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Engineering Pt nanoclusters on CeO₂ surface with abundant point defects by *in situ* confined-domain encapsulation strategy for the catalytic elimination of VOCs†

Siyi Ma,^{ab} Fang Dong,^{ac} Weiliang Han,^a Weigao Han^a and Zhicheng Tang^{id}*^a

Pt nanoclusters are a promising catalyst for VOC catalytic combustion, but they have been rarely studied so far. Herein, Pt nanoclusters (Pt NCs) and Pt nanoparticles (Pt NPs) were constructed by an *in situ* confined-domain encapsulation strategy, and then the reaction mechanism of Pt species on the catalytic combustion of VOCs was studied systematically. Interestingly, the addition process of Pt and Ce components greatly affected the dispersion and surface states of Pt species. The catalytic performance over Pt_{NC}@CeO₂ (0.01 wt% Pt loadings) was proved to be of outstanding activity and stability, and the reason was related to the contribution of Pt nanoclusters and more lattice oxygen and Ce³⁺ species, whose formation was inextricably linked to the strong interfacial effect between Pt and CeO₂. Notably, the *in situ* introduction approach of Pt species can effectively build up the point defects on the surface of CeO₂ to promote the dispersion and anchoring of Pt species. *In situ* DRIFT spectroscopy verified that the role of lattice oxygen was significant in accelerating the catalytic oxidation of VOCs, and the oxidation process of toluene followed the reaction path: toluene → benzyl alcohol → benzaldehyde → benzoic acid → phenol → maleic anhydride → carbon dioxide and water. Meanwhile, the rate-determining step in the oxidation of toluene may be the further decomposition of alcohol or carboxylic acid intermediates.

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1. Introduction

Volatile organic compounds (VOCs) have a significant effect on the atmosphere. As one of the contaminants in the atmosphere, VOCs can also cause relatively serious damage to human health.^{1,2} In fact, VOCs are essential precursors to pollutants like ozone, photochemical smog, and PM_{2.5} and are mostly produced by the production activities of industrial and human sources. Therefore, it is of great importance to convert VOCs into environmentally friendly substances to minimize the impact on human health and the environment. Toluene, as one of the typical indoor VOCs, is mainly used in various common materials, including paints, furniture, adhesives, upholstery materials and chemical solvents.^{3,4} The

most important point is that nowadays, people are exposed most of the time to toluene, so highly attentive efforts are required to eliminate toluene.⁵ Currently, catalytic oxidation is a more significant and effective method for VOC elimination.^{6,7} Moreover, as a key factor in the reaction process, the catalytic performance of catalysts has a positive relationship with the efficiency of VOC elimination.⁸ Obviously, designing a class of excellent and efficient catalysts can help promote the prevention and control of VOC pollutants.

Compared with non-precious metal catalysts, precious metal catalysts^{9–12} are selected to promote the catalytic oxidation efficiency of VOCs by virtue of their high catalytic activity, strong anti-inactivation ability, and low reaction temperature. Among the noble metal catalysts, platinum-based catalysts have better catalytic effects for hydrocarbon and aromatic hydrocarbon VOCs.^{13–15} Naturally, the key to preparing highly active platinum-based catalysts is to improve the active centers, which requires the assistance of a carrier. The typical active carrier cerium dioxide (CeO₂), with its unique characteristic of defect-prone structure and interconversion between different valence states of cerium,¹⁶ can act extensively in VOC catalytic combustion especially after the addition of the noble metal platinum (Pt).^{17,18} More

^a National Engineering Research Center for Fine Petrochemical Intermediates, and State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China.

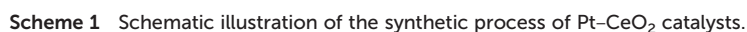
E-mail: tangzhicheng@licp.cas.cn; Tel: +86 931 4968083

^b University of Chinese Academy of Sciences, Beijing 100039, China

^c Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China

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Herein, Pt NCs and Pt NPs were constructed by an *in situ* confined-domain encapsulation strategy, and the reaction mechanism of the action of Pt species was systematically investigated. In order to carefully optimize Pt-CeO₂ catalysts, the effects of Pt and Ce species on the catalytic performance of Pt-CeO₂ catalysts were examined in this article. Scheme 1 shows the preparation process of each catalyst. Among them, adding sodium borohydride (NaBH₄) *in situ* to generate more Ce³⁺ species was beneficial to promote the catalytic performance.³⁵ With the aid of many characterization



methods, the $\text{Pt}_{\text{NC}}@\text{CeO}_2$ catalyst prepared by an *in situ* confined strategy demonstrated good catalytic performance. With more lattice oxygen and Ce^{3+} species over the $\text{Pt}_{\text{NC}}@\text{CeO}_2$ catalyst, an abundance of oxygen vacancies could be generated, thus effectively regulating the electronic structure. The formation of the interfacial effect between Pt and Ce by $\text{Pt}_{\text{NC}}@\text{CeO}_2$ was important, which caused changes in the surrounding coordination environment and also favored the anchoring of Pt nanoclusters. It was proved that the size and distribution of Pt species were impacted by the manner of the Pt and Ce introduction. In conclusion, we studied the toluene catalytic mechanism over $\text{Pt}_{\text{NC}}@\text{CeO}_2$ employing an *in situ* confined-domain encapsulation strategy to achieve the precise construction of noble metal catalysts, which showed a remarkable low-temperature activity as well as low Pt loading and good stability. As a result, this work provides Pt nanocluster catalysts with high catalytic activity, which would inspire researchers to pursue *in situ* confined methods to improve the catalytic activity of nanoclusters and offer some implications for the precise construction of highly dispersed Pt nanoparticles.

2. Experimental contents

2.1 Chemical reagents

Cerous nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), homophenic acid (H_3BTC), chloroplatinic acid (H_2PtCl_6), polyvinyl alcohol (PVA), sodium borohydride (NaBH_4), *N,N*-dimethylformamide (DMF) and other chemical reagents were used directly.

