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Synergistic effect of MgO and CeO_2 as a support for ruthenium catalysts in ammonia synthesis

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Nanocomposite materials in MgO–CeO_2 (Ce = 0–100 mol%) system were prepared as the support materials for Ru-based ammonia synthesis catalysts, so that the resultant catalytic activity was enhanced by mixing them together compared with that of the MgO or CeO_2 component was solely used as a support. Such high catalytic activity was due to two effects: electrodonating property of partially reduced $CeO_{2-\delta}$ to Ru metal and strong metal-support interaction derived from the unique catalyst morphology in this study.

KEY WORDS: ammonia synthesis; MgO–CeO_2 support; ruthenium catalyst; metal-support interaction; microstructure.

1. Introduction

Well dispersed ruthenium composites were reported as a favorable candidate of the catalysts for ammonia synthesis under mild conditions such as low pressure and temperature [1,2]. Many supports, such as magnesia [3–5], magnesium aluminum spinel oxide [6], zeolites [7] and active carbon [8–10] were studied from the viewpoint of metal-support interaction.

It is well known that lanthanide oxides act as effective promoters in ammonia formation over Ru/MgO catalysts [2] and also show good performance as the supports for ruthenium based catalysts. Furthermore, ceria has a special contribution to accelerate the reaction rate through the electrodonating from partially reduced $CeO_{2-\delta}$ to Ru metal [11]. However, ceria generally has the lower surface area than magnesia, so that the mixtures of them at nano-sized level are expected to be better supports for the Ru-based catalysts by high surface area derived from magnesia and electrodonating promotion from ceria.

In this study, the magnesia-ceria nanocomposite materials as supports for catalysts were prepared by co-precipitation method and characterized the synergistic effect of them for Ru-based ammonia synthesis catalysts.

2. Experimental

2.1. Preparation of catalysts

Mixtures of $Mg(OH)_2$–$Ce(OH)_{4-x}$ hydroxide gels were prepared from their acetate salt solutions as precursors of oxide supports by co-precipitation method. After washing the resultant gels with THF for three times, they were mixed with a THF solution of $Ru_3(CO)_{12}$ and stirred for 12 h to impregnate ruthenium component on them. The ruthenium loading amount was fixed to be 5 wt% for the resultant MgO–CeO_2 supports with 0, 25, 50, 75 and 100 mol% of CeO_2. The solvent was removed after impregnation and the gray powders obtained were dried in vacuum at 353 K for 12 h. Furthermore, they were heated at 393 K for 1 h and then at 723 K for 2 h (heating rate: 2 K/min) in vacuum to obtain black colored fine powders.

2.2. Ammonia synthesis and measurement of catalytic activity

The catalyst powders with various Ru contents were individually pressed into pellets (diameter = c.a. 1 mm, thickness = c.a. 0.5 mm), and 0.2 g of them were charged into U-type flow reactor tube (inner diameter = 10 mm) to perform the ammonia synthesis with stoichiometric reaction gas ($3H_2 + N_2$, SV: 18,000 mL g^{-1} h^{-1}, purity: >99.999%) at atmospheric pressure. Before the reaction, the charged catalyst was heated in a H_2 stream (50 mL min^{-1}) at 723 K for 2 h as activation treatment. The ammonia formation rate was measured by monitoring the pH value of dilute sulfuric acid solution trap (400 mL) used as an ammonia absorber.

2.3. Characterization of catalysts

XRD analysis for the resultant support materials was carried out on a Rigaku RINT-2200 X-ray diffractometer with Cu–Kα radiation. Amount of chemisorbed hydrogen on the catalysts were evaluated by the conventional pulse technique monitoring a thermal

