The influence of the precursor form on the ammonia synthesis activity of ruthenium zeolite catalysts

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At temperatures ranging from 300 to 450°C and under atmospheric pressure, Ru_3/KY and Ru_3/NaY catalysts prepared from sorbing $Ru(CO)_5$ generated by $Ru_3(CO)_{12}$ on KY and NaY zeolites were found to be much more active for ammonia synthesis than Ru/KY and Ru/NaY prepared from cation exchange with $Ru(NH_3)_6Cl_3$. Dynamic secondary ion mass spectrometric and X-ray photoelectron spectroscopic studies disclosed that the reduced Ru metal particles were mainly entrapped within the zeolite framework and that their nature is related to the precusor forms.

Keywords: Ru zeolites; ammonia synthesis; SIMS; XPS

1. Introduction

Supported ruthenium catalysts were found to have a higher catalytic activity for ammonia synthesis than the conventional iron catalyst [1,2] and through these catalysts ammonia may be synthesized from nitrogen and hydrogen at ambient temperature under atmospheric pressure. Such mild synthesis conditions were considered as an early key step in the artificial fixation of nitrogen [3]. The catalytic activity has been known to be quite sensitive to the nature of support and the existence of promoters [4–6]. Basic materials such as alkali metal salts, alkaline-earth oxides and lanthanides [6,7] are effective promoters by electron donation to the ruthenium, while chlorine is considered an inhibitor by retarding the hydrogen chemisorption [8]. Thus, several studies on alkali-promoted ruthenium catalysts supported on alumina indicated that Ru/Al_2O_3 catalyst prepared from Cl-free Ru–carbonyl was more active for ammonia synthesis than that prepared from $RuCl_3$ [4,7,9]. Since the dissociative adsorption of nitrogen molecules is generally accepted to be the rate determining step for ammonia synthesis [4], the reduced catalyst from supported metal–carbonyl clusters with controlling geometry of metal–metal bonds could be expected to facilitate the reaction. Using a zeolite as a host might stabilize Ru metal dispersion [2]. But, Lunsford et al. [10] found that the activity of Ru/KX from ion exchanging KX zeolite with $Ru(NH_3)_6Cl_3$ was greater in ammonia synthesis than that from the vapor deposition of $Ru_3(CO)_{12}$ on KX. Since $Ru_3(CO)_{12}$ with a diameter of 9.2 Å does not migrate easily into the supercages of faujasite zeolite through the 12-ring pore opening (diameter of 7.4 Å), our previous work [11] indicated that most of $Ru_3(CO)_{12}$ from a direct vapor deposition might be located on the zeolite surface instead of being incorporated into the supercage of faujasite zeolite. The encapsulated $Ru_3(CO)_{12}$ within the pores of faujasite zeolite can be obtained by first decomposing $Ru_3(CO)_{12}$ into the unstable monomer $Ru(CO)_5$ on the dehydrated zeolite under CO, and then reforming encaged $Ru(CO)_5$ to $Ru_3(CO)_{12}$ inside the supercage of faujasite under N_2 flow.

In this work, the catalytic activity for ammonia synthesis of reduced catalysts from $Ru(CO)_5$-loaded zeolites was compared with those from $Ru(NH_3)_6^{3+}$-exchanged zeolites. The nature and distribution of Ru were also characterized by XPS and dynamic SIMS respectively.

2. Experimental

2.1. Catalyst preparation

$Ru(NH_3)_6^{3+}$/NaY was prepared by ion-exchanging NaY and KY with an aqueous solution of $Ru(NH_3)_6Cl_3$ for 50 h at ambient temperature. $Ru_3(CO)_{12}$/NaY (V.I.) was prepared via vapor impregnation of $Ru_3(CO)_{12}$ with dehydrated NaY at 353 K. $Ru_3(CO)_{12}$ was pre-evacuated to 10^{-2}–10^{-3} Torr at ambient temperature. NaY was preheated to 673 K at 0.2 K/min under vacuum, kept at 673 K for 20 h and evacuated to 10^{-5} Torr. The white $Ru(CO)_5$/NaY or $Ru(CO)_5$/KY was obtained by reacting yellow $Ru_3(CO)_{12}$ with dehydrated NaY or KY under CO gas of 110 atm at 423 K in a Parr high pressure reactor. After being transferred

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into a N_2 dry box, part of $Ru(CO)_5$ was slowly changed into $Ru_3(CO)_{12}$ in zeolite with a color change from white to pale yellow. The samples were digested with mixed acids, and their chemical compositions were determined by ICP-AES on a GVM 1000. The Ru loading was 2.5–2.6 wt%.