2.2 Preparation of $\text{Pt}_{\text{NP}}@\text{CeO}_2$ sample

In deionized water (20 mL) at 90 °C, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (3.472 g) and a small quantity of PVA (PVA/noble metal mass ratio = 1.2:1.0) were dissolved. After cooling, solution A was created by adding 0.037 mL H_2PtCl_6 (19.3 mmol L^{-1}). 38.4 g of NaOH (6 mol L^{-1}) was diluted in 140 mL deionized water to form solution B, and then solution B was combined with solution A to create solution C. Drops of dissolved NaBH_4 (0.05 g) in deionized water were then added to solution C. After vigorous stirring for 30 min at ambient temperature, solution C was then added to a hydrothermal reactor (100 °C, 24 h). The resulting precipitate ($\text{Pt}_{\text{NP}}@\text{Ce}(\text{OH})_3$) was washed with distilled water before being vacuum-dried overnight at 80 °C and calcined in air for 4 h at 400 °C. The prepared sample was labeled as $\text{Pt}_{\text{NP}}@\text{CeO}_2$. On this basis, a catalyst without NaBH_4 incorporation was also synthesized, which is documented in the ESI.†

2.3 Preparation of $\text{Pt}_{\text{NC}}@\text{CeO}_2$ sample

A small amount of PVA (PVA/noble metal mass ratio = 1.2:1.0) and a certain amount of H_2PtCl_6 (0.037 mL) were mixed with distilled water at 90 °C. After cooling, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (3.472 g) was added to the chloroplatinic acid solution to form solution A. Meanwhile, 38.4 g of NaOH (6 mol L^{-1}) was diluted in 140 mL of deionized water to make solution B.

Then solution C was obtained by mixing solution B with solution A. Subsequently, 0.05 g of NaBH_4 dissolved in distilled water was added dropwise to solution C. Next, solution C was stirred vigorously for 30 min (25 °C) and poured into a hydrothermal reactor for 24 h at a constant temperature of 100 °C. The precipitate was subsequently treated in the same way as the $\text{Pt}_{\text{NP}}@\text{Ce}(\text{OH})_3$ precipitate. The prepared sample was labeled as $\text{Pt}_{\text{NC}}@\text{CeO}_2$.

2.4 Preparation of $\text{Pt}_{\text{NP}}@\text{CeO}_2$ -MOF sample

To verify the influence of Pt introduction methods on the catalysts, $\text{Pt}_{\text{NP}}@\text{CeO}_2$ -MOF catalyst was prepared. The catalyst was prepared using the same process as for the $\text{Pt}_{\text{NP}}@\text{CeO}_2$ sample and the only difference was the composition of solution B. The main additions to solution B were 1.681 g H_3BTC , 5 mL of deionized water and 20 mL of DMF. In addition, the dried $\text{Pt}_{\text{NP}}@\text{Ce}$ -MOF sample was roasted at 400 °C.

2.5 Preparation of $\text{Pt}_{\text{NP}}/\text{CeO}_2$ sample

The $\text{Pt}_{\text{NP}}/\text{CeO}_2$ sample was also synthesized in the same way as the $\text{Pt}_{\text{NP}}@\text{CeO}_2$ sample, except that H_2PtCl_6 was added in a different way. The $\text{Pt}_{\text{NP}}/\text{CeO}_2$ sample was impregnated with H_2PtCl_6 (0.023 mL) onto 0.861 g CeO_2 .

2.6 Characterization technique

We used *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to probe the reaction mechanism. The results were obtained using a VERTEX 70 spectrometer which consists of an MCT detector and a CaF_2 window *in situ* cell. The frequency range of the spectra is mainly from 4000 to 600 cm^{-1} . For the adsorption of VOCs, the $\text{Pt}_{\text{NC}}@\text{CeO}_2$ catalyst (200 mg) was pretreated for 30 min at 300 °C under N_2 . After cooling to 100 °C, the catalyst was exposed to VOCs/ N_2 (20 mL min^{-1}) and reached adsorption saturation for some time. Subsequently, N_2 was passed through and *in situ* DRIFTS spectra of the catalysts were collected at different temperatures (150 °C, 200 °C, 250 °C, 300 °C and 350 °C). Next, the same pretreatment and adsorption process was applied to the fresh $\text{Pt}_{\text{NC}}@\text{CeO}_2$ catalyst, and then air with a flow rate of 20 mL min^{-1} was fed at 100 °C to obtain *in situ* DRIFTS results at different temperatures.

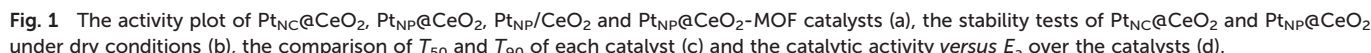
The details of other characterization techniques, such as transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, N_2 adsorption-desorption, inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray photoelectron spectroscopy (XPS), O_2 temperature-programmed desorption (O_2 -TPD), NH_3 temperature-programmed desorption (NH_3 -TPD), and H_2 temperature-programmed reduction (H_2 -TPR) are described in the ESI.†

3. Results and discussion

3.1 Catalytic performance

The catalysts were synthesized utilizing various methods. Fig. 1 displays the outcomes of the analysis. In Fig. 1a, the

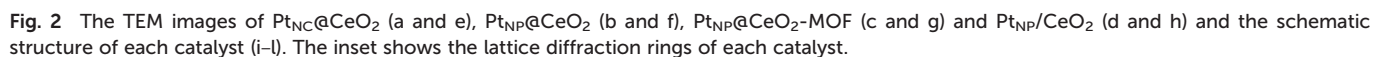




Subsequently, the thermal stability of Pt_{NC}@CeO₂ and Pt_{NP}@CeO₂ samples was tested under dry conditions at high and low conversions (Fig. 1b), respectively. For the Pt_{NC}@CeO₂ catalyst, the toluene conversion remained at 60-70% for 15 h at 220 °C, while that was maintained essentially above 90% at 260 °C. As for the Pt_{NP}@CeO₂ catalyst, the toluene conversion was kept between 60% and 65% for 15 h at 240 °C, while at 300 °C the toluene conversion was around 90% for 15 h, and slightly decreased after 10 h. Besides, we also performed stability tests (*T*₉₀) on Pt_{NC}@CeO₂ and Pt_{NP}@CeO₂ catalysts for up to 40 h (Fig. S1b†). The Pt_{NC}@CeO₂ sample still maintained 90% conversion, while the conversion of the Pt_{NP}@CeO₂ sample was maintained above 85%. It was clear that the Pt_{NC}@CeO₂ catalyst exhibited better durability at a high temperature than the Pt_{NP}@CeO₂ catalyst. The strategy of *in situ* introduction of Pt species could effectively promote the catalytic activity as shown in Fig. 1a. In Fig. 1c, a comparison of *T*₅₀ and *T*₉₀ for each catalyst was drawn. The temperature order of the low conversions for each catalyst was similarly consistent with the order of the high conversions, and the Pt_{NC}@CeO₂

