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Introduction

Due to its abundance, renewability and zero-emission, hydrogen has been given extensive attention as an energy carrier. However, the storage of hydrogen is still a great challenge in the scientific community.^{1,2} Ammonia, a basic chemical for production of fertilizers, has been considered as one of the most promising carriers for hydrogen. In this regard, NH₃ decomposition is expected to be a simple and efficient approach for generation of high-purity CO_x-free H₂ from NH₃.^{3,4} To date, a variety of supported metal catalysts (e.g. Ru, Fe, Co, Ni) have been extensively studied for NH₃ decomposition reaction.⁵⁻⁹ However, decomposition of NH₃ in the presence of a catalyst is still greatly hampered by the sluggish kinetics. Therefore, designing an efficient catalyst that performs well at relatively low temperatures is urgently needed for the effective and economic production of H₂ from NH_3 .

Metal–support interaction-modulated catalytic activity of Ru nanoparticles on Sm₂O₃ for efficient ammonia decomposition[†]

Xilun Zhang,^{ab} Lin Liu, ¹⁰*^a Ji Feng,^{ab} Xiaohua Ju,^a Jiemin Wang,^{ac} Teng He ¹⁰^a and Ping Chen^{*a}

Development of efficient catalysts is important for production of CO_x -free hydrogen from ammonia decomposition. Herein, a highly active catalyst with uniform Ru nanoparticles dispersed on Sm_2O_3 nanorods is developed *via* a facile precipitation method. Under a relatively high weight hourly space velocity of 30 000 mL g⁻¹ h⁻¹, Ru/Sm₂O₃ can catalyze ammonia decomposition reaction with a H₂ formation rate as high as 25.9 mmol g_{cat}⁻¹ min⁻¹ at 450 °C, which is superior to most of conventional oxide-supported Ru catalysts. Moreover, we find that the activity of Ru/Sm₂O₃ is highly dependent on the preparation method. The Ru/Sm₂O₃ catalyst prepared by precipitation methods. Characterization results demonstrate that the superior catalytic performance of Ru/Sm₂O₃ achieved from precipitation method should originate from much enhanced interaction between Ru nanoparticles and Sm₂O₃ support. These findings offer promise to explore Ru/Sm₂O₃ catalyst as a new kind of efficient catalyst for ammonia decomposition and to improve the catalytic performance by modulating the metal–support interaction of the catalyst.

Ru-based catalysts are highly active for the decomposition of NH₃.^{10,11} During the past years, Ru nanoparticles (NPs) loaded on high surface area supports have been widely investigated in NH₃ decomposition. Among them, oxidesupported Ru catalysts have been explored and display high activity and stability for NH₃ decomposition. Many kinds of oxides, including SiO₂, TiO₂, Al₂O₃, MgO, La₂O₃, CeO₂, ZrO₂ and barium hexaaluminate, have been used as supports for Ru-based catalysts.^{5,12–17} To expand the scope of Ru-based catalysts, developing new efficient oxide-supported Ru catalysts and understanding the relationship between the activity and structure of these catalysts are needed.

In oxide-supported metal catalysts, the function of oxide supports is not only to disperse and stabilize metal particles but also to generate interface phenomena through metaloxide interaction. Controlling metal-support interaction has been recognized as an efficient strategy to tune the surface geometries and electronic structure of supported metal particles and further enhance the catalytic performances of supported metal catalysts.^{18,19} Discovering support material which can effectively enhance Ru dispersion and metal-oxide interaction is a major concern for construction of efficient Ru-based catalysts. In recent years, rare earth oxides such as Pr_6O_{11} , La₂O₃ and CeO₂ have attracted increasing interests as superior supports for Ru-based NH₃ decomposition catalysts.^{14,20-29} As a typical rare earth oxide, samarium oxide

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^a Dalian National Laboratory for Clean Energy, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. E-mail: liulin@dicp.ac.cn, pchen@dicp.ac.cn

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China

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(Sm₂O₃) has been applied as a catalyst for oxidative coupling of methane,^{30,31} oxidation of ethane and ethylene,³² CO hydrogenation reaction³³ and dehydration of alcohols.³⁴ Because of its intrinsic features of chemical stability, high melting point and low volatility, Sm₂O₃ has also been applied as a support, promoter, stabilizer or dopant in a variety of Au-, Ru-, Pt- and Rh-based catalysts.³⁵⁻³⁸ However, to date, little attention has been paid to the utilization of Sm₂O₃ as a catalyst support for Ru-based catalysts in NH_3 decomposition.

In this paper, we explored Sm₂O₃ as a support and developed an efficient Ru/Sm2O3 catalyst by deposition of uniform Ru NPs on Sm₂O₃ through a precipitation method. The catalyst has been characterized and evaluated in NH₃ decomposition reaction. The Ru/Sm₂O₃ catalyst exhibits high activity and stability for the decomposition of NH3 at relatively low temperatures (400-450 °C). The effect of metalsupport interaction on the activity of the Ru/Sm2O3 catalyst was also studied in detail. By synthesizing Ru/Sm2O3 analogues consisting of nearly identical Ru NPs and Sm₂O₃ nanorods via impregnation and solid milling methods, we find that the catalytic activity of the Ru/Sm2O3 catalysts differs substantially, which manifests the crucial role of the interaction between Ru and Sm₂O₃ in regulating the activity of the Ru/Sm₂O₃ catalysts. These findings can inspire the development of new efficient oxide-supported Ru catalysts for NH₃ decomposition by modulating the metal-support interaction of the catalysts.

