Catalytic Oxidation of Nitric Oxide to Nitrogen Dioxide on Ru-FAU

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Abstract Ru-FAU samples were prepared by wet impregnation and studied as promising catalysts for NO oxidation. The existence of rare earth ions in FAU structure showed positive effect on NO oxidation while the existence of alkali metal ions on cation sites showed negative effect. As a result, Ru-REY exhibited the best activity and a maximal NO conversion of ca. 94% was obtained at 250 °C at a very high WHSV of 180,000 h⁻¹.

Keywords NO oxidation · Ru catalysts · FAU zeolite · REY

1 Introduction

Nitrogen oxides are known to be associated with several environmental and health hazards, including photochemical smog and acid rain. Due to the increasingly stringent regulations on nitrogen oxide emissions, various post-treatment methods have been attempted for the reduction of NO_x emissions in excess oxygen [1]. In the case of stationary sources, the selective catalytic reduction of NO_x by ammonia (NH₃-SCR), a state-of-the-art technology for NO_x abatement, has been extensively studied. In the case of mobile sources, the selective catalytic reduction of NO_x by hydrocarbons (HC-SCR) and NO_x storage and reduction

(NSR) are two major techniques and draw much attention. During the above-mentioned processes, it becomes more and more evident now that NO₂ plays a decisive role. For NO_x storage and reduction, NO is first oxidized to NO₂ over the noble metal component and then stored as nitrates or nitrites on the basic component [2]. For the selective catalytic reduction of NO_x, NO is partially oxidized to NO₂, which subsequently reacts with hydrocarbon or NH₃ to give out N₂ [3]. More important, the so-called “fast” SCR reaction ($4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$), in contrast to standard ammonia SCR reaction ($4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$), is drawing more and more attention in recent years [4–8]. The reaction between equimolar NO–NO₂ and NH₃ is ca. 10 times faster than the reaction between NO and NH₃ at low temperatures (200–300 °C). Therefore, the fast SCR reaction is considered as a feasible means to boosting the denitrification efficiency at lower temperatures as well as to reducing the catalyst costs of SCR system. However, it is known that nitrogen oxides produced from emission sources mainly consist of NO (>90%). Thus, the oxidation of NO to NO₂ becomes a key step to realize the fast SCR process and catalysts with sufficient activity for NO oxidation are being researched.

During the research of NO oxidation catalysts, supported platinum catalysts drew much attention. Pt/SiO₂ [9, 10] and Pt/Al₂O₃ [11, 12] have been reported to be highly active for NO oxidation, and up to now supported platinum catalysts are still regarded as model catalysts for NO oxidation. As for supported platinum catalysts, the deactivation in strong oxidizing conditions remains a big problem to be solved [13]. Moreover, the high cost of noble metal platinum materials also restricts the application of supported Pt catalysts to a great extent. Therefore, alternative catalysts for NO oxidation are under investigation. For example, supported cobalt catalysts have been

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reported to be very active for NO oxidation by several groups [14–16].

In this work, less expensive ruthenium is selected as the alternative active component for NO oxidation and zeolites with FAU structure are employed as catalytic supports. Ru-FAU samples are prepared by simple impregnation and tested as promising catalysts for NO oxidation. The effects of zeolite supports choice, optimal ruthenium loading and experimental conditions on NO oxidation activity are discussed in details.

2 Experimental

2.1 Catalysts Preparation

Commercial zeolites with FAU structure, NaY (Si/Al = 3.8), HY (Si/Al = 5.4), ultra-stable Y (USY, Si/Al = 11.6) and rare earths Y (REY, Si/Al = 7.2, RE₂O₃ wt% = 5.2) were provided by Sinopec. Co and directly used as catalyst supports. Ruthenium species were introduced to the support by wet impregnation using RuCl₃ as precursor. In a typical synthesis, 1 g zeolite support was impregnated with a certain amount of 2 mM RuCl₃ aqueous solution under vigorous stirring at a constant temperature of 80 °C. The as-prepared samples were dried at 100 °C over night and then calcined at 450 °C in flowing air for 4 h.

For reference, Ru/TiO₂ with Ru weight loading of ca. 2% and Pt/Al₂O₃ with Pt weight loading of ca. 2% were also prepared by similar wet impregnation process.

2.2 Catalyst Characterization

The Ru, Si and Al loadings in Ru-FAU samples were determined by ICP–AES using an Optima 2000 spectrometer.