have a length of 50–100 nm with a width of about 10 nm. The Pt_{NP}@CeO₂-MOF sample displayed an elongated rod-like structure with a length of 50–100 nm, and the Pt_{NP}/CeO₂ sample showed polyhedral structures of about 10 nm in diameter, demonstrating that the preparation methods had a massive effect on the morphology of catalysts. For Pt_{NC}@CeO₂ and Pt_{NP}@CeO₂, the differed introduction methods of Pt and Ce species did not affect the catalyst morphology but altered the size of Pt species over the Pt/CeO₂ catalyst (Fig. 2e and f). Generally speaking, when the particle size is reduced to a nanocluster, the lattice is not easily identified and eventually disappears.³⁶ Therefore, it is clear that Pt_{NC}@CeO₂ had more Pt nanoclusters (Pt NCs) and the diameter of the nanoclusters was mainly less than 1 nm as seen by HRTEM.³⁷ The Pt_{NP}@CeO₂ sample exhibited the presence of nanoparticles (>1 nm) as shown in Fig. 2f, which could also be confirmed by Fig. S3.† In addition, the presence of Pt nanoparticles (Pt NPs) on Pt_{NP}@CeO₂-MOF and Pt_{NP}/CeO₂ samples is revealed in Fig. 2g and h. Combined with the catalytic performance, the production of Pt NCs was one of the crucial elements to enhance the catalytic activity. It may be because the metal atoms in nanoclusters were mainly located at the corners and edges with a large contact surface,³⁸ which increased the active sites' exposure and thus promoted the catalytic activity. Moreover, the irregularity of the microstructure may be the reason for the poor activity of the Pt_{NP}/CeO₂ catalyst.^{39,40}

Fig. 2 displays the micromorphology of each catalyst and the dispersion conditions of the Pt species by TEM. Pt_{NC}@CeO₂ and Pt_{NP}@CeO₂ exhibited short rod-shaped structures which



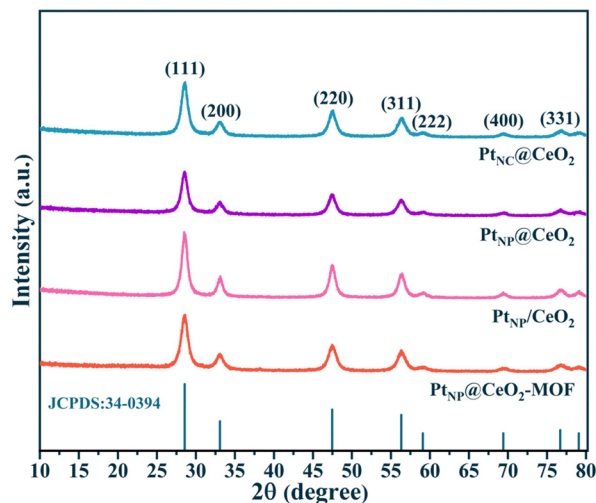


Fig. 3 The XRD patterns of the four catalysts.

The XRD patterns are shown in Fig. 3. The derived peaks of 28.6°, 33.1°, 47.5°, 56.3°, 59.1°, 69.4°, and 76.7° (2θ) were attributed to the (111), (200), (220), (311), (222) and (331) crystal planes of CeO₂ with face-centered cubic structure, respectively. The results could be compared with the XRD peaks of CeO₂ (JCPDS 34-0394), indicating that the four catalysts contained primarily the crystal structure of CeO₂. At the same time, the XRD patterns showed no Pt-related diffraction peak, which may be related with the low Pt content or the existence of highly dispersed Pt nanoparticles. In common, the presence of wider peaks in the XRD diffraction peaks indicated that the active metal components exhibited high dispersion,⁴¹ which facilitated the emergence of more active sites and thus promoted the catalytic oxidation process. In contrast to the Pt_{NP}@CeO₂ sample, Pt_{NC}@CeO₂ showed a border peak width, which implied that it had a smaller grain size contributing to the generation of lattice defects.^{42,43} The XRD results demonstrated that the different

methods of Pt and Ce introduction had an impact on the crystal sizes of the catalysts.

To gain insight into the molecular structure, Raman measurement was performed on the catalysts (Fig. 4). There were two main peaks for each catalyst in the Raman spectrum. The peak at around 458–464 cm^{-1} could be attributed to the Ce–O–Ce mode of the fluorite-type CeO_2 structure (F_{2g}).³¹ The peak of 579 cm^{-1} was attributed to the defect-induced (D) mode, which was associated with Ce^{3+} -induced oxygen vacancies. Metal–support interactions, in general, influenced the energy produced by the band in the D mode, implying that various amounts of oxygen vacancies were formed. It can be seen in Fig. 4a that more oxygen vacancies were exhibited in the $\text{Pt}_{\text{NC}}@\text{CeO}_2$ catalyst, which may be related to the presence of Ce^{3+} or may be due to the vibrations generated when the highly dispersed PtO interacts with the cerium oxide carrier to form Pt–O–Ce bonds, thus creating defects in the cerium oxide lattice, which was also consistent with the XRD result. Apparently, the D-mode peak of the $\text{Pt}_{\text{NP}}@\text{CeO}_2\text{-MOF}$ sample was relatively weak compared to that of the other three catalysts, which may also be caused by the insignificant interaction between the precious metal (Pt) and the carrier (CeO_2). More importantly, through the magnified schematic of Raman (Fig. 4b), compared with the $\text{Pt}_{\text{NP}}@\text{CeO}_2\text{-MOF}$ sample, we found that the F_{2g} mode bands of $\text{Pt}_{\text{NC}}@\text{CeO}_2$, $\text{Pt}_{\text{NP}}@\text{CeO}_2$ and $\text{Pt}_{\text{NP}}/\text{CeO}_2$ catalysts showed a certain degree of red shift and the peak intensity also decreased to a certain degree. This suggested that the structure of fluorite might have changed, which was confirmed to be due to the emergence of Pt–O–Ce bonds. It is possible that the introduction of the reducing agent promoted the construction of point defects in the carrier, thus contributing to the SMSI effect.⁴⁴ The Raman result elucidated that the formation of the SMSI effect in the $\text{Pt}_{\text{NC}}@\text{CeO}_2$ catalyst caused the production of additional Pt–O–Ce bonds. At the same time, the $\text{Pt}_{\text{NC}}@\text{CeO}_2$ catalyst generated more oxygen vacancies, which provided the active