Experimental

Preparation of the Ru/Sm₂O₃ catalysts from different methods

 $\rm Sm(OH)_3\,$ nanorods were synthesized by a hydrothermal method according to the previous literature. 39

 RuO_2 NPs were prepared using a precipitation method. In a typical synthesis, 0.06 g of KOH was dissolved in 30 mL of water. Then, 10 mL of $RuCl_3$ solution (0.015 M) was slowly added to the solution under vigorous stirring. The resulting mixture was kept at room temperature for 2 h under stirring. The obtained product was filtered and washed with excess water and ethanol. After that, the product was dried in an oven at 80 °C for 8 h.

Ru/Sm₂O₃-p catalysts with Ru mass loadings of 1–4 wt% were prepared by precipitation of aqueous solutions of RuCl₃ with KOH solution. Briefly, 0.35 g of Sm(OH)₃ was dispersed into 30 mL of water containing 0.06 g of KOH. After stirring for 30 min, 10 mL of RuCl₃ solution (0.015 M) was slowly added to the above solution under vigorous stirring. After stirring at room temperature for 2 h, the precipitates were filtered, washed with water, and finally dried at 80 °C for 8 h. The obtained sample was reduced in a 5% H₂/Ar stream at 500 °C for 2 h, and the reduced sample was denoted as 1–4% Ru/Sm₂O₃-p.

For comparison, a sample, in which Ru NPs dispersed on an inert SBA-15 support with a Ru mass loading of 4 wt%, was also prepared with the same procedure as that of the Ru/Sm₂O₃-p sample. The obtained sample was reduced in a 5% H₂/Ar stream at 500 °C for 2 h, and the reduced sample was denoted as 4% Ru/SBA-15-p.

Ru/Sm₂O₃ catalyst with a Ru mass loading of 4% was also prepared using an impregnation method. In a typical synthesis, 0.35 g of Sm(OH)₃ was impregnated with an appropriate amount of ethanol solution of RuO₂ NPs. The mixture was sonicated for 30 min. The suspension was stirred at 25 °C until the ethanol was evaporated. The obtained sample was reduced in a 5% H₂/Ar stream at 500 °C for 2 h, and the reduced sample was denoted as 4% Ru/Sm₂O₃-i.

A 4% Ru/Sm₂O₃ reference catalyst was also prepared by a solid milling method with the use of Sm(OH)₃ and RuO₂ NPs. An appropriate amount of RuO₂ and Sm(OH)₃ was milled in a mortar by hand for 10 min. The obtained sample was reduced in a 5% H₂/Ar stream at 500 °C for 2 h, and the reduced sample was denoted as 4% Ru/Sm₂O₃-m.

Characterization

Powder X-ray diffraction (XRD) patterns of the catalysts were measured on an X'Pert Pro (PANAlytical) diffractometer with Cu K α radiation, operating at 40 kV and 40 mA.

Nitrogen sorption was performed at -196 °C using a Micromeritics ASAP 2020 analyser after evacuation at 250 °C for 2 h. The specific surface area of the sample was calculated by the Brunauer-Emmett-Teller (BET) method.

The actual Ru loadings of the catalysts were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 7300DV, Perkin-Elmer, USA).

Transmission electron microscopy (TEM) images were taken on a JEOL 2100X microscope.

 H_2 temperature-programmed reduction (H_2 -TPR) profiles of the catalysts were collected on a fixed-bed reactor equipped with a gas chromatograph. About 50 mg of the catalyst was loaded into a tubular quartz reactor. The analysis was performed in a 5% H_2 /Ar stream (30 mL min⁻¹), ramping the temperature from room temperature to 800 °C at a heating rate of 10 °C min⁻¹.

The Ru dispersion of the catalyst was determined by CO chemisorption on an AutoChem II 2920 instrument (Micromeritics). About 100 mg of the catalyst was loaded and reduced with 10% H_2/Ar (30 mL min⁻¹) at 400 °C for 1 h, and then it was purged with He (30 mL min⁻¹) for another 1 h. After the sample was cooled to 50 °C in He, a high-purity CO pulse was introduced. The CO uptake was measured using a gas chromatograph equipped with a TCD detector. The Ru dispersion was calculated by assuming a CO:Ru stoichiometry of 1:1.

An X-ray photoelectron spectroscopy (XPS) study was performed on an ESCALAB MK-II spectrometer using monochromatic Al K α radiation. Carbonaceous C 1s line (284.8 eV) was used as the reference to calibrate the binding energy.

Catalytic performance measurement

The catalytic activity for the decomposition of ammonia was studied in a fixed-bed quartz reactor under atmospheric pressure. Prior to the reaction, the dried catalysts (catalyst: 50 mg, 20–40 mesh) were reduced in an NH₃ flow at 500 °C for 2 h. The gas reactant was pure NH₃ with a flow rate of 25 mL min⁻¹, corresponding to a weight hourly space velocity (WHSV) of 30 000 mL g_{cat}^{-1} h⁻¹. The reaction temperature was set in the range of 300–500 °C. Product gas composition was analysed online using a GC-7890 gas chromatograph equipped with a TCD detector. The conversion of NH₃ (C_{NH_3}) was calculated by the following equation:

$$C_{\mathrm{NH}_3}(\%) = \frac{A_{\mathrm{NH}_3,\mathrm{in}} - A_{\mathrm{NH}_3,\mathrm{out}}}{A_{\mathrm{NH}_3,\mathrm{in}}}$$

where $A_{\rm NH_3,in}$ and $A_{\rm NH_3,out}$ are the total amount of NH₃ in the inlet and outlet, respectively. The H₂ formation rate was calculated from the NH₃ conversion ($C_{\rm NH_3}$) as shown below:

H₂ formation rate (mmol
$$g_{cat}^{-1}$$
 min⁻¹) = $\frac{WHSV \times C_{NH_3} \times 1.5}{24.45 \times 60}$

where WHSV is the weight hourly space velocity (30 000 mL g_{cat}^{-1} h⁻¹), C_{NH_3} is the conversion of NH₃, and 24.45 mL mmol⁻¹ is the molar volume of the gas at 25 °C and 1 atm.

