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A novel catalyst for NO reduction by CO

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A silica-pillared layered niobate (Si-Nb_3O_8) has been prepared by intercalating layered niobate with $NH_2(CH_2)_3Si(OEt)_3$. The results of XRD and BET measurement showed that the obtained product was a porous material with a high specific surface area and high thermal stability, and its layered structure remained unchanged after treatment with 5 vol% water vapor at 500 °C for 3 h. Using Si-Nb_3O_8 as support, a 2 wt% Cu/Si-Nb_3O_8 catalyst was prepared by impregnation of $Cu(NO_3)_2$ solution and the catalytic reduction of NO by CO was examined. The results showed that the catalyst had a good activity and selectivity, and the pretreatment of 5 vol% water vapor could obviously improve the conversion of NO reduction, while the selectivity of NO to N_2 almost kept unchanged.

KEY WORDS: pillaring; layered niobate; silica; copper oxide; nitrogen monoxide; catalytic reduction; carbon monoxide; water vapor.

1. Introduction

Air pollution induced by nitrogen oxide (NO_x) in the exhaust gases from automobiles and power plants has become a serious problem. Atmospheric emissions of NO_x not only have a detrimental effect on human health, but also have adverse effects on the ecosystems in which we live. Therefore, the development of excellent catalysts to remove NO_x is of great importance. The use of CO for the catalytic reduction of NO was one of the first possibilities investigated to eliminate NO from automotive exhaust gas [1–4]. To date, although many catalysts, such as base metal oxides, mixed metal oxide compounds like perovskites, supported metal catalysts, and metal zeolites have already been investigated, the difficulty of achieving long-term stability of the catalysts in the presence of H_2O and SO_2 means that few systems can be used in practice [5].

Metal-oxide-pillared layered materials are two-dimensional zeolite-like materials. They are usually prepared by intercalating large inorganic hydroxycations, which are polymeric or oligomeric hydroxy metal cations formed by the hydrolysis of metal oxides or salts. Upon heating, the metal hydroxy cations undergo dehydration and dehydroxylation, forming stable metal oxide clusters which act as pillars keeping the matrix layers separated, creating interlayer space of molecular dimensions. Since these materials have a number of attractive features such as high porosity, high surface area and high thermal stability, they have attracted considerable attention as catalysts and adsorbents. In particular, smectite clays pillared by metal oxides have been successfully used as dehydrogenation and selective oxidation catalysts [6–8] and acid catalysts in several organic reactions as well [9]. Ion-exchanged pillared clays also have been found to be active for the selective catalytic reduction of NO by NH_3 or hydrocarbons [10–13]. On the other hand, pillared derivatives of some layered phosphates [14,15], titanates [16], lanthanum-niobates [17] and titanoniobates [18] have also been prepared, but their applications in catalysis have hardly been investigated. Hydrated Nb_2O_5 is making an impact in its application as an unusual solid acid catalyst [19]. However, a low surface area often limits its application in catalysis. In this paper, a silica-pillared layered niobate (represented by Si-Nb_3O_8) was prepared by the reaction of HNb_3O_8 powder with an aqueous solution of $NH_2(CH_2)_3Si(OEt)_3$. This product is a new porous material with a high specific surface area, thermal stability and hydrothermal stability, and therefore could be a promising support of catalysts. Herein, by using silica-pillared layered niobate as support, a 2 wt% Cu/Si-Nb_3O_5 catalyst was first prepared for the NO + CO reaction. It was found that the catalyst had a relatively high activity for NO reduction and good selectivity to N_2. Besides, the pretreatment with 5 vol% water vapor before the reaction could obviously improve the catalytic activity of NO reduction, while the selectivity remained unchanged.

2. Experimental

2.1. Synthesis of silica-pillared layered niobate and preparation of catalyst

KNb_3O_8 was prepared by the solid-state reaction of a stoichiometric mixture of Nb_2O_5 and KNO_3 powder at 900 °C for 3 h according to Nedjar *et al.* [20]. HNb_3O_8 was obtained by a two-step cation-exchange reaction.