2.2. *Dynamic SIMS*

All depth profiles of SIMS analyses were obtained with a CAMECA IMS-4f ion microscope using 12.5 keV O_2 ions, probe current of 185 nA and typical acquisition time of 700 s. The sample was pressed on an indium foil. The beam was raster scanned over an area of 225×225 μm^2. Under these conditions, the sputtering ratio is 4.2 Å/s. A matrix species like $^{30}Si^+$ was used to provide the normalization in order to remove small differences between analyses.

2.3. *NH_3 synthesis*

Approximately 0.3 g of ruthenium catalyst was charged into a micro-reactor of 6 mm diameter. The sample was slowly heated (about 1°C/min) to 400°C in flowing hydrogen and then maintained at 400°C for 4 h. A gas mixture of H_2 and N_2 (3 : 1) was passed through the reactor, at a flow rate of 40 ml/min. Prior to activity measurements, 20 min was allowed for the system to reach stabilization. The evolved ammonia was trapped in a solution of boric acid and NH_4Cl, and was titrated with 0.02 N sulfamic acid on an on-line automatic pH titrator. Typical reaction was under atmospheric pressure at 300–450°C and products were collected between 1/2 and 2 h. No evidence of deactivation on catalysts was observed after the running time of 10 h in the temperature range of 300–450°C. Activity was calculated as molecules of ammonia produced per Ru atom per second.

2.4. *XPS*

The photoelectron spectra were obtained from a SSI X probe (HP SSX100/206) spectrometer using monochromatic Al Kα X-rays (powered at 20 mA and 10 kV). The analyzed area was about 1.4 mm^2 and the constant pass energy in the hemispherical analyzer 50 eV. The vacuum during spectra acquisition was better than 1×10^{-8} mbar. Since the zeolite sample is an insulating material, a flood gun with 6 eV was used for charge compensation.

The Ru-containing zeolite, after reduction in H_2 at 400°C for 2 h, was pressed in stainless-steel sample holders of 4 mm in diameter under the protection of an isooctane solution [12]. Spectra were obtained for the Si_{2s}, Al_{2s}, O_{1s}, Ru_{3d}, Ru_{3p}, C_{1s}, Na_{1s} and K_{2s} regions. The intensities were calculated by integrating each peak after Shirley's background subtraction method. The atomic concentration ratios were calculated by taking into account the experimental sensitivity factors. The binding energy was referred to $C_{1s} = 284.6$ eV. The reproducibility was estimated to be $+0.1$ eV.

3. Results and discussion

The SIMS depth profiles for $Ru(NH_3)_6^{3+}$/NaY, $Ru_3(CO)_{12}$/NaY and $Ru(CO)_5$/NaY are presented in fig. 1. The surface enrichment of $^{102}Ru^+/^{30}Si^+$ ratio was observed on $Ru_3(CO)_{12}$/NaY (V.I.), not on $Ru(NH_3)_6^{3+}$/NaY and $Ru(CO)_5$/NaY. This indicates that most likely $Ru_3(CO)_{12}$ of $Ru_3(CO)_{12}$/NaY (V.I.) is located on the catalyst surface and may not migrate into the supercage of the Y zeolite, and that the $Ru_3(CO)_{12}$ deduced from $Ru(CO)_5$ may be located inside the zeolite framework as $Ru(NH_3)_6^{3+}$. A linear relationship was observed between the $^{102}Ru^+/^{30}Si^+$ ratio on the surface by SIMS and in the bulk by ICP-AES (fig. 2). The relative sensitivity of the $^{102}Ru^+/^{30}Si^+$ ratio is dependent on the form of Ru and in the order of $Ru(NH_3)_6^{3+}$/NaY > $Ru(CO)_5$/NaY > $Ru_3(CO)_{12}$/NaY (V.I.). These results may be derived from the effect of ion-induced local heating on samples, since $Ru_3(CO)_{12}$ is easily vaporized and can be decomposed at 150°C. The relative ion intensities on SIMS are controlled by the relative stabilities of ions in their vapour phase, which was also found on transition-metal oxides and mixed oxides by Allen et al. [13]. The distortion of the Na_{2s} line shape on faujasites subjected to very mild electron bombardment ($E_k > 6$ eV) was ascribed to the reduction of Na^+ ions to the metallic state [14].