 TOF_{H_2} was calculated from the H₂ formation rate divided by the exposed surface Ru atoms on the catalysts, shown as follows:

$$\text{TOF}_{\text{H}_2}(\text{s}^{-1}) = \frac{\text{H}_2 \text{ formation rate} \times 10^{-3}}{60 \times \text{Ru content} \times D_{\text{Ru}}/\text{Ru}_{\text{at}}}$$

where D_{Ru} is the Ru dispersion of the catalyst determined by CO chemisorption and H₂ formation rate (mmol g_{cat}^{-1} min⁻¹), and Ru_{at} is the molar mass of Ru (101.07 g mol⁻¹).

Results and discussion

Structural characterization of the Ru/Sm2O3 catalysts

In this study, RuO₂ NPs were firstly synthesized using a precipitation method (Fig. 1a). Fig. S1a and b⁺ show the TEM images of the RuO₂ NPs at different scales. The spherical and uniform-sized RuO₂ NPs with an average particle size of $1.9 \pm$ 0.2 nm can be facilely obtained (Fig. S1c†). The high resolution TEM image shows that the RuO₂ NPs are in the partially crystalline state (Fig. S1a[†]), which agrees well with the XRD result (Fig. S2[†]). Here, well-crystallized Sm(OH)₃ nanorods with lengths of 100-600 nm and widths of 30-60 nm (Fig. S3[†]) were used as support precursors to disperse and support RuO₂ NPs. Three preparation methods including precipitation, impregnation and solid milling were applied to disperse RuO₂ NPs onto the Sm(OH)₃ support precursor (Fig. 1b-d). The actual Ru mass loadings of the catalysts were determined by ICP-OES analysis (Table 1). The structures of the catalyst precursors were characterized by XRD. As shown in Fig. S4,† the characteristic peaks of all



Fig. 1 Schematic illustration of (a) the preparation of the RuO_2 NPs; deposition of the Ru NPs on the Sm_2O_3 support by the different methods: (b) precipitation method, (c) impregnation method and (d) solid milling method.

the catalyst precursors are nearly identical with that of $Sm(OH)_3$ support precursor (JCPDS 01-083-2036), indicating that the introduction of RuO_2 NPs does not cause any structural change in $Sm(OH)_3$.

The three catalyst precursors were reduced at 500 °C to obtain the Ru/Sm₂O₃ catalysts, which were denoted as 4% Ru/Sm₂O₃-p, 4% Ru/Sm₂O₃-i and 4% Ru/Sm₂O₃-m, respectively. During the reduction process, the Sm(OH)₃ precursor was decomposed into Sm₂O₃ and the RuO₂ NPs were reduced to Ru NPs. The surface areas of 4% Ru/Sm₂O₃-p and 4% Ru/Sm₂O₃-i are 38.4 and 43.8 m² g⁻¹, respectively, which are larger than that of the pristine Sm₂O₃ support (25.8 m² g⁻¹, Table 1). Corresponding N_2 adsorption– desorption isotherms are shown in Fig. S5.[†] The increase in surface area may be attributed to the reconstruction of support in the solution during the preparation processes. The structures of the different 4% Ru/Sm2O3 catalysts were studied by XRD. As shown in Fig. 2, characteristic diffraction peaks at 2θ of 28.3°, 32.8°, 47.0° and 55.8° can be observed for all the 4% Ru/Sm2O3 samples, which match well with the diffraction peaks from the (222), (400), (440) and (622) lattice planes of cubic Sm2O3 (JCPDS 00-015-0813). The XRD patterns of the different 4% Ru/Sm2O3 samples show similar diffraction peaks to that of the Sm₂O₃ support. No observable diffraction peaks corresponding to the Ru species can be detected, indicating the high dispersion of Ru NPs in the three 4% Ru/Sm₂O₃ samples.

The morphologies and sizes of the Ru NPs in the 4% Ru/ Sm_2O_3 catalysts prepared by different methods were characterized by TEM. As shown in Fig. 3, the Sm_2O_3 supports in the three 4% Ru/ Sm_2O_3 samples possess fine crystallinity. TEM images reveal that an inter-planar space of

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 Table 1
 Physical properties of the Sm₂O₃ and Ru/Sm₂O₃ samples

Sample	Ru loading ^a (wt%)	Surface area $(m^2 g^{-1})$	TEM results		CO chemisorption results			
			Particle size ^{b} (nm)	Ru dispersion ^{b} (%)	CO uptake (µmol g^{-1})	Ru dispersion ^c (%)	Particle size ^c (nm)	
4% Ru/Sm ₂ O ₃ -p	3.8	38.4	3.0	37.3	127.4	32.2	3.5	
4% Ru/Sm ₂ O ₃ -i	3.7	43.8	2.9	38.3	145.0	36.6	3.1	
4% Ru/Sm ₂ O ₃ -m	3.5	28.5	3.3	34.6	132.8	33.5	3.3	
Sm ₂ O ₃	_	25.8	_	_	_	_	_	

^{*a*} Determined by ICP-OES analysis. ^{*b*} Determined by TEM study by the equation of Borodziński and Bonarowska.⁴⁰ ^{*c*} Determined by CO chemisorption, assuming a CO:Ru stoichiometry of 1:1.