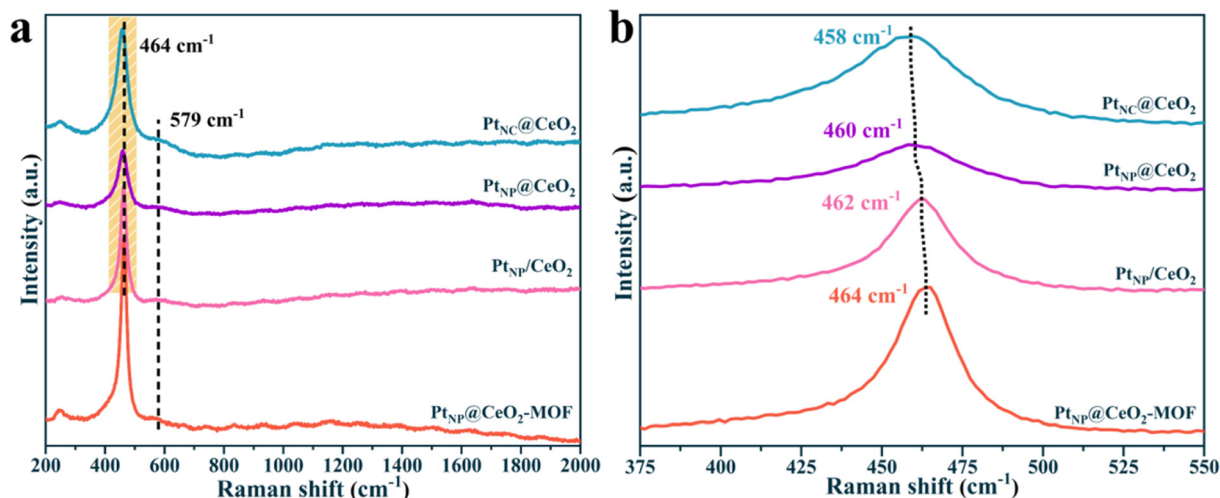


Fig. 4 Raman diagrams of the catalysts.



Fig. 5 The N_2 physisorption isotherms of catalysts (a) and the BJH pore size distributions of catalysts (b).

centers and promoted the catalytic reaction of VOCs. It was also verified that the $Pt_{NC}@CeO_2$ catalyst had the best activity, which was in agreement with the activity result.

Furthermore, the molecular structure and chemical bonds in the catalysts can be identified in the range of 500–4000 cm^{-1} by Fourier transform infrared spectroscopy (FTIR). The FTIR results of $Pt_{NC}@CeO_2$, $Pt_{NP}@CeO_2$, Pt_{NP}/CeO_2 and $Pt_{NP}@CeO_2$ -MOF are displayed in Fig. S4.† The broad peak at 3420 cm^{-1} was mainly attributable to the physically adsorbed water (H_2O), while the band at 1578 cm^{-1} corresponded to the $\delta(OH)$ vibration of H_2O molecules. The narrow band in the 2825–2990 cm^{-1} range was mainly associated with the incorporation of PVA. The presence of two broad bands within 990–1420 cm^{-1} was mainly related to the formation of “carbonate-like” materials on the surface of CeO_2 , possibly caused by residues in the catalysts,⁴⁵ and the peak at 848 cm^{-1} corresponded to the metal–oxygen bond. Notably, the $Pt_{NP}@CeO_2$, Pt_{NP}/CeO_2 and $Pt_{NP}@CeO_2$ -MOF catalysts showed an asymmetric stretching vibration band of CO_2 at 2352 cm^{-1} , but the $Pt_{NC}@CeO_2$ catalyst did not exhibit the corresponding peak. This indicated that CO_2 from the calcination process was not easily adsorbed on the surface of the $Pt_{NC}@CeO_2$ catalyst,⁴⁶ suggesting that CO_2 could be quickly desorbed. This may imply that the CO_2 products during the catalytic reaction are easily desorbed, thus facilitating the catalytic reaction of VOCs.

Naturally, the data on the pore structure and specific surface of each catalyst are also important parts of the analysis of catalytic microstructure. Thus, the BET data of each sample were calculated and the outcomes are presented in Fig. 5 and S5† and Table 1. According to the IUPAC classification, the N_2 adsorption–desorption isotherms of each catalyst exhibited distinct type IV isotherms with H3-type hysteresis loops of elongated crack-like structures.^{47,48} Table 1 shows the detailed BET data for $Pt_{NC}@CeO_2$, $Pt_{NP}@CeO_2$, Pt_{NP}/CeO_2 and $Pt_{NP}@CeO_2$ -MOF catalysts. The BET surface area of $Pt_{NC}@CeO_2$ with Pt nanoclusters was 112.22 $m^2 g^{-1}$, the pore volume was 0.37 $cm^3 g^{-1}$, and the average pore diameter was 13.04 nm. Most importantly, $Pt_{NC}@CeO_2$ had a larger specific surface, pore volume and average pore size than $Pt_{NP}@CeO_2$, Pt_{NP}/CeO_2 and $Pt_{NP}@CeO_2$ -MOF samples. Moreover, the order of the specific surface area was $Pt_{NC}@CeO_2$ (112.22 $m^2 g^{-1}$) > $Pt_{NP}@CeO_2$ (104.69 $m^2 g^{-1}$) > Pt_{NP}/CeO_2 (98.44 $m^2 g^{-1}$) > $Pt_{NP}@CeO_2$ -MOF (97.13 $m^2 g^{-1}$). It is worth noting that there was a direct relationship with the activity of the catalysts. In Fig. 5b and the enlarged schematic, it can be seen that there are two distinct peaks in the pore size between 0 and 50 nm and the $Pt_{NC}@CeO_2$ catalyst has the largest average pore size (13.04 nm) according to the data in Table 1. The $Pt_{NC}@CeO_2$ sample prepared by an *in situ* confined-domain encapsulation method with the larger pore size was more

