and CuY\_CBV500 (d).

lifetime and surface concentration of the main intermediates (not of any inactive (spectator) species) can be determined. The SSITKA studies were carried out at 100, 125, and 150 °C. Compared to our previous work,<sup>21</sup> we applied two measurement times: 5 and 10 minutes in order to check how the rates of change in these kinetic parameters differ among the studied catalysts. For all materials, the average surface lifetime of reversibly adsorbed  $\text{NH}_3$  increased with time; however, it did not change significantly with the applied temperature. On the other hand, the surface concentration of reversibly adsorbed  $\text{NH}_3$  decreases with increasing temperature, suggesting that the concentration of inactive  $\text{NH}_3$  molecules on the catalyst surface decreases. These changes agreed with the catalytic activity results (Fig. 3a) – the most active catalyst (CuY\_CBV100) adsorbs the lowest amounts of inactive  $\text{NH}_3$  molecules, while the least active catalyst (CuY\_CBV500) adsorbs the highest quantities of inactive ammonium molecules. In the case of CuY\_CBV300 and CuY\_CBV400, the values of the surface concentration of reversibly adsorbed  $\text{NH}_3$  are very similar to each other, because their activity is also very similar.

Based on the SSITKA results, the average surface lifetime and surface concentration of nitrogen and its intermediates involved in nitrogen formation were also

calculated (Fig. 6b, d, f and h). The average surface lifetime values for the analysed temperatures (100, 125, and 150 °C) are very similar, whereas some slight differences are observed between the studied catalysts. The most interesting behaviour is observed for the values of the surface concentration of nitrogen and its intermediates involved in nitrogen formation. Extending the analysis time to 10 min allowed for obtaining higher values of the average-surface lifetime and surface concentrations, but did not vary the trend of their changes with temperature.

The highest values were obtained for CuY\_CBV100, which is the most active catalyst. This means that, on its surface, there are the most considerable amounts of active centres. In the case of CuY\_CBV300 and CuY\_CBV400, these values are similar but lower than those for CuY\_CBV100. These two catalytic materials (CuY\_CBV300 and CuY\_CBV400) exhibit practically the same, but lower, activity in the  $\text{NH}_3$ -SCR-DeNO<sub>x</sub> process. The worst catalytic material (CuY\_CBV500 catalyst) shows the lowest (below 20 mmol g<sup>-1</sup>) surface concentration of nitrogen and its intermediates involved in nitrogen formation in all the studied measurements.

To summarize this part, it can be stated that although all catalytic materials adsorb large amounts of ammonia (Fig. 2c), only a part of these sites becomes active for the