0.32 nm, corresponding to the lattice fringe of the (222) facet of Sm_2O_3 , can be clearly identified for all the three samples. As the Z-contrast of the Ru atoms is smaller than that of Sm in the Sm₂O₃ support, it is challenging to directly distinguish the dispersion and geometry of the Ru NPs from the more condensed Sm₂O₃ support, especially when the particle size of the Ru NPs is relatively small. As a result, only the Ru NPs on the edge of the Sm2O3 support can be identified in the TEM images. By counting ca. 100 Ru particles on the edge of Sm₂O₃ in different regions, as shown in the TEM images (Fig. 3d-f), statistical results of the size distributions of the Ru NPs of the three Ru/Sm2O3 catalysts were obtained (Fig. 3g-i). The average particle sizes of 4% Ru/Sm₂O₃-p, 4% Ru/Sm₂O₃-i and 4% Ru/Sm₂O₃-m are estimated to be ca. 3.0, 2.9, and 3.3 nm, respectively, revealing similar particle sizes of Ru in the three Ru/Sm₂O₃ samples. In addition, the Ru NPs in Ru/Sm₂O₃-p shows a lower crystallinity by comparing the lattice finger of the Ru NPs (insets of Fig. 3a-c). No obvious agglomeration of Ru NPs into large particles could be observed, showing that Sm₂O₃ is capable of preserving a highly dispersed geometry of Ru NPs. A CO pulse chemisorption method was also used to estimate the Ru dispersion and the average particle size of the different 4% Ru/Sm₂O₃ samples. As shown in Table 1, the Ru dispersions



Fig. 2 XRD patterns of the Sm_2O_3 support and 4% Ru/Sm₂O₃-m, 4% Ru/Sm₂O₃-i and 4% Ru/Sm₂O₃-p catalysts.

of the three Ru/Sm_2O_3 samples are similar based on the CO pulse chemisorption results. Accordingly, the Ru particle sizes of 4% Ru/Sm_2O_3 -p, 4% Ru/Sm_2O_3 -i and 4% Ru/Sm_2O_3 -m estimated by CO pulse chemisorption are determined to be about 3.5, 3.1 and 3.3 nm, respectively, agreeing well with the TEM results.

Catalytic performance for ammonia decomposition

The catalytic activities of 4% Ru/Sm₂O₃-p, 4% Ru/Sm₂O₃-i and 4% Ru/Sm₂O₃-m in NH₃ decomposition were evaluated. As shown in Fig. 4a, the Sm₂O₃ support is inactive in NH₃ decomposition. When the Ru NPs are anchored on the surface of Sm₂O₃, remarkably high catalytic activity can be obtained. Compared with the 4% Ru/Sm2O3-i and 4% Ru/ Sm₂O₃-m samples, 4% Ru/Sm₂O₃-p exhibits significantly enhanced activity under identical conditions (Fig. 4a). In detail, the NH₃ decomposition over 4% Ru/Sm₂O₃-p starts at 300 °C and reaches ca. 100% conversion at 500 °C. By contrast, obvious activity can only be detected at temperatures above 375 °C over 4% Ru/Sm2O3-i and 4% Ru/ Sm₂O₃-m. At 450 °C, the NH₃ conversion over 4% Ru/Sm₂O₃p is 84.6%, while the NH₃ conversions over 4% Ru/Sm₂O₃-i and 4% Ru/Sm2O3-m are 21.5% and 15.7% at 450 °C, respectively. At 400 °C, the NH₃ conversion over 4% Ru/ Sm₂O₃-p is 7.5 and 11.1 times higher than that over 4% Ru/ Sm₂O₃-i and 4% Ru/Sm₂O₃-m, respectively. These data demonstrate the superior catalytic performance of the Ru/ Sm₂O₃-p catalyst.

Due to the same composition of the different 4% Ru/ Sm_2O_3 samples, comparison of the TOF value on each exposed Ru atom is useful to evaluate the intrinsic catalytic nature of Ru NPs in the different catalysts. It is also realized that the size of Ru NPs plays a crucial role in determining the catalytic performance of supported Ru-based catalysts in NH₃ decomposition. Many previous studies suggest that the TOF_{H₂} value varies with the sizes and shapes of Ru NPs.⁴¹⁻⁴⁴ Our TEM results reveal that the average Ru particle sizes of the three 4% Ru/Sm₂O₃ samples are similar (Fig. 3), but their TOF_{H₂} values vary greatly under identical reaction conditions (Fig. 4b). The 4% Ru/Sm₂O₃-m sample, which has an average size of 3.3 nm, shows a smallest TOF_{H₂} value of 0.7 s⁻¹ at 450 °C among the three size is 3.0 nm. However, a markedly



Fig. 3 Representative HRTEM and TEM images, and particle size distributions of 4% Ru/Sm₂O₃-p (a, d and g), 4% Ru/Sm₂O₃-i (b, e and h), and 4% Ru/Sm₂O₃-m (c, f and i).