Table 1 The data of specific surface, pore structure, and Pt content of catalysts

Catalysts	BET surface area ($m^2 g^{-1}$)	Pore size (nm)	Pore volume ($cm^3 g^{-1}$)	Pt content (wt%)
$Pt_{NC}@CeO_2$	112.22	13.04	0.37	0.0075
$Pt_{NP}@CeO_2$	104.69	12.19	0.32	0.0113
Pt_{NP}/CeO_2	98.44	9.60	0.24	0.0073
$Pt_{NP}@CeO_2$ -MOF	97.13	7.49	0.18	0.0097
CeO_2 -OH	107.42	7.96	0.26	—
CeO_2 -MOF	87.03	8.33	0.23	—

3.3 Analysis of surface chemical properties and redox behaviors of catalysts

a Ce 3d XPS spectra showing intensity (a.u.) versus binding energy (eV) for Pt_{NC}@CeO₂, Pt_{NP}@CeO₂, Pt_{NP}/CeO₂, and Pt_{NP}@CeO₂-MOF. Peaks are labeled u''', u'', u', u, v''', v'', v', and v.

b O 1s XPS spectra showing intensity (a.u.) versus binding energy (eV) for Pt_{NC}@CeO₂, Pt_{NP}@CeO₂, Pt_{NP}/CeO₂, and Pt_{NP}@CeO₂-MOF. Peaks are labeled O_{ads}, O_{latt}, and O_{OH}.

c Bar chart of oxygen species ratios (%) for Pt_{NC}@CeO₂, Pt_{NP}@CeO₂, Pt_{NP}/CeO₂, and Pt_{NP}@CeO₂-MOF. The ratios are: O_{latt} (pink), O_{ads} (blue), and O_{OH} (orange).

Catalyst	O _{latt} (%)	O _{ads} (%)	O _{OH} (%)
Pt _{NC} @CeO ₂	74.12	25.88	3.58
Pt _{NP} @CeO ₂	66.23	30.19	5.02
Pt _{NP} /CeO ₂	66.8	26.27	6.93
Pt _{NP} @CeO ₂ -MOF	66.4	33.6	-

d 3D bar chart of active species ratios (%) for Pt_{NC}@CeO₂, Pt_{NP}@CeO₂, Pt_{NP}/CeO₂, and Pt_{NP}@CeO₂-MOF. The ratios are: Ce³⁺ (purple) and O_{latt} (orange). The chemical reaction scheme is: Ce³⁺ + O_{latt} → Ce⁴⁺ + O_v.

Catalyst	Ce ³⁺ (%)	O _{latt} (%)
Pt _{NC} @CeO ₂	19.90%	74.12%
Pt _{NP} @CeO ₂	18.23%	70.91%
Pt _{NP} /CeO ₂	15.16%	66.80%
Pt _{NP} @CeO ₂ -MOF	14.08%	66.40%

Fig. 6 The XPS spectra about Ce 3d (a) and O 1s (b), the oxygen species ratios (c) and the active species ratios (d) of catalysts.

Table 2 The XPS data of catalysts

Catalysts	Ce ³⁺ /Ce _{total}	Ce ⁴⁺ /Ce _{total}	O _{latt} /O _{total}	O _{ads} /O _{total}	O _{OH} /O _{total}
Pt _{NC} @CeO ₂	19.90	80.10	74.12	25.88	—
u-Pt _{NC} @CeO ₂	14.64	85.36	66.23	30.19	3.58
Pt _{NP} @CeO ₂	18.23	81.77	70.91	24.07	5.02
u-Pt _{NP} @CeO ₂	15.16	84.84	66.80	26.27	6.93
Pt _{NP} /CeO ₂	16.57	83.43	69.17	30.83	—
Pt _{NP} @CeO ₂ -MOF	14.08	85.92	66.40	33.60	—
CeO ₂ -OH	16.38	83.62	68.99	24.87	6.14
CeO ₂ -MOF	14.03	85.97	65.57	34.43	—

species effectively promoted the generation of Ce³⁺ species, which contributed to the production of more oxygen vacancies, as seen in Table 2. It is worth mentioning that the introduction of reducing agents promoted the creation of Ce³⁺. Therefore, the presence of more reactive Ce³⁺ species in the catalyst implied the formation of more oxygen vacancies. Moreover, combined with the Raman results, it is clearly pointed out that oxygen vacancies were essential for toluene molecules. It meant that the Pt_{NC}@CeO₂ sample contained more active Ce³⁺ species, which promoted the production of more oxygen vacancies and unsaturated chemical bonds. The Pt_{NC}@CeO₂ catalyst had more outstanding activity than the other three catalysts. Thus, having more active Ce³⁺ species could effectively propel the activity at a lower temperature, and it was also confirmed that the presence of Ce³⁺ species was one of the beneficial factors to boost the catalytic reaction.