The catalytic activities of supported ruthenium catalysts on ammonia synthesis are dependent on the reaction temperature, as shown in fig. 3. The Ru_3/NaY and Ru_3/KY catalysts prepared from decarbonylation of supported $Ru(CO)_5$ on zeolite have higher activities

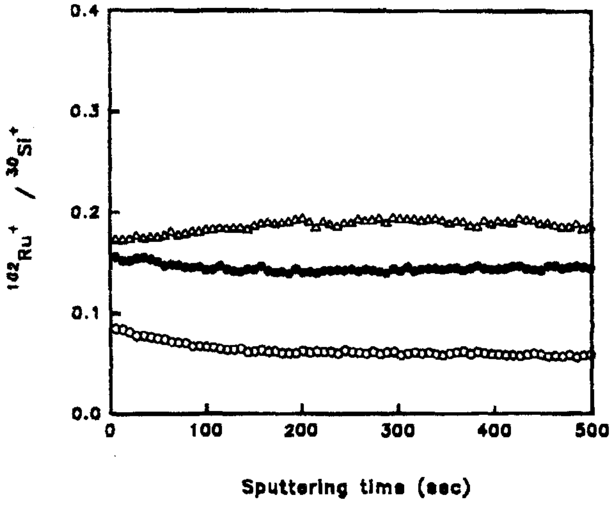

Fig. 1. SIMS depth profiles of $Ru(NH_3)_6^{3+}$/NaY (△), $Ru_3(CO)_{12}$/NaY (○) and $Ru(CO)_5$/NaY (●).

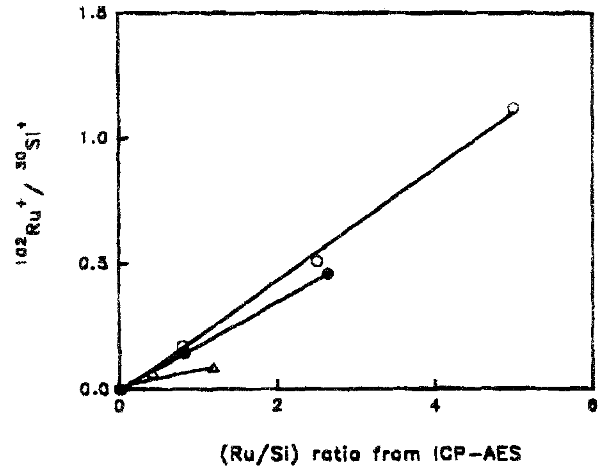

Fig. 2. The plot of $^{102}Ru^+/^{30}Si^+$ ratio from SIMS versus Ru loading from ICP-AES for $Ru(NH_3)_6^{3+}/NaY$ (○), $Ru_3(CO)_{12}/NaY$ (△) and $Ru(CO)_5/NaY$ (●).

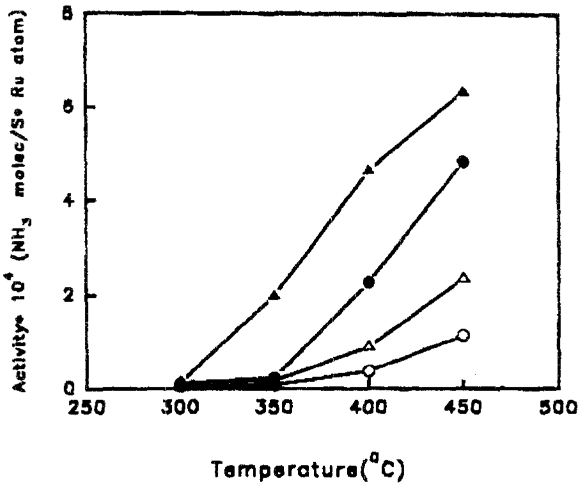

Fig. 3. Activities of ammonia synthesis versus reaction temperature on Ru/NaY (○), Ru/KY (△), Ru_3/NaY (●) and Ru_3/KY (▲).