increased TOF_{H₂} value of 3.6 s⁻¹ at 450 °C can be observed, which is 5.2 and 4.3 times higher than that of the 4% Ru/ Sm₂O₃-m and 4% Ru/Sm₂O₃-i samples, respectively. The superior catalytic performance of Ru/Sm₂O₃-p in NH₃ decomposition is further justified by comparison of the apparent activation energies (E_a) of the different catalysts. Correlating well with the activity results, obvious differences in the E_a values can be observed for the different 4% Ru/ Sm₂O₃ samples. As shown in Fig. 4c, the Arrhenius plots reveal that the E_a value of the 4% Ru/Sm₂O₃-p catalyst is 85.1 kJ mol⁻¹, which is lower than that of the 4% Ru/Sm₂O₃-i (96.0 kJ mol⁻¹) and 4% Ru/Sm₂O₃-m (100.2 kJ mol⁻¹) catalysts.

The activities of Ru/Sm₂O₃-p with different Ru mass loadings were also investigated, and the activity increases with the increase of the Ru loading from 1 to 4 wt% (Fig. S6a†). Moreover, similar E_a values can be observed for the Ru/Sm₂O₃-p samples with Ru mass loadings in the range of 1–4 wt% (Fig. S6b†), indicating the similar structure of active sites in the Ru/Sm₂O₃-p samples with different Ru mass loadings.

The specific H_2 formation rate per unit Ru or mass of catalyst is a meaningful index to compare the activities of various Ru-based catalysts. We thus collected, calculated and compared the activity data of some representative supported Ru catalysts. As shown in Table 2, the H_2 formation rate of the 4% Ru/Sm₂O₃-p catalyst at 450 °C is 25.9 mmol g_{cat}⁻¹

min⁻¹, which outperforms most of promoter-free Ru-based catalysts under similar reaction conditions. It is worth to note that the H₂ formation rate per unit of Ru over the 1% Ru/Sm₂O₃-p catalyst at 450 °C is as high as 1338 mmol g_{Ru}^{-1} min⁻¹, which is even higher than that of the highly active potassium promoted K–Ru/CNT and K–Ru/MgO-DP catalysts. In addition to the catalytic activity, stability is another crucial parameter for evaluating the catalytic performance of a catalyst. Here, the 4% Ru/Sm₂O₃-p catalyst was selected for the stability test at 475 °C. Fig. 4d shows the catalytic behaviour of the 4% Ru/Sm₂O₃-p catalyst as a function of time on stream. The ammonia conversion remains nearly constant during a test period of 60 h. With its superior activity and stability, the Ru/Sm₂O₃-p catalyst has a practical potential in NH₃ decomposition for H₂ production.

Metal–support interactions of the different 4% Ru/Sm₂O₃ catalysts

 $\rm NH_3$ decomposition over Ru-based catalysts has been recognized to be a structure sensitive reaction. Currently, the B5 sites on the surface of Ru nanoparticles have been widely accepted as the active sites of Ru-based catalysts for $\rm NH_3$ decomposition.^{43,45,46} It is well known that the surface structure and chemical state of Ru NPs determine the catalytic performance of supported Ru catalysts in $\rm NH_3$



Fig. 4 Catalytic performance of the Ru/Sm₂O₃ catalysts for ammonia decomposition. (a) Temperature-dependent NH₃ conversion and H₂ formation rate. (b) Turnover frequency (TOF_{H₂}). (c) Arrhenius plots of the 4% Ru/Sm₂O₃-p, 4% Ru/Sm₂O₃-i and 4% Ru/Sm₂O₃-m catalysts. (d) Long-term stability test of the 4% Ru/Sm₂O₃-p catalyst at 475 °C. WHSV = 30 000 mL g_{cat}^{-1} h⁻¹.

Table 2	NH ₃ decomposition	activities of variou	s Ru-based	catalysts at 4	150 °C
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Catalyst	$\begin{array}{l} \text{WHSV} \\ \left(\text{mL } {g_{cat}}^{^{-1}} \ h^{^{-1}} \right) \end{array}$	Ru loading (wt%)	NH ₃ conversion (%)	H_2 formation rate (mmol $g_{cat}^{-1} min^{-1}$)	H_2 formation rate (mmol $g_{Ru}^{-1} min^{-1}$)	Ref.
Ru/SiO ₂	30 000	10	36.4	11.2	112	47
Ru/CNTs	30 000	4.8	43.3	13.3	277	5
K-Ru/CNTs	30 000	4.8	97.3	29.9	622	5
Ru/MgO-CNTs	60 000	4.85	30	18.4	379	48
Ru/Al_2O_3	30 000	4.8	23.3	7.1	149	5
Ru/AC	30 000	4.8	28.7	8.8	183	5
Ru/CaAlO _x -w	30 000	3.5	20	6.1	175	49
Ru/BHA	30 000	2.74	42	12.9	470	16
Ru/MgO-DP	30 000	3.5	56.5	17.3	495	15
K-Ru/MgO-DP	36 000	3.5	87.0	32.1	914	15
Ru/c-MgO	30 000	4.7	80.6	24.7	526	50
K-Ru/Mg ₂ Al-LDO	30 000	4.6	42.7	13.1	285	51
Ru-K/CaO	9000	2.8	90	8.3	296	52
Ru/Rb-Y zeolite	30 000	1.96	24	7.3	376	53
Ru/CeO ₂	22 000	1.0	100	22.5	2249	26
Ru/La ₂ O ₃ -700-i	18 000	4.8	58.2	10.7	221	14
Ru/Sm ₂ O ₃ -p	30 000	1.0	43.6	13.4	1338	This work
Ru/Sm ₂ O ₃ -p	30 000	2.0	59.7	18.3	916	This work
Ru/Sm ₂ O ₃ -p	30 000	3.8	84.6	25.9	683	This work
Ru/Sm ₂ O ₃ -i	30 000	3.7	21.5	6.6	179	This work
Ru/Sm ₂ O ₃ -m	30 000	3.5	15.7	4.9	137	This work

decomposition. Generally, many factors such as dispersion, size and morphology of Ru NPs, interaction between Ru NPs and support, and surface properties of support can influence the surface structure and chemical state of Ru NPs, leading to the remarkable difference in the catalytic activity.