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15 g KNb_3O_8 powder was added to 400 ml 7 M HNO_3 solution under stirring at room temperature for 2 days, followed by centrifugation, and washed with distilled water twice. The obtained solid product was then added to 400 ml 7 M HNO_3 solution again under the same condition for one day so that K^+ could be completely exchanged by H^+. The final product was fully washed with distilled water, and then dried at 50 °C for 24 h.

Silica-pillared layered niobate was prepared by adding 10 g HNb_3O_8 powder, under stirring, to 700 ml freshly-prepared 10 wt% aqueous solution of $NH_2(CH_2)_3Si(OEt)_3$ (Si : Nb = 10 : 1). The dispersion was refluxed for 60 h, followed by centrifugation, and fully washed with distilled water, then air-dried at 50 °C for 24 h, and finally calcined in air at 500 °C for 12 h.

2 wt% Cu catalyst supported on silica-pillared layered niobate (represented by 2 wt% Cu/Si-Nb_3O_8) was prepared by the impregnation of Si-Nb_3O_8 powder with an aqueous solutions of $Cu(NO_3)_2$. 2 g Si-Nb_2O_8 powder was soaked into 4 ml corresponding aqueous solutions of $Cu(NO_3)_2$ under stirring at room temperature for 1.5 h, then evaporated at 60 °C for 2 h, dried at 100 °C overnight, and finally calcined at 500 °C in air for 3 h.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on a Shimadzu XD-3A diffractometer operating with Cu K_α radiation and an Ni filter. The Brunauer–Emmett–Teller (BET) surface area and N_2 adsorption–desorption isotherm of the sample were measured volumetrically at liquid-nitrogen temperature on a Micromeritics ASAP-2000 instrument. The sample was evacuated at 300 °C to reach a vacuum below 3 μmHg before the measurements were made.

NH_3-TPD was carried out on a home-built device. The sample (60–80 mesh) was pretreated in He flow (30 ml/min) at 100 °C for 2 h and then NH_3 was added until the peak of NH_3 remained constant for 30 min. Temperature programmed desorption was then performed at a heating rate of 10 °C/min using a TCD detector.

H_2-TPR studies were carried out using 100 mg 60–80 mesh sample on a home-built device, The samples were pretreated at 500 °C for 2 h in air. A 15 vol% H_2/Ar mixture was passed through the sample in a temperature range from 50 to 650 °C at a heating rate of 10 °C/min.

2.3. Catalytic activity measurement

The catalytic experiment was carried out in a fixed-bed flow reactor at atmospheric pressure. A quartz glass tube (4 mm i.d.) was used as a reactor, and the temperature was monitored by a chromel-alumel thermocouple. 0.1 g catalyst (60–80 mesh) was placed in the reactor and supported by quartz wool. The reactant gas contained 1.0 vol% NO, 1.5 vol% CO and He as the balance. The flow rate was controlled by a rotameter. Prior to the reaction, the catalyst was pretreated in a flow of He at 500 °C for 2 h in order to remove the impurities on the catalyst surface, then cooled to 100 °C in an He stream, and then reactant gas was introduced. Water vapor for the catalyst treatment was generated by passing He through a temperature-controlled gas-wash bottle containing deionized water. The reaction temperature was increased stepwise in 50 or 100 °C intervals from 200 to 600 °C. After the reaction was carried out at each temperature for 1 h, the products were analyzed on-line by a gas chromatograph (FULI GC 9790) at 50 °C with a 5 Å molecular sieve column for NO, N_2 and CO, and in a Porapak Q column for N_2O and CO_2.