The surface areas of Ru-FAU catalysts were analyzed by low temperature N₂ adsorption/desorption using a Quantachrome NOVA-1200 gas absorption analyzer and the specific surface areas were calculated using the BET equation.

The dispersion of ruthenium on FAU support was determined by CO pulse adsorption on a chemisorption analyzer (Chemisorb 2720, Micromeritics). In a typical experiment, ca. 100 mg sample in the quartz reactor was first reduced in 5% H₂/He at 450 °C for 1 h and pre-treated in He at 450 °C for 1 h to remove H₂ adsorbed on the surface of samples. After cooling down to room temperature in flowing He, pulses of 5% CO/He were injected to the reactor one pulse per minute until no further changes in signal intensity of outlet CO. The dispersion of ruthenium was calculated assuming the equimolar adsorption of CO on ruthenium metal.

The X-ray diffraction patterns of samples were recorded on a Rigaku powder diffractometer (D/MAX-RB) using

Cu-K α radiation ($\lambda = 0.15418$ nm) at a scanning rate of 4°/min in $2\theta = 5$ –80°.

The temperature-programmed reduction experiments of samples were carried out on a chemisorption analyzer (Chemisorb 2720, Micromeritics) with 5 vol % H₂/Ar at a heating rate of 10 °C/min from 50 to 700 °C. Prior to reduction, the sample (100 mg) was treated in He at 450 °C for 1 h.

The temperature-programmed desorption of oxygen (O₂-TPD) were also performed on the chemisorption analyzer. The samples were pre-treated in 5 vol % O₂/He at 450 °C for 1 h and then cooled down to room temperature in the same flow. After He purge for 30 min at 50 °C, the temperature-programmed desorption experiments were conducted in He flow from 50 to 700 °C at a heating rate of 10 °C/min.

Transmission electron microscopy images of samples were acquired on a JEOL 3010 transmission electron microscope at an acceleration voltage of 200 kV. Samples were crushed and deposited on a carbon-coated copper grid, and then evaporate at room temperature.

2.3 Catalytic Oxidation of Nitric Oxide

The catalytic oxidation of NO was carried out in a fixed-bed flow micro reactor at atmospheric pressure. A 0.15 g sample (sieve fraction of 0.17–0.25 mm, small enough to exclude internal mass transfer limitations) was placed in a quartz reactor (4 mm i.d.) and pretreated in 5% O₂/He at 450 °C for 1 h. After cooling to 150 °C in He, the reactant gas was fed to the reactor. A typical reactant gas composition was 400 ppm NO, 10% O₂, and balance He. The total flow rate of the gas mixture was maintained at 450 mL min^{−1}, corresponding to a WHSV of 180,000 mL/g_{cat}h. The inlet and outlet gases were monitored on-line using a gas chromatograph (HP 6820 series, for N₂ and N₂O analysis) and a chemiluminescence NO_x analyzer (Ecotech EC 9841, for NO and NO₂ analysis).

3 Results and Discussion

3.1 Characterization Results of Ru-FAU Samples

The physical properties of as-prepared Ru-FAU samples are characterized and the results are summarized in Table 1. It is seen that the Si/Al ratios in each samples increase to some degree in comparison with parent zeolite, indicating the dealumination (up to 10%) during preparation process. Besides, the surface areas of Ru-FAU are observed to be in the range of 400–550 m² and the dispersion of ruthenium on different zeolites is found to be 40–60%.

Table 1 Physical properties of Ru-FAU samples

Catalyst	Ru loading (wt%)	Si/Al	Surface area (m ² /g)	Ru dispersion (%)
Ru-NaY	1.93	4.3	447.8	49.5
Ru-HY	1.98	5.9	548.1	52.3
Ru-USY	1.95	13.1	537.4	55.2
Ru-ReY	1.91	7.5	431.2	54.7
Ru-REY-0.5%	0.54	7.9	445.2	59.2
Ru-REY-1%	0.97	7.4	439.4	56.5
Ru-REY-4%	3.85	8.1	419.8	40.8