We first examined the chemical state of the Ru NPs on Sm₂O₃ by XPS. Here, a 4% Ru/SBA-15-p catalyst, in which Ru NPs dispersed on an inert SBA-15 support, was used as a reference for XPS characterization. Due to the overlapping of the Ru 3d_{3/2} and C 1s peaks at ca. 284.8 eV, the Ru state is analysed by the Ru $3d_{5/2}$ and $3p_{3/2}$ peaks. The Ru $3d_{5/2}$ peak of 4% Ru/SBA-15-p is found to be centred at 280.0 eV, indicating the dominant metallic state of the Ru NPs (Fig. 5a). $\tilde{^{54-56}}$ The Ru $3d_{5/2}$ peak of 4% Ru/Sm₂O₃-p, on the other hand, shifts to a higher value of 280.4 eV. At the same time, the binding energy of the Ru 3p_{5/2} peaks of 4% Ru/ Sm₂O₃-p (461.9 eV) is also higher than that of 4% Ru/SiO₂ (461.2 eV) (Fig. 5b). These results demonstrate that the chemical state of the Ru NPs in 4% Ru/Sm2O3-p shows an obvious difference from that of the Ru NPs in 4% Ru/SBA-15-p. We infer that the Ru NPs in 4% Ru/Sm₂O₃-p has stronger interaction with Sm₂O₃ than that of the Ru NPs in 4% Ru/SBA-15-p. As widely acknowledged, metal-support interactions in oxide-supported metal catalysts play a critical role in regulating the activity of catalysts.^{18,19}



Fig. 5 Ru 3d (a) and 3p (b) core level XPS spectra of the 4% Ru/ $\rm Sm_2O_3\text{-}p$ and 4% Ru/SBA-15-p catalysts.

Here, we are also curious about the origin of the different performances of the three Ru/Sm₂O₃ catalysts prepared using the same Sm(OH)₃ support and RuO₂ NP precursor but *via* different preparation methods. TEM observation (Fig. 3) and CO chemisorption results (Table 1) confirm that the Ru NPs in the three 4% Ru/Sm₂O₃ analogues give similar particle sizes (3.1–3.5 nm) and dispersions (32.2–36.6%). Thus, the particle size effect can be preliminary excluded. Considering the similar particle size of the Ru NPs in the three 4% Ru/Sm₂O₃ samples, we propose that the extent of interaction between Ru NPs and Sm₂O₃ varies greatly under the preparation conditions applied.

To probe the metal-support interaction of the Ru/Sm₂O₃ catalysts obtained from the different preparation methods, H₂-TPR was conducted (Fig. 6). For RuO₂ NPs, there are two broad peaks centred at around 127 and 213 °C, corresponding to a two-step reduction process from the RuO₂ NPs to the metallic Ru NPs.⁵⁷⁻⁵⁹ For the 4% Ru/Sm₂O₃-m sample obtained from the physical mixture of Ru NPs and Sm(OH)₃, five broad peaks centred at 123, 167, 240, 382 and 457 °C can be observed. Based on the H₂-TPR profiles of the RuO_2 NPs and $Sm(OH)_3$, we can reasonably conclude that the reduction peaks at temperatures below 320 °C may be attributed to the reduction of the RuO₂ NPs, while the reduction peaks at temperatures above 320 °C may be attributed to the reduction of surface oxygen on the Sm(OH)₃/Sm₂O₃ support. Here, the presence of the three reduction peaks at temperatures below 320 °C indicates that the RuO₂ NPs exist in different states. The RuO₂ NPs interacting weakly with Sm(OH)₃ can be reduced at lower temperatures, while other RuO2 NPs that strongly interact with the support can only be reduced at higher temperatures. Similar with 4% Ru/Sm₂O₃-m, the majority of the RuO₂ NPs in 4% Ru/Sm₂O₃-i can be reduced at temperatures below 320 °C. The onset reduction temperature of the 4% Ru/Sm₂O₃-i sample is about 53 °C. For the 4% Ru/Sm₂O₃-p sample, four



Fig. 6 TPR profiles of RuO_ NPs, 4% Ru/Sm_2O_3-m, 4% Ru/Sm_2O_3-i, 4% Ru/Sm_2O_3-p and Sm(OH)_3.

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main reduction peaks centred at 161, 273, 355, and 430 °C were observed. The first two reduction peaks around 161 and 273 °C should be associated with the reduction of the RuO₂ NPs. The two reduction peaks centred at around 355 and 430 °C may be assigned to the reduction of surface oxygen species. In comparison with that of the 4% Ru/Sm₂O₃-i and 4% Ru/Sm₂O₃m samples, the reduction of the RuO2 NPs in the 4% Ru/ Sm₂O₃-p sample shifts towards higher temperatures, while the reduction of the support shifts to lower temperatures, providing strong evidence for the much enhanced interaction between the RuO₂ NPs and Sm(OH)₃ support. We suggest that the enhanced metal-support interaction in 4% Ru/Sm₂O₃-p via the precipitation method could allow Sm₂O₃ to exert stronger influence on modulating the electronic structure of Ru NPs. As a result, the 4% Ru/Sm₂O₃-p sample shows the highest catalytic activity among the three 4% Ru/Sm₂O₃ analogues.