over the temperature range from 300 to 450°C than the catalyst prepared from $Ru(NH_3)_6^{3+}$ ion-exchanged zeolites. While Lunsford et al. [10] considered that the source of Ru is unimportant for the activity of Ru/KX prepared from $Ru(NH_3)_6Cl_3$ or $Ru_3(CO)_{12}$, Moggi et al. [8] reported that the catalyst derived from $Ru_3(CO)_{12}$ cluster was more active than the catalyst prepared from $RuCl_3$ on Al_2O_3. Two factors may account for the high catalytic activities of Ru_3/KY and Ru_3/NaY from $Ru(CO)_5$/Y: (1) After dehydration and reduction, the Brønsted acid site can be formed on Ru/KY and Ru/NaY but not on the Ru_3/KY and Ru_3/NaY catalysts; however, the activity in ammonia synthesis increases with the basicity of support and it may be retarded by Brønsted acidity. (2) Ru–Ru bonding may be retained in the Ru_3/KY or Ru_3/NaY catalyst after decarbonylation, and it may favor N≡N bond breaking. Moreover, the Raman spectrum of Ru–Ru bond in $Ru_3(CO)_{12}$/NaY formed from $Ru(CO)_5$/NaY has been observed at 189 cm^{-1} and it is comparable with the frequency of Ru–Ru in $Ru_3(CO)_{12}$ at 187 cm^{-1}. The catalytic activities of Ru zeolite catalysts at 350°C are listed in table 1. The activity of our Ru_3/KY sample is about five times that of the activity of Ru/KY reported by Lunsford et al. [10]. Dumesic et al. [15] indicated that the activity for ammonia synthesis could be affected by metal dispersion: as the dispersion of Fe on Fe/MgO catalysts decreased, the turnover frequency increased. But, Aika et al. [16] suggested that the influence of crystalline size should not be as important as that of the electronic effect.

XPS results of Ru-containing Y zeolites reduction in hydrogen at 400°C are shown in table 1. The binding energies (BE) of supported Ru catalysts were in the order Ru/NaY = Ru/KY > Ru_3/NaY = Ru_3/KY. This result indicates that the binding energy of $Ru_{3d_{5/2}}$ is dependent on the precursor form and not on the nature of the alkali cation. Our binding energies for the $Ru_{3d_{5/2}}$ peak shift 0.8–1.4 eV to 280.0 eV of unsupported Ru^0 and are close to the 281.0 eV for RuNaY after reduction in flowing H_2 at 400°C reported by Lunsford et al. [17]. Based on the previous result of H_2 chemisorption, the metal dispersion for Ru/NaY (H/Ru = 0.52) was higher than that for Ru_3/NaY (H/Ru = 0.32). Table 1 shows that the binding energy of the $Ru_{3d_{5/2}}$ peak decreases with increased particle size of ruthenium. Espinos et al. [18] observed a similar phenomenon namely that $Ni_{2p_{3/2}}$ binding energies decreased with increasing size of metal

Table 1
Binding energies and peak ratios of XRD and activities of ammonia synthesis for reduced Ru zeolite catalysts

Catalysts	Binding energy of $Ru_{3d_{5/2}}$ (eV) [a]	$Ru_{3p_{3/2}}/Si_{2s}$	Atomic ratio		Activity [c] $\times 10^4$
			Na_{1s}/Si_{2s}	K_{2s}/Si_{2s}	
2.5% Ru/NaY	281.4	0.054	0.37	–	0.09
2.6% Ru/KY	281.3	0.084	–	0.189	0.18
2.6% Ru_3/NaY	280.8	0.049	0.67	–	0.23
2.5% Ru_3/KY	280.9	0.12	–	0.31	2.07
2.0% Ru/KY [b]	–	–	–	–	0.44

[a] Using C_{1s} = 284.6 eV as a reference.
[b] Data from ref. [10].
[c] Reaction at 350°C and acitivy represented in TOF, molec. NH_3 s^{-1} (Ru atm)$^{-1}$.

particles from ~ 30 to 250 Å. Because of the poor coupling between the metallic particles and support valence band, such as SiO_2, Wertheim et al. [19] suggested that the BE shift would be the positive charge left behind on the particle as the photoelectron escapes. If the substrate is a conductor , the core hole in the particle can be fully screened, so that an electron from the substrate may hop onto the particle leading to complete delocalization of the hole. In addition , $Ru_{3p_{3/2}}/Si_{2s}$ ratios for Ru-containing Y zeolites were as follows: $Ru_3/KY > Ru/KY > Ru/NaY > Ru_3/NaY$. The $Ru_{3p_{3/2}}/Si_{2s}$ ratio for potassium-exchanged Y zeolite is higher than that for sodium-exchanged Y zeolite. The activity of ammonia synthesis depends on the content of surface ruthenium, which, in turn, can be enhanced by potassium ions.

In summary, this work shows that Ru_3/KY and Ru/KY with K^+ promotion showed much higher activity than Ru_3/NaY and Ru/NaY. To improve the support effect the K^+ ion-exchange in zeolite is quite significant on the catalyst derived from ruthenium–carbonyl precusor. It is clear that the potassium ion-promoted ruthenium zeolite that is derived from encaged Ru–carbonyl cluster is a promising catalyst for ammonia synthesis.

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