Fig. 1 XRD patterns of various Ru-FAU samples

Figure 1 shows XRD patterns of various Ru-FAU catalysts. It is seen that Ru-NaY, Ru-HY and Ru-USY show almost identical diffraction lines, corresponding to the typical structure of FAU zeolites [17]. As for Ru-REY, the intensities of all diffraction lines corresponding to FAU structure decrease to some extent and especially the two diffraction lines at 10.3° and 12.0° almost disappear. It is thus indicated the introduction of rare earths to FAU zeolite may result in the partial destruction of zeolite structure. Besides, a weak diffraction line at 12.4° is also observed in the XRD pattern of Ru-REY, corresponding to the rare earth ions inside the super cages [18]. Generally, rare earth ions may be located both inside the super cages and inside the sodalite cages of REY. In this work, the diffraction line at 12.4° corresponding to rare ions inside the super cages is clearly observed and the diffraction line at 11.8° corresponding to rare ions inside the sodalite cages is very weak. Therefore, we believe that most rare earth ions are located inside the super cages of REY. For all Ru-FAU samples, no diffraction lines corresponding to ruthenium oxides are observed, which can be ascribed to the poor crystallization or good dispersion of ruthenium oxides.

The H₂-TPR profiles of Ru-FAU samples are shown in Fig. 2. The reduction peaks at below 250 °C should be

ascribed to the reduction of different types of Ru oxides since the support materials cannot be reduced within this temperature range. For Ru-USY, two reduction peaks at 100 °C and 130 °C are observed, which can be ascribed to the reduction of highly dispersed amorphous RuO₂ and bulk amorphous RuO₂ [19, 20], respectively. As for Ru-NaY, the reduction of highly dispersed amorphous RuO₂ and bulk amorphous are observed at higher temperature than that on Ru-USY, e.g., at 120 °C and 155 °C, respectively. The existence of alkali metal ions Na⁺ in FAU structure significantly retards the reduction of ruthenium oxides by hydrogen, consistent with literature results [21]. As for Ru-REY, a reduction peak at ca. 70 °C is observed and ascribed to the reduction of amorphous ruthenium oxides. It is noted that the reduction temperature of amorphous ruthenium oxides on Ru-REY is much lower than that on Ru-USY, probable due to the interaction between ruthenium oxides and rare earth ions. Besides, two reduction peaks at 580 °C and 610 °C corresponding to the reduction of rare earth ions are observed on Ru-REY.

The H₂ consumption during the reduction of ruthenium species (reduction peaks at below 250 °C) in Ru-FAU is calculated and displayed in Fig. 2. The H₂ consumption indicates that most ruthenium species exist in the state of Ru⁴⁺, i.e., RuO₂ and are reduced to metallic Ru during TPR process. From the H₂-TPR profiles of Ru-FAU samples, following two aspects can be easily concluded. Firstly, ruthenium species exist in Ru-FAU in the form of amorphous RuO₂ that can be reduced at below 200 °C. Secondly, the alkali metal ions Na⁺ in FAU structure retard the reduction of ruthenium species by hydrogen while the rare earth ions promote the reduction of ruthenium species by hydrogen in Ru-FAU.

The O₂-TPD profiles of the Ru-FAU samples are shown in Fig. 3. In the temperature range of 100–300 °C, there are two desorption peaks over each sample. These peaks are ascribed to the desorption of surface oxygen species, the peak at lower temperature to O²⁻ and the peak at higher temperature to O⁻ [22, 23]. It is seen that the desorption of surface oxygen is facilitated by the existence of rare earth ions while it is retarded by the existence of alkali metal ions, considering the temperature difference for surface

Fig. 2 H₂-TPR profiles of various Ru-FAU samples

Fig. 3 O₂-TPD profiles of various Ru-FAU samples

oxygen desorption. On Ru-REY and Ru-USY, an oxygen desorption peak at high temperature of ca. 410 °C is observed, which should be ascribed to the desorption of lattice oxygen from ruthenium oxides. There are no similar peaks observed on Ru-NaY, due to the interaction between Na⁺ and ruthenium oxides. The O₂-TPD results in this work are employed to illustrate the interaction between ruthenium oxides and rare earth ions or alkali metal ions in Ru-FAU.