Conclusions

In summary, we demonstrate that Ru NPs on Sm_2O_3 catalysts show superior activity and excellent stability for NH_3 decomposition. The activity of Ru/Sm_2O_3 with identical composition shows high dependence on the preparation method. The Ru/Sm_2O_3 catalyst obtained from a precipitation method exhibits much higher activity than the analogues from impregnation and solid milling methods. These findings offer promise to explore Ru/Sm_2O_3 catalyst as a new kind of superior catalyst for NH_3 decomposition. Furthermore, this work also highlights the important role of metal–support interaction in enhancing the activity of Ru/Sm_2O_3 catalysts in NH_3 decomposition and provides opportunity to improve the catalytic performance of catalysts by delicately modulating metal–support interactions of oxidesupported metal catalysts.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 D. Mori and K. Hirose, Int. J. Hydrogen Energy, 2009, 34, 4569-4574.
- 2 K. Mazloomi and C. Gomes, *Renewable Sustainable Energy Rev.*, 2012, **16**, 3024–3033.
- 3 A. Klerke, C. H. Christensen, J. K. Nørskov and T. Vegge, J. Mater. Chem., 2008, 18, 2304.
- 4 R. Lan, J. T. S. Irvine and S. Tao, *Int. J. Hydrogen Energy*, 2012, 37, 1482–1494.

- 5 S. F. Yin, B. Q. Xu, W. X. Zhu, C. F. Ng, X. P. Zhou and C. T. Au, *Catal. Today*, 2004, **93–95**, 27–38.
- 6 X. Duan, G. Qian, X. Zhou, Z. Sui, D. Chen and W. Yuan, *Appl. Catal., B*, 2011, **101**, 189–196.
- 7 W. Zheng, J. Zhang, Q. Ge, H. Xu and W. Li, *Appl. Catal., B*, 2008, **80**, 98–105.
- 8 D. Varisli and N. G. Kaykac, *Appl. Catal., B*, 2012, **127**, 389–398.
- 9 S. Mukherjee, S. V. Devaguptapu, A. Sviripa, C. R. F. Lund and G. Wu, *Appl. Catal.*, *B*, 2018, **226**, 162–181.
- 10 S.-F. Yin, Q.-H. Zhang, B.-Q. Xu, W.-X. Zhu, C.-F. Ng and C.-T. Au, J. Catal., 2004, 224, 384–396.
- 11 J. C. Ganley, F. S. Thomas, E. G. Seebauer and R. I. Masel, *Catal. Lett.*, 2004, 96, 117–122.
- 12 X. Li, W. Ji, J. Zhao, S. Wang and C. Au, *J. Catal.*, 2005, 236, 181–189.
- 13 S. F. Yin and B. Q. Xu, ChemPhysChem, 2003, 4, 277-281.
- C. Huang, Y. Yu, J. Yang, Y. Yan, D. Wang, F. Hu, X. Wang,
 R. Zhang and G. Feng, *Appl. Surf. Sci.*, 2019, 476, 928–936.
- 15 X. Ju, L. Liu, P. Yu, J. Guo, X. Zhang, T. He, G. Wu and P. Chen, *Appl. Catal.*, *B*, 2017, **211**, 167–175.
- 16 Z. Wang, Z. Cai and Z. Wei, ACS Sustainable Chem. Eng., 2019, 7, 8226–8235.
- 17 S. F. Yin, B. Q. Xu, X. P. Zhou and C. T. Au, *Appl. Catal., A*, 2004, 277, 1–9.
- 18 T. W. van Deelen, C. Hernández Mejía and K. P. de Jong, *Nat. Catal.*, 2019, 2, 955–970.
- 19 Y. Lou, J. Xu, Y. Zhang, C. Pan, Y. Dong and Y. Zhu, *Mater. Today Nano*, 2020, **12**, 100093.
- 20 K. Nagaoka, K. Honda, M. Ibuki, K. Sato and Y. Takita, *Chem. Lett.*, 2010, **39**, 918–919.
- 21 K. Nagaoka, T. Eboshi, N. Abe, S.-i. Miyahara, K. Honda and K. Sato, *Int. J. Hydrogen Energy*, 2014, **39**, 20731–20735.
- 22 H. Muroyama, C. Saburi, T. Matsui and K. Eguchi, *Appl. Catal.*, *A*, 2012, **443–444**, 119–124.
- 23 S. Podila, H. Driss, S. F. Zaman, Y. A. Alhamed, A. A. AlZahrani, M. A. Daous and L. A. Petrov, *J. Mol. Catal. A: Chem.*, 2016, **414**, 130–139.
- 24 Y. Xun, X. He, H. Yan, Z. Gao, Z. Jin and C. Jia, *J. Rare Earths*, 2017, **35**, 15–23.
- 25 I. Lucentini, A. Casanovas and J. Llorca, Int. J. Hydrogen Energy, 2019, 44, 12693–12707.
- 26 X.-C. Hu, X.-P. Fu, W.-W. Wang, X. Wang, K. Wu, R. Si, C. Ma, C.-J. Jia and C.-H. Yan, *Appl. Catal.*, B, 2020, 268, 118424.
- 27 Y. Yu, Y.-M. Gan, C. Huang, Z.-H. Lu, X. Wang, R. Zhang and G. Feng, *Int. J. Hydrogen Energy*, 2020, 45, 16528–16539.
- 28 T. Furusawa, H. Kuribara, K. Kimura, T. Sato and N. Itoh, *Ind. Eng. Chem. Res.*, 2020, **59**, 18460–18470.
- 29 C. Huang, Y. Yu, X. Tang, Z. Liu, J. Zhang, C. Ye, Y. Ye and R. Zhang, *Appl. Surf. Sci.*, 2020, **532**, 147335.
- 30 K. Otsuka, K. Jinno and A. Morikawa, *Chem. Lett.*, 1985, 14, 499–500.
- 31 K. Otsuka and T. Komatsu, Chem. Lett., 1987, 16, 483-484.
- 32 V. T. Amorebieta and A. J. Colussi, *J. Am. Chem. Soc.*, 1996, **118**, 10236–10241.