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conductivity detector (TCD) of gas chromatograph (Shimadzu, GC-8A). To reduce Ru metal particle and eliminate adsorbed species completely, all the samples were pretreated in a H_2 stream (50 mL min^{-1}) at 723 K for 2 h and then degassed in Ar stream (50 mL min^{-1}) at 723 K for 2 h before the above-mentioned pulse experiments. The metal dispersiveness and particle size were evaluated according to sphere metal-particle model from the results of H_2 chemisorption experiments. Hydrogen consumption profiles were also observed by temperature-programmed reduction (TPR) experiments to estimate the reduction behavior of catalysts using the TCD. Prior to the TPR experiments carried out in a H_2 stream (80 mL min^{-1}) from room temperature to 923 K (heating rate 5 K min^{-1}), the catalysts were oxidized in an air stream (50 mL min^{-1}) at 823 K for 2 h. Specific surface area values were measured by BET method on a Micrometrics Flow Sorb 2300II. Microstructures of the catalysts were observed on a JEOL JEM-2010F transmission electron microscope.

3. Results and discussion

Figure 1 shows the XRD patterns of Ru/MgO, Ru/CeO_2 and Ru/(MgO–CeO_2) powders derived from $Ru(CO)_n/(Mg(OH)_2–Ce(OH)_4)$. The MgO peaks in the XRD patterns faded out with increase of CeO_2 content and finally disappeared at the CeO_2 content more than 50 mol%. Magnesia and ceria are known to form no solid solutions [11] and the MgO peaks appeared after heating in air at 873 K. These results suggest that the MgO component is in amorphous or fine particle state due to the suppression of crystal growth by CeO_2 addition even by heat treatment at 723 K *in vacuo* [12].

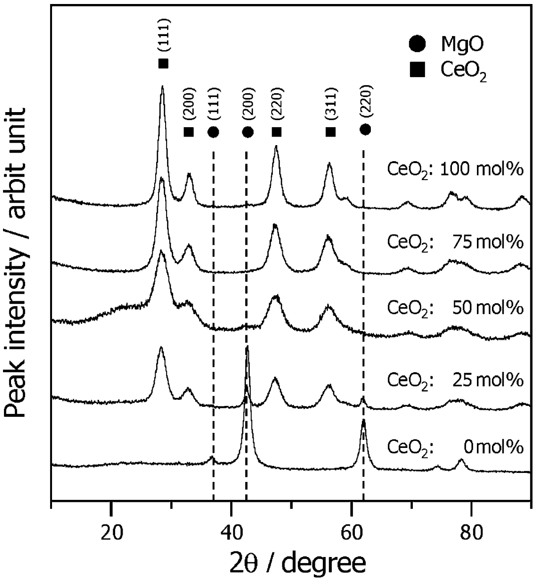


Figure 1. XRD profiles of Ru/(MgO–CeO_2) (CeO_2: 0, 25, 50, 75 and 100 mol%) catalysts. Symbols ● and ■ represent the diffraction peaks from MgO and CeO_2, respectively.

TPR profiles shown in figure 2 represent the behavior of partial reduction of CeO_2 on the surface layer of catalysts. Compared with the reduction temperature of sole CeO_2 and Ru/CeO_2 samples (790 K and 670 K, respectively), the reduction on Ru/(MgO–CeO_2) apparently took place at low temperature (550 K). Since the decrease in the reduction temperature caused by presence of precious metals such as Rh has been ascribed to SMSI effect [13], it is found that the hybridization of MgO and CeO_2 enhances such SMSI effect and accelerates the reduction of CeO_2. Partially reduced ceria, $CeO_{2-\delta}$, is known to be an *n*-type semiconductor [14] and mobile electrons in $CeO_{2-\delta}$ can be donated to Ru metal particles in the equation, $Ce^{3+} + RuCe^{4+} + Ru(e^-)$, to promote the cleavage of $N \equiv N$ triple bond [15].

The temperature dependences of ammonia formation rate measured on the Ru/(MgO–CeO_2) catalysts at various reaction temperatures are shown in figure 3. The ammonia formation rate (c.a. 4 mmol g^{-1} h^{-1}) was enlarged by the above-mentioned strong SMSI effect and maximized on the samples with 50 mol% CeO_2 at 648 K. For the Ru/(MgO–CeO_2) catalysts, the catalytic activity in the higher temperature range was in the thermodynamic equilibrium state, resulting in the limitation of ammonia formation.