3.2 NO Oxidation Over Ru-FAU Catalysts

The temperature dependence of steady-state NO oxidation over Ru-FAU, Ru/TiO₂ and Pt/Al₂O₃ are shown in Fig. 4. For reference, the thermodynamic equilibrium for NO–NO₂ under given conditions is also shown in the figure (in dashed). The main product for NO oxidation is NO₂, and the formation of other N-containing product, such as N₂O and N₂, can be neglected. The NO conversion to NO₂ over catalysts was kinetically limited at low temperatures and equilibrium limited at higher temperatures. For Ru-FAU catalysts, Ru-REY shows the highest activity, followed by Ru-HY and Ru-USY, and then Ru-NaY. For the best Ru-REY catalyst, a 50% NO conversion to NO₂ was achieved at ca. 230 °C and the maximal NO conversion of ca. 94.5% is achieved at ca. 250 °C. At above 250 °C, the NO conversion dropped gradually along the thermodynamic equilibrium. It should be noted that the NO oxidation activity of Ru-REY is obtained at a very high WHSV of 180,000 mL/g_{cat}h and the activity is higher than that on other supported ruthenium catalysts, e.g., Ru-TiO₂ [20]. The activity of Ru-REY is also much higher than that on Pt/Al₂O₃ model catalyst (pre-reduced) for NO oxidation under similar conditions, as shown in Fig. 4. Ru-HY and Ru-USY exhibit similar activity for NO oxidation despite of the different Si/Al ratios of HY and USY. It is thus deduced that the Si/Al ratios of FAU zeolites is not a key factor controlling the NO oxidation activity of Ru-FAU catalysts. From the catalytic results, we clearly see that the existence of rare earth ions shows positive effect on NO oxidation while the existence of alkali metal ions on cation sites shows negative effect.

Fig. 4 Catalytic activities for NO oxidation on Ru-FAU, Ru/TiO₂ and Pt/Al₂O₃. Reaction conditions: 0.15 g catalyst, 400 ppm NO, 10% O₂ and the balance He, WHSV = 180,000 mL/g_{cat}h

The nature of ruthenium species is changed by interaction with rare earth ions or alkali metal ions, as indicated by the H_2 -TPR and O_2 -TPD results. Correlating the catalytic results and H_2 -TPR results, it is found that ruthenium oxides reducible at lower temperatures shows higher activity for NO oxidation.

3.3 Effects of Initial NO and O_2 Concentration on NO Oxidation

The effects of initial NO and O_2 concentration on NO oxidation are investigated and the results are displayed in Fig. 5. It is seen that NO conversion to NO_2 slightly decreases from ca. 46% to ca. 30% with initial NO concentration increasing from 100 to 1,000 ppm at the constant temperature of 225 °C (O_2 concentration fixed at 10%). The NO conversion increases from ca. 15% to ca. 38% with increasing oxygen concentration from 1 to 10% at 225 °C with fixed NO concentration of 400 ppm. Further increase in oxygen concentration to 20% does not bring corresponding increase in NO conversion as expected. It is evident that oxygen plays a distinct positive role on NO oxidation for $\text{O}_2 < 10\%$.

3.4 Effects of H_2O and SO_2 on NO Oxidation Over Ru-REY

For practical application, Ru-REY catalysts are expected to work under the conditions with SO_2 and water vapor in the stream. So, it is necessary to clarify their effects on NO

Fig. 5 Influence of initial NO and O_2 concentration on NO conversion at 225 °C. Reaction conditions: 0.15 g catalyst, 100–1,000 ppm NO, 1–20% O_2 and the balance He, WHSV = 180,000 mL/g_{cath}h

Fig. 6 Influence of H_2O and SO_2 in the stream on NO conversion over Ru-REY. Reaction conditions: 0.15 g catalyst, 400 ppm NO, 10% O_2 0 or 2% H_2O , 0 or 40 ppm SO_2 , and the balance He, WHSV = 180,000 mL/g_{cath}h

oxidation. As seen in Fig. 6, the presence of 2% H_2O in the reaction system shows slight negative effect on NO oxidation. For example, the light-off-temperatures (when T_{50} is achieved) slightly increase from 230 to 236 °C. The inhibition effect of H_2O on NO oxidation is presumably originated from the competitive adsorption of H_2O on the active sites. The presence of 40 ppm SO_2 shows more serious negative effect on NO oxidation. Typically, the light-off-temperatures increase from 230 to 321 °C with the addition of 40 ppm SO_2 . SO_2 poisoning is known as the most serious problem for NO catalytic oxidation since catalysts preferred to convert SO_2 to SO_3 ($2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$) instead of oxidation of NO. The formed SO_3 may not only occupy the active sites for NO oxidation but also cover the support materials by forming sulfates [9]. It is seen that the inhibition effect of SO_2 on NO oxidation over Ru-REY is not as serious as that over some Pt catalysts [24]. A possible explanation is that Ru is not as active as Pt for SO_2 oxidation.