3. Results and discussion

3.1. Silica-pillared layered niobate

The silica-pillared layered niobate was obtained after calcination of the as-prepared intercalate in air at 500 °C for 12 h. Figure 1 shows the XRD patterns of the as-prepared sample after calcination at different temperatures in air. It can be seen that the diffraction peaks attributed to HNb_3O_8 disappear and the new (002) diffraction peak ($2\theta = 4.8°$) characteristic of a layered structure shows up, suggesting that the organosilicon compound has been intercalated into the layers of HNb_3O_8. After calcination at 500 °C for 12 h, the interlayer distance of the sample decreases remarkably as a result of the decomposition of the organosilicon in the interlayer space ($2\theta = 6.2°$). TGA and DTA results showed that the organosilicon began to decompose around 315 °C to form silica [16], indicating that the intercalate had fully decomposed into silica-pillared layered niobate after calcination at 500 °C for 12 h. The (002) peak characteristic of the layered structure is still retained upon heat treatment in air at 600 °C and disappeared after calcination at 700 °C, indicating that

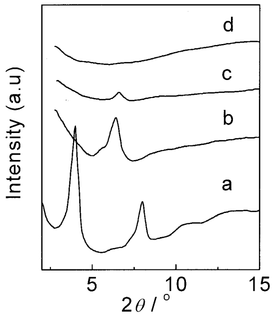

Figure 1. X-ray diffraction patterns of HNb_3O_8 after reaction with $NH_2(CH_2)_3Si(OEt)_3$ aqueous solution: (a) air-dried at 50 °C, (b) calcined at 500 °C for 12 h, (c) 600 °C, 3 h and (d) 700 °C, 3 h.

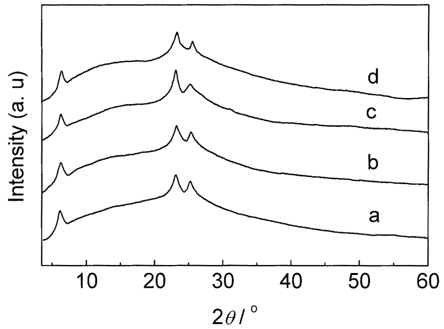

Figure 2. X-ray diffraction patterns of (a) Si-Nb_3O_8, (b) Si-Nb_3O_8 after treatment with water vapor at 500 °C for 3 h, (c) Cu/Si-Nb_3O_8 and (d) Cu/Si-Nb_3O_8 after treatment with water vapor at 500 °C for 3 h.

the obtained silica-pillared layered niobate has a relatively high thermal stability beyond 600 °C.

The N_2 adsorption isotherm of the silica-pillared layered niobate calcined in air at 500 °C for 12 h was of type IV in the classification of Brunauer, Deming, Deming and Teller (BDDT), indicating the presence of both micropores and mesopores. The N_2 adsorption–desorption isotherm of the sample showed an apparent hysteresis loop of H3 type as classified by Sing *et al.* [21], suggesting that the material possessed a porous structure associated with the aggregates of plate-like particles giving rise to slit-shaped pores. Table 1 gives some physical parameters of Si-Nb_3O_8. It can be seen that the sample has a high specific surface area and a pore volume with an average pore diameter of 27.5 Å. On the contrary, the starting material KNb_3O_8 is nonporous, with a very low BET surface area of 2.5 $m^2\,g^{-1}$. The large microporous surface area (98.9 $m^2\,g^{-1}$) also confirmed the successful insertion of silica pillars between the niobate layers.

Figure 2(b) gives the XRD result of the silica-pillared layered niobate after treatment at 500 °C for 3 h in a flow of mixed H_2O and He (5 vol% H_2O). It can be seen that the XRD pattern of the treated sample is the same as that of the original sample (figure 2(a)), and the (002) diffraction peak characteristic of the layered structure is retained.

NH_3-TPD results (figure 3) showed that there were two desorption peaks on the surface of Si-Nb_3O_8. After treatment with 5 vol% water vapor, the low-temperature desorption peak shifted to higher temperatures, from 238 °C to 274 °C, and the position of the high-temperature peak did not have an obvious change around 680 °C. Both areas of the peaks showed a substantial change. These results revealed that the treatment of water vapor could affect the number of acidic sites and acidic strength on the surface of Si-Nb_3O_8.