Figure 4 shows the TEM photograph of Ru/(MgO–CeO_2) catalyst with 50 mol% CeO_2. Fine CeO_2 grains with sizes of 10–30 nm in diameter (dark blocks) were isolated by the amorphous or fine MgO phase (light gray area) and fine Ru metal particles (1–2 nm) were well dispersed on the surface of MgO or CeO_2 oxides (indicated in gray points). Furthermore, the surface area of Ru metal particles evaluated by H_2 chemisorption was much lower than that of conventional catalyst prepared by impregnating metal component to an anhydrous CeO_2 support materials (table 1). The calculated metal

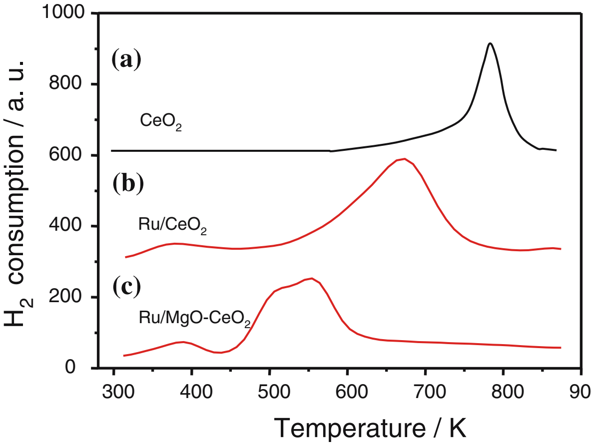


Figure 2. TPR profiles of (a) CeO_2 ([13]), (b) Ru/CeO_2 and (c) Ru/(MgO–CeO_2) (CeO_2: 50 mol%) catalysts.

Table 1
BET surface area, H_2 chemisorption data and turn-over frequencies for Ru/(MgO–CeO$_2$) catalysts

Support materials (MgO: CeO$_2$)	Ru loading [wt%]	BET surface area [m^2 g^{-1}]	H_2 uptake [μmol g^{-1}]	Calculated Ru metal particle size[a] [nm]	TOF at 598 K [s^{-1}]
0:100 (CeO$_2$)[b]	1.0	54	32	1.6	2.6×10^{-3}
0:100 (CeO$_2$)	5.0	121.8	24.8	13.3	3.4×10^{-3}
25:75	5.0	157.6	52.5	6.3	6.3×10^{-3}
50:50	5.0	144.8	43.0	7.7 (1.6)	8.0×10^{-3}
75:25	5.0	142.3	63.0	5.2	4.9×10^{-3}
100:0 (MgO)	5.0	200.3	21.4	15.4	1.8×10^{-3}

[a] Data are calculated based on H:Ru = 1:1, sphere shape of metal particle.
[b] Calculated on Ru metal impregnated on anhydrous CeO$_2$ from reference [15], reaction temperature is 588 K.
[c] Size of the Ru metal particle directly observed by TEM.

particle sizes were about 5–15 nm in diameter, but TEM observation revealed the Ru particle size was about 1–2 nm in diameter. It proves that the sphere metal particle model is not appropriate for the samples derived from Ru(CO)$_n$/M(OH)$_x$ precursor, so that Ru metal particles should be partially covered with the support as illustrated in figure 5a. The dehydroxylation process also helped to isolate CeO$_2$ fine grains with surrounding amorphous MgO matrices. On the other hand, with conventional impregnation method by which metal components are loaded onto calcined supports, both Ru metal particle sizes as observed on the TEM micrographs and evaluated from the H_2 chemisorption data have reported to be almost same as each other [4] and metal particles contact to support weakly (figure 5b).