3.5 Effects of Ru Loading on NO Oxidation Over Ru-REY

In order to obtain the effects of Ru loadings on the NO oxidation activity, Ru-REY catalysts with different Ru loadings are studied and the results are shown in Fig. 7. Higher activity is observed with higher ruthenium loadings, as Ru-REY-4% > Ru-REY-2% > Ru-REY-1% > Ru-REY-0.5%. The light-off-temperatures increase from 227 to 277 °C with Ru loadings decrease from 4 to 0.5%. It should be noted that Ru-REY-4% only exhibited a little higher activity than Ru-REY-2% and Ru-REY-1% also exhibited a little higher activity than Ru-REY-0.5%

Fig. 7 Catalytic activities for NO oxidation on Ru-REY catalysts with different Ru loadings. Reaction conditions: 0.15 g catalyst, 400 ppm NO, 10% O₂ and the balance He, WHSV = 180,000 mL/g_{cath}

though the ruthenium loading was doubled. In contrast, Ru-REY-2% shows distinct higher activity than Ru-REY-1%. Obviously, NO oxidation activity over Ru-REY is not linearity dependent on ruthenium loadings. By taking both the activity and the cost of catalyst into account, the optimal ruthenium loading is ca. 2%. For reference, the activity of Ru-HY with ruthenium loadings of 1 and 2% are also shown in Fig. 7. It is seen that Ru-HY-1% exhibits similar activity to Ru-REY-1% while Ru-HY-2% exhibits much lower activity than Ru-REY-2%. A possible explanation is that the promotion effect of rare earth ions on NO oxidation does not operate with ruthenium loading of 1%.

The TEM images of Ru-REY with different ruthenium loadings are shown in Fig. 8. For Ru-REY-0.5%, no obvious ruthenium oxides can be distinguished, probably due to low ruthenium loading and high dispersion of ruthenium species. For Ru-REY-1%, very small ruthenium oxides clusters of below 2 nm can be found after careful observation. In the TEM image of Ru-REY-2%, ruthenium oxides clusters of 2–4 nm with good dispersion in REY zeolite are clearly

Fig. 8 TEM images of Ru-REY catalysts with different ruthenium loadings

observed. As for Ru-REY-4%, ruthenium oxides of above 5 nm are observed. It is easily seen that the size of ruthenium oxides clusters on REY increases with increasing ruthenium loadings.

Compared to that on Ru-REY-2%, the NO oxidation activity on Ru-REY-0.5% and Ru-REY-1% is rather low (see Fig. 7) though ruthenium and rare earth ions both present. It is proposed that the interaction between rare earth ions and ruthenium oxides are formed only if ruthenium loading exceeds a certain value. As for Ru-REY-4%, much higher NO oxidation activity than Ru-REY-2% is not obtained as expected though the interaction between rare earth ions and ruthenium oxides are formed and the ruthenium loading is doubled. A possible explanation can be given from the decrease in ruthenium dispersion from 54.7 to 40.8%, as seen in Table 1.

4 Conclusion

Zeolites NaY, HY, USY and REY with the similar FAU structure were employed as catalyst supports and ruthenium was introduced on the supports by simple wet impregnation. The as-prepared Ru-FAU samples were studied as promising catalysts for NO oxidation. Ru-REY exhibited the highest activity for NO oxidation, followed by Ru-HY and Ru-USY and then Ru-NaY. As for Ru-REY catalyst, a maximal NO conversion of ca. 94% could be obtained at 250 °C under a very high WHSV of 180,000 h⁻¹. Based on the H₂-TPR and O₂-TPD results on Ru-FAU, it is found that both the rare earth ions in REY and alkali metal ions in NaY could interact with ruthenium oxides and subsequently change the nature of ruthenium oxides on FAU zeolites. As a consequence, rare earth ions show positive effect on NO oxidation over Ru-FAU while alkali metal ions Na⁺ showed negative effect. The optimal ruthenium loading in Ru-REY catalyst for NO oxidation is determined to be ca. 2%. The presence of H₂O in reaction system shows mild negative effect on NO oxidation while the presence of SO₂ shows great negative effect on NO oxidation.

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