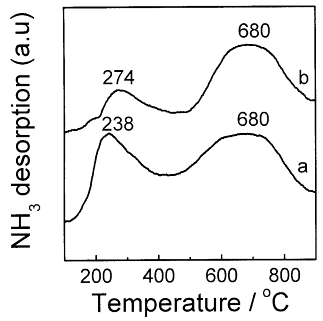

Figure 3. NH_3-TPD curves of Si-Nb_3O_8 (a) before and (b) after treatment with water vapor at 500 °C for 3 h.

3.2. 2.0 wt% Cu/Si-Nb_3O_8 catalyst

Figure 2(c) and (d) show the XRD results of 2.0 wt% Cu/Si-Nb_3O_8 catalyst before and after treatment with 5 vol% water vapor at 500 °C for 3 h. It is shown that the diffraction peaks are the same as those of the unsupported Si-Nb_3O_8, which shows a basic (002) diffraction peak and two diffraction peaks of two-dimensional crystal surface, indicating that the layered structure of the support Si-Nb_3O_8 was still retained in the preparation of the catalyst. From figure 2(c) and (d), there appear no new diffraction peaks compared with the support, suggesting that copper oxide may be well dispersed on the surface of the support, and after the treatment with water vapor, the existing states of copper oxide are not changed obviously, showing a water-tolerant ability of the catalyst.

As a first step, the NO + CO reaction was examined over Si-Nb_3O_8, and the results showed that the conversion of NO could hardly be observed in the temperature range of 200–600 °C, indicating that the support Si-Nb_3O_8 itself had no catalytic activity for the reduction of NO by CO.

A 2.0 wt% Cu/Si-Nb_3O_8 catalyst was then studied in the temperature range from 200 to 600 °C at a space velocity of 18 000 $cm^3\,g^{-1}\,h^{-1}$ and the conversion of NO reduction is shown in figure 4. The space velocity was defined as the total flow rate over the weight of the catalyst. It can be found that the catalyst has a high activity of NO reduction and selectivity to N_2 by CO, suggesting that CuO species are active sites in this

Table 1
Some physical parameters of silica-pillared layered niobate calcined in air at 500 °C for 12 h

Interlayer distance (Å)	Pillaring height (Å)	Average pore diameter (Å)	Specific area (BET, $m^2\,g^{-1}$)	Microporous area ($m^2\,g^{-1}$)	Pore volume ($ml\,g^{-1}$)
14.3	6.8	27.5	115.0	98.9	0.11

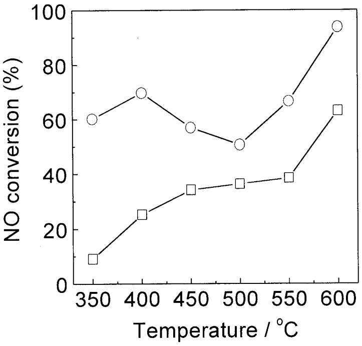

Figure 4. Effect of water treatment on the conversion of NO reduction over 2.0% Cu/Si-Nb_3O_8 catalyst, (□) 0% H_2O, (○) 5% H_2O. The reaction conditions: 1.0 vol% NO, 1.5 vol% CO, SV = 18 000 ml g^{-1} h^{-1}.

reaction. The conversion of NO increases with the reaction temperature below 450 °C, then almost keeps constant with further increase of the temperature up to 550 °C, and finally increases rapidly at a temperature above 550 °C. The selectivity of NO reduction to N_2 is shown in figure 5. It can be seen that the selectivity first decreases with the reaction temperature and reaches a minimum at 500 °C, then starts to increase with the temperature again.