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- 33 L. Shi, G. Dong and D. He, *Catal. Commun.*, 2007, 8, 359–365.
- 34 G. A. M. Hussein, J. Chem. Soc., Faraday Trans., 1994, 90, 3693.
- 35 L. Zhang, J. Lin, J. Ni, R. Wang and K. Wei, *Catal. Commun.*, 2011, 15, 23–26.
- 36 D. Duan, C. Hao, L. Wang, M. Adil, W. Shi, H. Wang, L. Gao, X. Song and Z. Sun, *J. Alloys Compd.*, 2020, 818, 152879.
- 37 R. B. Duarte, M. Nachtegaal, J. M. C. Bueno and J. A. van Bokhoven, J. Catal., 2012, 296, 86–98.
- 38 R. B. Duarte, S. Damyanova, D. C. de Oliveira, C. M. P. Marques and J. M. C. Bueno, *Appl. Catal.*, *A*, 2011, **399**, 134–145.
- 39 X. Wang and Y. Li, Angew. Chem., Int. Ed., 2002, 41, 4790-4793.
- 40 A. Borodziński and M. Bonarowska, *Langmuir*, 1997, **13**, 5613–5620.
- 41 W. Raróg-Pilecka, D. Szmigiel, A. Komornicki, J. Zieliński and Z. Kowalczyk, *Carbon*, 2003, **41**, 589–591.
- 42 W. Zheng, J. Zhang, H. Xu and W. Li, *Catal. Lett.*, 2007, **119**, 311–318.
- 43 F. R. García-García, A. Guerrero-Ruiz and I. Rodríguez-Ramos, *Top. Catal.*, 2009, **52**, 758–764.
- 44 A. M. Karim, V. Prasad, G. Mpourmpakis, W. W. Lonergan,
 A. I. Frenkel, J. G. Chen and D. G. Vlachos, *J. Am. Chem. Soc.*,
 2009, 131, 12230–12239.
- 45 C. J. H. Jacobsen, S. Dahl, P. L. Hansen, E. Tornqvist, L. Jensen, H. Topsoe, D. V. Prip, P. B. Moenshaug and I. Chorkendorff, *J. Mol. Catal. A: Chem.*, 2000, 163, 19–26.

- 46 W. Rarogpilecka, E. Miskiewicz, D. Szmigiel and Z. Kowalczyk, J. Catal., 2005, 231, 11–19.
- 47 T. Choudhary, C. Sivadinarayana and D. Goodman, *Catal. Lett.*, 2001, 72, 197–201.
- 48 S. F. Yin, B. Q. Xu, S. J. Wang, C. F. Ng and C. T. Au, *Catal. Lett.*, 2004, 96, 113–116.
- 49 J. Zhao, S. Xu, H. Wu, Z. You, L. Deng and X. Qiu, *Chem. Commun.*, 2019, 55, 14410–14413.
- 50 X. Ju, L. Liu, X. Zhang, J. Feng, T. He and P. Chen, *ChemCatChem*, 2019, **11**, 4161–4170.
- 51 Q. Su, L. L. Gu, A. H. Zhong, Y. Yao, W. J. Ji, W. P. Ding and C. T. Au, *Catal. Lett.*, 2018, **148**, 894–903.
- 52 S. Sayas, N. Morlanés, S. P. Katikaneni, A. Harale, B. Solami and J. Gascon, *Catal. Sci. Technol.*, 2020, **10**, 5027–5035.
- 53 J. Cha, T. Lee, Y.-J. Lee, H. Jeong, Y. S. Jo, Y. Kim, S. W. Nam, J. Han, K. B. Lee, C. W. Yoon and H. Sohn, *Appl. Catal.*, *B*, 2021, 283, 119627.
- 54 K. Kim, J. Catal., 1974, 35, 66-72.
- 55 C. L. Bianchi, V. Ragaini and M. G. Cattania, *Mater. Chem. Phys.*, 1991, **29**, 297–306.
- 56 V. Mazzieri, Appl. Surf. Sci., 2003, 210, 222-230.
- 57 P. Koopman, J. Catal., 1981, 69, 172–179.
- 58 I. Rossetti, N. Pernicone and L. Forni, *Appl. Catal., A*, 2003, **248**, 97–103.
- 59 X.-C. Hu, W.-W. Wang, R. Si, C. Ma and C.-J. Jia, *Sci. China: Chem.*, 2019, **62**, 1625–1633.