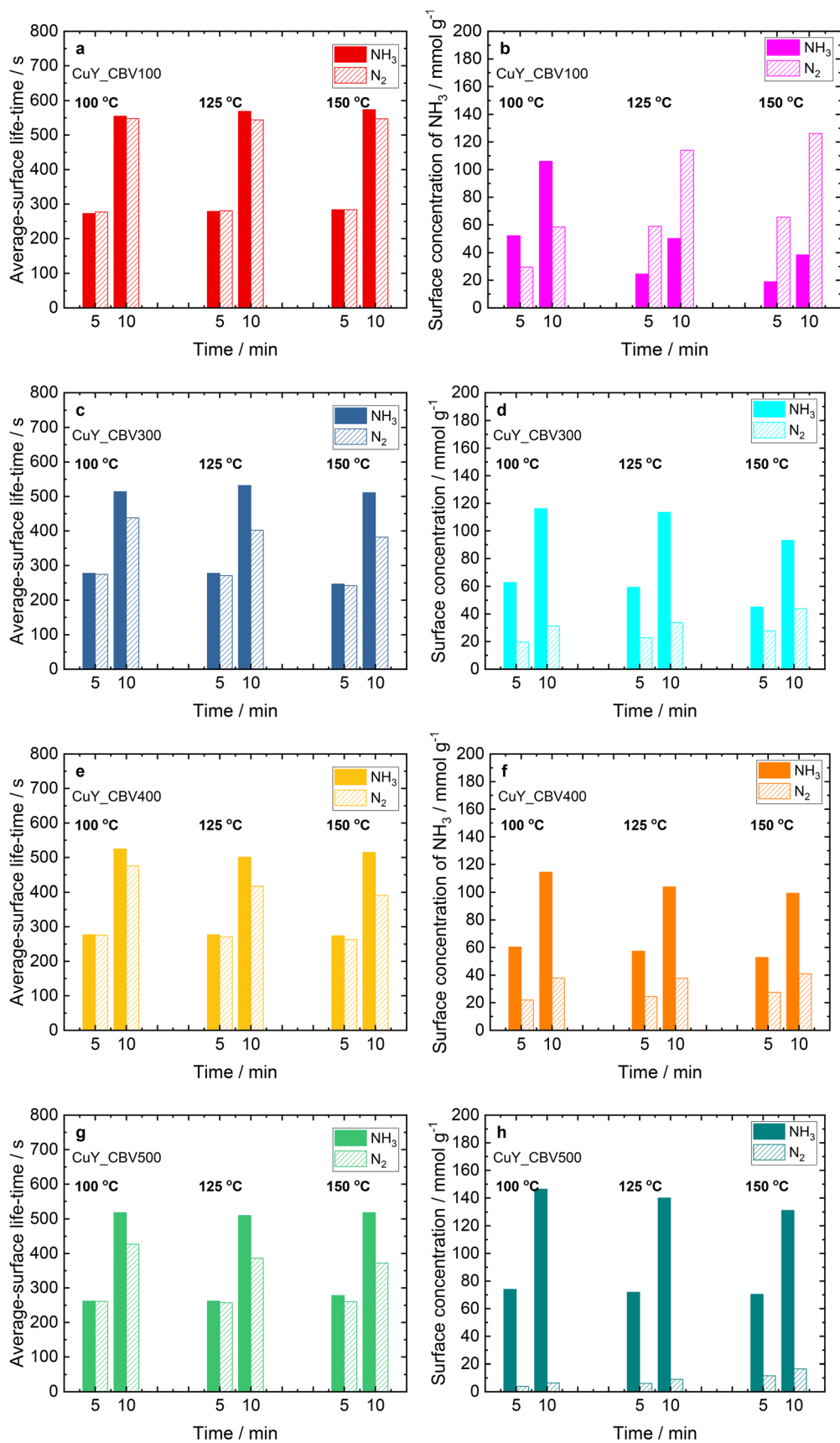


Fig. 6 a, c, e and g) Average-surface lifetime of reversibly adsorbed ammonia, adsorbed nitrogen molecules, and intermediates leading to the formation of nitrogen and b, d, f and h) surface concentration of reversibly adsorbed ammonia, adsorbed nitrogen molecules, and intermediates leading to the formation of nitrogen.



NH<sub>3</sub>-SCR-DeNO<sub>x</sub> process. This behavior is correlated with the increase in acidity (*i.e.*, Lewis acid sites) of the catalytic materials.

## 4. Conclusions

A series of copper-modified commercial zeolite Y catalysts were investigated for their activity and N<sub>2</sub> selectivity in the NH<sub>3</sub>-SCR-DeNO<sub>x</sub> reaction. Modulated excitation *in situ*/operando infrared (IR) spectroscopy and phase-sensitive detection (PSD) were applied to study the reaction intermediates that formed on the Cu-containing Y zeolite samples during transient experiments. For CuY\_CBV100, after NO exposure to the NH<sub>3</sub> preadsorbed surface, the NH<sub>3</sub> adsorbed on Lewis acid sites (L-NH<sub>3</sub>) decreases, while new Brønsted acid sites form (B-NH<sub>3</sub>). Then, some L-NH<sub>3</sub> moves to the BAS. Thus, the LAS domains govern the NH<sub>3</sub>-SCR-DeNO<sub>x</sub> reaction. For modulation excitation results, for CuY\_CBV300, CuY\_CBV400, and CuY\_CBV500, the intensity of the response to the NO pulse is obviously lower than that of CuY\_CBV100. As for CuY\_CBV500, the situation is different; we can see that the B-NH<sub>3</sub> peak is quite strong, which means a large number of BAS exist on the CuY\_CBV500 surface. NO can react with both L-NH<sub>3</sub> and B-NH<sub>3</sub> (whose presence facilitates high N<sub>2</sub> selectivity).

By the application of SSITKA, we determined the average-surface lifetime and surface concentration of NH<sub>3</sub>, nitrogen and intermediates leading to the formation of nitrogen at different temperatures and times of exchange of NH<sub>3</sub>. The number of active sites was found as the key parameter for the activity of CuY\_CBV100 in NH<sub>3</sub>-SCR-DeNO<sub>x</sub>, while N<sub>2</sub> selectivity is determined by slower rates of ammonia consumption during the reaction, as for CuY\_CBV500.

## Author contributions

Magdalena Jabłońska: conceptualization, methodology, investigation, data curation, writing – original draft and review & editing, supervision, data management, project management, and resources. Rujito S. R. Suharbiansah: investigation, data curation, and writing – review & editing. Jie Yang: investigation, data curation, and writing – review & editing. Marek Rotko: data curation and review. Pranjit Das: investigation, data curation, and writing – review & editing. Marko Bertmer: investigation and data curation. Jacek Grams: investigation and data curation. Junjiang Zhu: review. Andreas Pöppel: review.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI).

Supplementary information is available. See DOI: <https://doi.org/10.1039/d5cy01536g>.

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