Moreover, the O 1s spectra of each catalyst are displayed in Fig. 6. The fine peaks at 529.2–529.4 eV, 531.3–531.5 eV and 532.9 eV corresponded to lattice oxygen (O_{latt}), surface adsorbed oxygen (O_{ads}) and surface hydroxyl (O_{OH}), respectively.^{52,53} The four catalysts contained mainly O_{latt} and O_{ads} with a small amount of O_{OH} (Fig. 6b). We also performed XPS on the oxygen species content of fresh and used Pt_{NC}@CeO₂ and Pt_{NP}@CeO₂ catalysts, and the results are illustrated in Fig. S8;† there was a significant reduction of O_{latt} content in the used catalysts. Subsequently, the percentages of oxygen species for each

catalyst were summarized and recorded in Table 2 and Fig. 6c for more visual analysis of the O_{latt}, O_{ads} and O_{OH}. Therefore, it is evident that the content of O_{latt} presented the following order: Pt_{NC}@CeO₂ (74.12%) > Pt_{NP}@CeO₂ (70.91%) > Pt_{NP}/CeO₂ (69.17%) > CeO₂-OH (68.99%) > Pt_{NP}@CeO₂-MOF (66.40%) > CeO₂-MOF (65.57%). Similarly, the introduction of Pt species favored the generation of lattice oxygen. According to previous studies,^{54,55} O_{latt} plays a key role in many thermocatalytic reactions. O_{latt} can oxidize the reducing molecules and then create oxygen vacancies, which are subsequently filled with the activation of molecular oxygen. The ratio of O_{latt} could explain that Pt_{NC}@CeO₂ had the best catalytic performance. It has been proven that more O_{latt} generated sufficient oxygen vacancies, thus promoting toluene adsorption and activation. As shown in Fig. 6d, it can be concluded from the percentage of active species of each catalyst that Ce³⁺ and O_{latt} were the main active components to improve the activity of the Pt_{NC}@CeO₂ catalyst. Also, the addition of Pt species effectively promoted the generation of Ce³⁺ species and lattice oxygen, which contributed to the production of more oxygen vacancies. Moreover, Ce³⁺ also facilitated the generation of unsaturated bonds and more Ce species would interact with Pt species, thus building Pt–Ce interfaces to promote the catalytic oxidation of VOCs.

To determine the types of oxygen species for each catalyst, O₂-TPD curves are recorded in Fig. 7a. The peak at 100–325 °C was considered to be O_α, which was mainly present at the

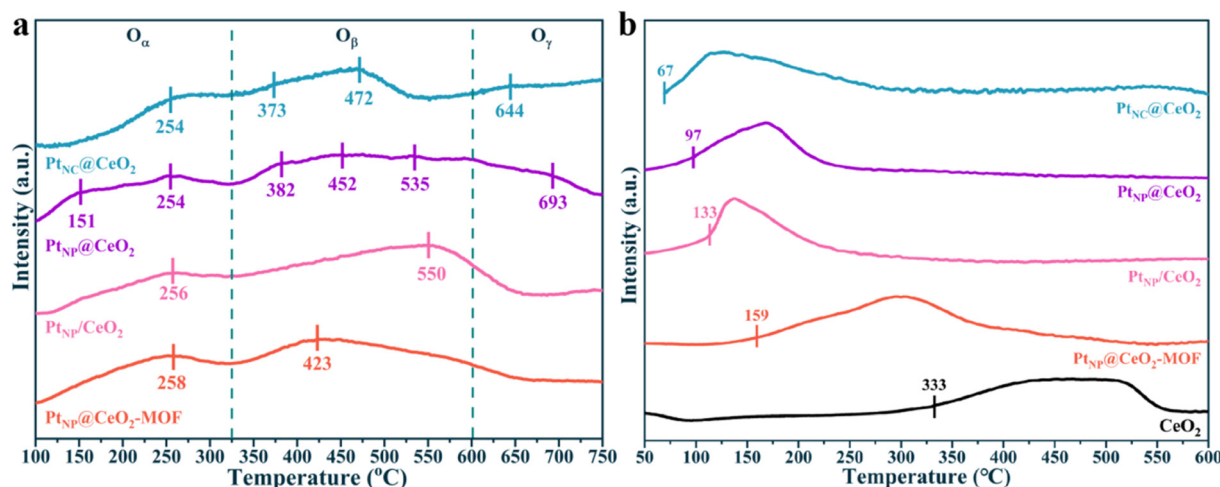
**Fig. 7** O₂-TPD curves (a) and H₂-TPR curves (b) of samples.



Fig. 8 NH₃-TPD profiles (a) and percentages of surface acid sites (b) of catalysts.

surface oxygen vacancies. The peak between 325 and 600 °C was caused by the desorption of O_β, and this oxygen species was distributed at the surface lattice. The peak above 600 °C corresponded to O_γ, which was mainly found in the lattice bulk phase.⁵⁶ For Pt_{NC}@CeO₂ and Pt_{NP}@CeO₂, the types of oxygen species were essentially the same. However, the O₂-TPD curve of the Pt_{NC}@CeO₂ sample exhibited higher mobility of O_β and O_γ. Combined with the results of activity, it was revealed that O_β and O_γ transfer from the body to the catalyst surface was accelerated during the reaction process,⁵⁷ thus promoting the activation of VOCs. It has been shown that the methods of *in situ* introduction of Pt and Ce could alter the mobility of oxygen species. It was discovered that the Pt_{NC}@CeO₂ catalyst contained different types of oxygen species. This indicated that the method of Pt and Ce introduction also had a great influence on the type of oxygen species produced by Pt–Ce-based catalysts. In short, the lattice oxygen was significant for the catalytic performance of the Pt_{NC}@CeO₂ catalyst and might be probably due to the interaction between Pt nanoclusters and the carrier. According to the results of the above work, we suggested that the presence of more Ce³⁺ species and a substantial amount of lattice oxygen species on the Pt_{NC}@CeO₂ catalyst may be one of the key factors to enhance the catalytic performance.