Figures 4 and 5 also show the activity of NO reduction and the selectivity to N_2 over 2.0% Cu/Si-Nb_3O_8 catalyst after pretreatment with 5 vol% water vapor for 3 h, respectively. It is obvious that the conversion of NO increases greatly after water treatment compared with that of the untreated catalyst over the whole reaction temperature range, while the selectivity of NO reduction to N_2 is almost the same as that of the untreated catalyst. Figure 6 shows H_2-TPR profiles of Cu/Si-Nb_3O_8 before and after treatment with water vapor at 500 °C for 3 h, along with Si-Nb_3O_8 and unsupported CuO for comparison. The support Si-Nb_3O_8 itself has no reduction behavior, while unsupported CuO only had a very narrow peak centered at 277 °C. For Cu/Si-Nb_3O_8 before pretreatment with water, there are two reduction peaks centered at 245 and 294 °C, respectively. They can be ascribed to the reduction of fine CuO particles well dispersed on the support and isolated Cu^{2+} ions [22]. After pretreatment with water, a main peak at 249 °C and a tail from 280 to 360 °C were observed. In addition, the total area was reduced to some extent. It may be concluded that water treatment led to the rearrangement of copper species on the surface of the support and partial reduction of isolated Cu^{2+} ions to Cu^{+} ions. The formation of Cu^{+} after water pretreatment was also confirmed by UV-DRS. A new absorption band appeared between 400 and 500 nm, which is characteristic of the emission or absorption of photons from three-dimensional Cu^{+} [23]. Together with NH_3-TPD results, it seems that the treatment with water vapor leads to the change of acidic sites and acidic strength on the surface of the support, and therefore has an effect on the interaction between the support and CuO species, and then the reduction behavior and finally the activity of CuO species on the surface. Since water is inevitable and its effect is rather complicated in the practical process, further investigation about the role of water in the process is needed in order to understand the mechanism of this catalytic reaction.

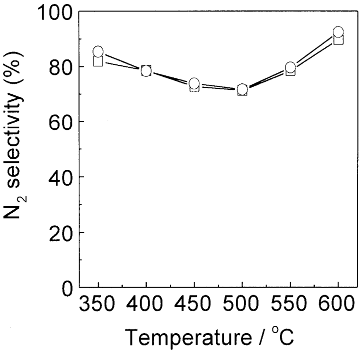

Figure 5. Effect of water treatment on the selectivity of NO into N_2 over 2.0% Cu/Si-Nb_3O_8 catalyst, (□) 0% H_2O, (○) 5% H_2O. The reaction conditions: 1.0 vol% NO, 1.5 vol% CO, SV = 18 000 ml g^{-1} h^{-1}.

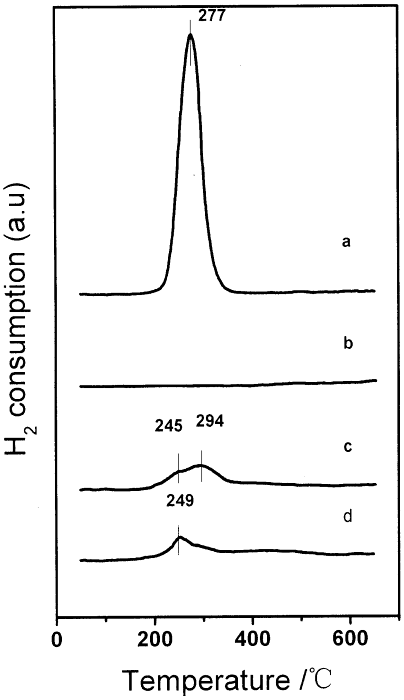

Figure 6. H_2-TPR profiles of (a) unsupported CuO, (b) Si-Nb_3O_8, (c) Cu/Si-Nb_3O_8 and (d) Cu/Si-Nb_3O_8 after treatment with water vapor at 500 °C for 3 h.

4. Conclusions

The silica-pillared layered niobate prepared by intercalating layered niobate with an aqueous solution of $NH_2(CH_2)_3Si(OEt)_3$ was a porous material with a high specific area and a hydrothermal stability. Using Si-Nb_3O_8 as support, 2 wt% Cu/Si-Nb_3O_8 catalyst showed a high catalytic activity of NO reduction and selectivity to N_2 in the reaction of $NO + CO$. The pretreatment with water vapor could remarkably facilitate the conversion of NO reduction by CO over a wide reaction temperature range.

Acknowledgments

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