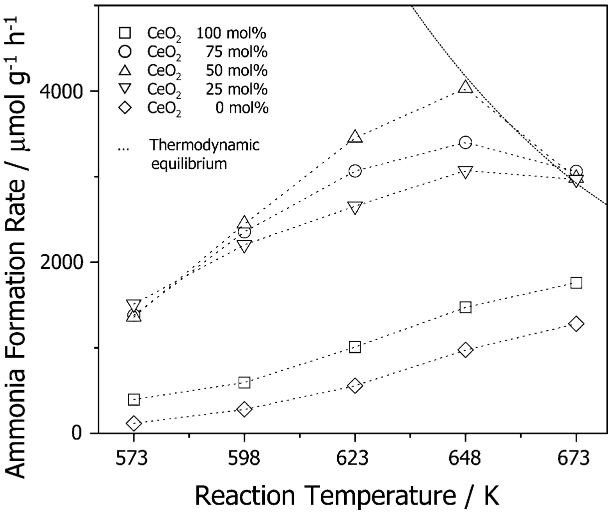


Figure 3. Temperature dependencies of ammonia formation rates on Ru/(MgO–CeO$_2$) catalysts with various contents of CeO$_2$.

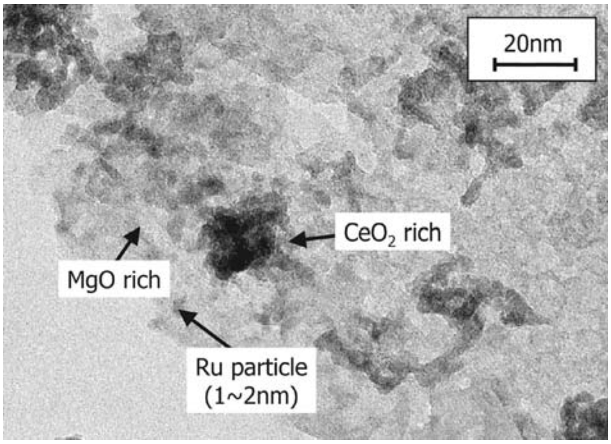
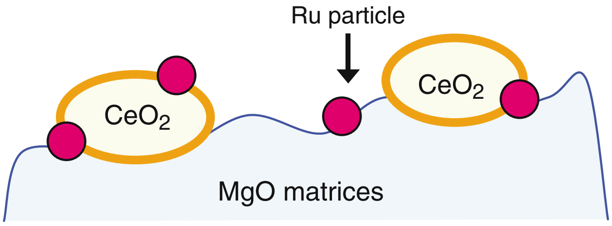


Figure 4. A TEM micrograph of Ru/(MgO–CeO$_2$) (CeO$_2$: 50 mol%) catalyst.

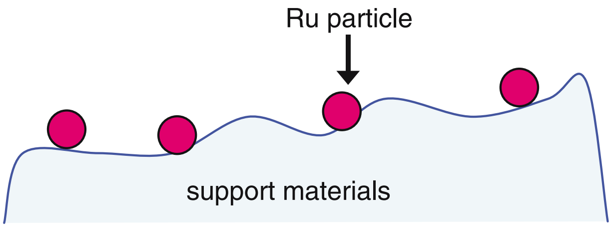
The implantation of Ru metal particles into supports enlarges the contact area between the metal and support, so that turn-over frequency (TOF) for ammonia synthesis is enhanced over the Ru/(MgO–CeO$_2$) catalysts with the strengthened metal-support interaction (SMSI). Compared with the Ru/CeO$_2$ catalyst prepared by conventional impregnation method the TOF value was increased by about 30%. In addition, through the hybridization with MgO, the TOF value was enlarged about 2.5 times more than that of Ru/MgO catalyst.

4. Conclusions

The ammonia synthesis over Ru-based catalyst is accelerated by employment of MgO and CeO$_2$



(a) Hydrogel impregnating



(b) Conventional impregnating

Figure 5. Schematic models around the surfaces of Ru/(MgO–CeO$_2$) catalysts: (a) prepared in this study, (b) prepared with conventional method.

nanocomposite materials as the catalyst support. The catalyst with 50 mol% of CeO_2 content provides the highest ammonia formation rate which is about eight times higher than that of Ru/MgO. Such high catalytic activity is due that the Ru metal particles are well dispersed and buried on the supports composed of the CeO_2 nanograins isolated with amorphous or fine MgO. This surface morphological property is responsible for simultaneous dehydration of the hydroxide gels consisting of $Mg(OH)_2$ and $Ce(OH)_4$ and the subsequent decomposition of $Ru_3(CO)_{12}$.

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