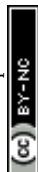
The reducibility of each species in the catalysts was tested by H₂-TPR, and the results are presented in Fig. 7b and S10.† Each catalyst showed a wide reduction temperature interval (Fig. 7b), and the H₂ consumption of the catalysts is shown in Table S2.† The finely fitted peaks of each catalyst are displayed in Fig. S10.† In general, the first reduction peak was classified as the reduction of adsorbed oxygen on the surface of CeO₂. The second peak belonged to the reduction of adsorbed oxygen on the subsurface of CeO₂.^{58–60} It is obvious from Fig. 7b that the reduction peaks of CeO₂ shifted toward lower temperatures after the addition of Pt, and the onset reduction temperatures of each catalyst were in the order Pt_{NC}@CeO₂ (67 °C) < Pt_{NP}@CeO₂ (97 °C) < Pt_{NP}/CeO₂ (133 °C) < Pt_{NP}@CeO₂-MOF (159 °C) < CeO₂ (333 °C). In

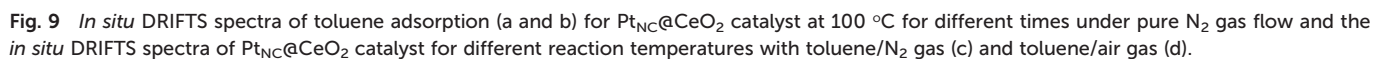
addition, the lower onset reduction temperature indicated that the Pt species in the catalysts were more likely to produce active hydrogen and transfer it to the CeO₂ carrier, thus greatly decreasing the reduction temperature of CeO₂.⁶¹ Obviously, the H₂-TPR of each catalyst confirmed the existence of a hydrogen overflow phenomenon. It should be noted that the onset reduction temperature of each catalyst remained positively correlated with the activity of each catalyst, indicating that the Pt_{NC}@CeO₂ catalyst established a strong Pt–O–Ce interaction and more Pt active sites, which facilitated the production of more active hydrogen, thus significantly reducing the reduction temperature of CeO₂ and promoting the activation of VOCs.⁶² However, the difficulty in reaching 90% toluene conversion of the Pt_{NP}@CeO₂-MOF sample may also be due to extremely poor redox ability, which did not establish a solid interfacial effect between Pt NPs and CeO₂, thus resulting in a decrease in activity.⁶³ In conclusion, H₂-TPR confirmed that the Pt_{NC}@CeO₂ catalysts had a strong interaction between Pt and CeO₂, so the main reasons for the best activity of the Pt_{NC}@CeO₂ sample could be the formation of the SMSI effect and the highly dispersed Pt nanoclusters. Combined with Fig. 1a and 7b, it can be visualized that the low-temperature reduction peaks had a significant impact on the activity of the catalysts.

The results of NH₃-TPD are exhibited in Fig. 8, S11,† and Table 3. The acid sites could be roughly divided into three types from Fig. 8a. The peaks below 200 °C belonged to weak

Table 3 The proportion of surface acid sites of each catalyst

Catalyst	Weak acid (%)	Medium strong acid (%)	Strong acid (%)
Pt _{NC} @CeO ₂	63.14	24.90	11.96
Pt _{NP} @CeO ₂	41.25	16.04	42.71
Pt _{NP} /CeO ₂	38.89	10.36	50.75
Pt _{NP} @CeO ₂ -MOF	—	27.44	72.56
CeO ₂ -OH	67.34	24.30	8.36
CeO ₂ -MOF	46.47	6.38	47.15





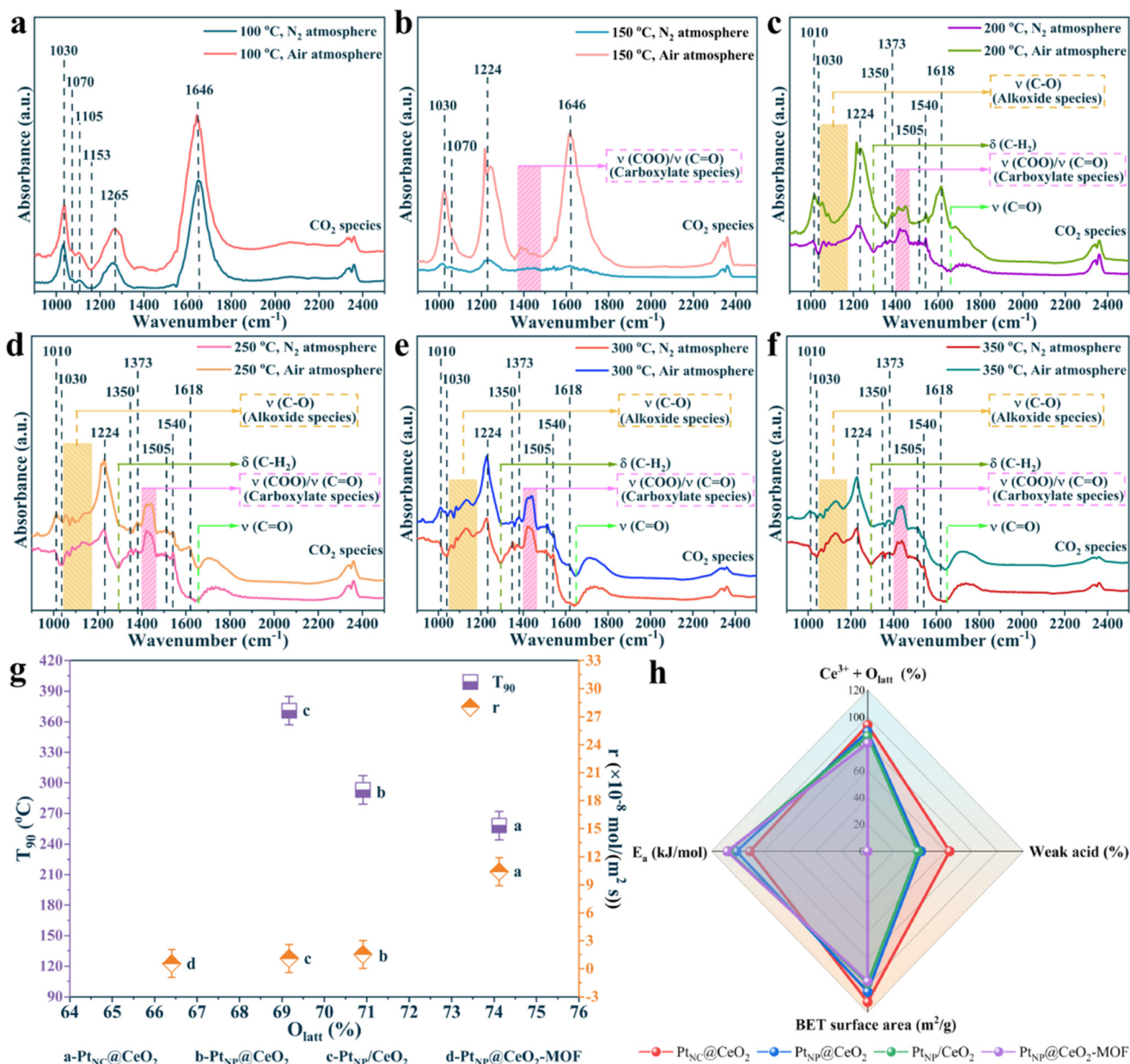


Fig. 10 *In situ* DRIFTS spectra under different atmospheres at different temperatures (a–f), the reaction rate and T_{90} versus O_{lat} (g), and the schematic diagram of E_a and frame of active sites over the catalysts (h).

mechanism. During the catalytic process, abundant oxygen vacancies were generated due to the consumption of lattice oxygen which was continuously replenished with the help of gas-phase oxygen, thus achieving a reciprocal cycle of reactions.⁷² It is of interest that the relationship between the lattice oxygen and the reaction rate and the relationship between T_{90} and lattice oxygen (Fig. 10g) both confirmed well the critical effect of lattice oxygen in the toluene elimination. Furthermore, the highly dispersed Pt nanoclusters in the Pt_{NC}@CeO₂ catalyst could be beneficial for adsorbing and becoming activated for the reactants, which may also be the reason for the ability of this type of catalyst to produce various intermediates at 100 °C. Hence, the Pt_{NC}@CeO₂

catalyst promoted the emission reduction of toluene due to the formation of Pt nanoclusters, which could expose more metal active sites derived from the rich Pt–O–Ce interface.

In short, the generation of Pt nanoclusters, more Ce³⁺ species, more lattice oxygen, more weak acid sites, larger specific surface area, and strong interfacial effect between Pt and CeO₂ combined to construct the Pt_{NC}@CeO₂ catalyst with the most excellent activity (Fig. 10h). To verify the activity for the catalysts, kinetic studies were performed (Fig. 11). It can be found that the R_s and R_m values of Pt_{NC}@CeO₂ were much higher than those of Pt_{NP}@CeO₂ under the same conditions in Fig. S12,[†] which also implied that Pt_{NC}@CeO₂ had superior catalytic activity.



Scheme 2 Proposed mechanism over Pt nanocluster catalyst for toluene oxidation.

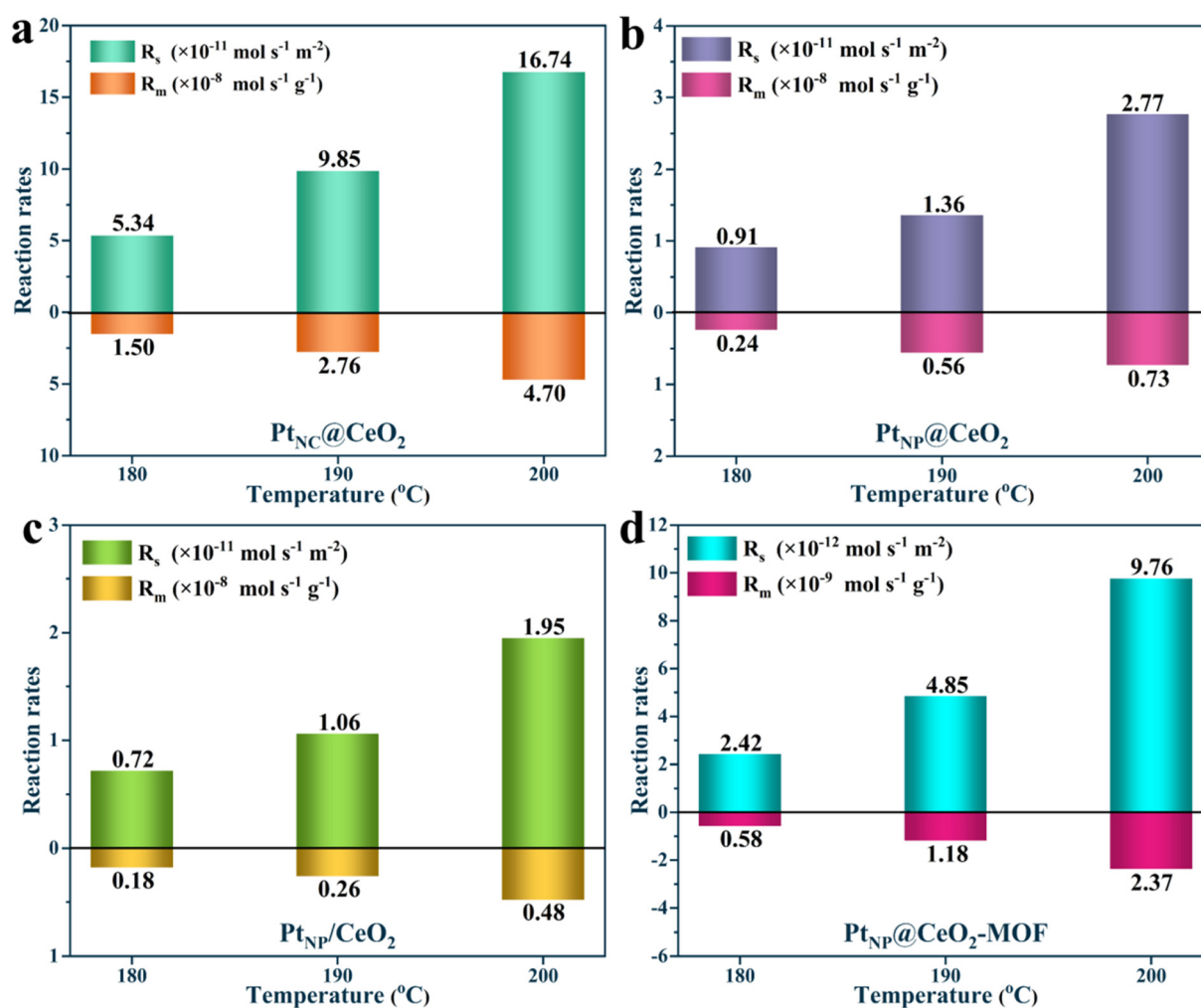


Fig. 11 Measurement of the specific toluene reaction rates of the catalysts.



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