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Wetness method preparation of catalysts for selective catalytic reduction of NO by propane

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A wetness method preparation of Co/ZSM-5 catalysts for selective catalytic reduction of NO by propane is shown to be comparable to ion-exchange preparation at the optimum catalytic conversion temperature of 450°C and superior to ion-exchange preparation at lower temperatures. Modification of Co/ZSM-5 catalysts with Ca^{2+} or Sr^{2+} significantly improves the catalytic activity.

Keywords: aluminosilicate zeolites, wetness method, aqueous solution, ion exchange, cobalt ion, catalytic activity

1. Introduction

The selective catalytic reduction (SCR) of nitrogen oxides with hydrocarbons is considered one of the most effective ways of NO_x ($NO_2 + NO$) abatement from the exhaust gases of lean burn engines and stationary sources such as power plants, industrial boilers, etc. Iwamoto et al. [1] and Held et al. [2] demonstrated that the most effective catalyst for this reaction is Cu/ZSM-5. However, Cu/ZSM-5 catalyst does not show good durability for practical application, and its hydrothermal stability is low [3–5]. A Co/ZSM-5 catalyst appears to be more practical; Armor and Farris showed that it exhibits high hydrothermal stability [6], and that its loss of catalytic activity in the presence of water vapor is reversible. Furthermore, NO can be easily reduced over Co/ZSM-5 with methane [7,8].

To date, only a few studies have dealt with the efficiency or ease of the catalyst preparation method. From a practical viewpoint, it is important to prepare catalysts economically and simply. In this work, an easy and convenient "wetness method" preparation of M/ZSM-5 catalysts, where M is a metal ion, is shown. These catalyst preparations are shown to be efficient for the removal of NO_x via selective catalytic reduction by propane. The wetness method seems more rapid and simpler than more conventional ion-exchange preparations.

2. Experimental

Catalysts were prepared by the wetness method by using only enough aqueous solution containing active metal cations to fill the pore volume of the zeolite support. The amount of aqueous solution required to fill only the pore volume of the support in the wetness method was determined experimentally. The aqueous solution was added dropwise to a given weight of support, which was mixed thoroughly between the drops by a glass rod. The support maintained a powdery texture until the pore volume was filled, at which point the next drop would produce a slurry containing a minimum amount of aqueous solution. This procedure looks like an accurate titration technique. Anhydrous ZSM-5 was prepared by drying at 105 ± 5°C for 3 h, and then storing it in a desiccator at room temperature. NH_4ZSM-5 was obtained by ion-exchanging HZSM-5 ($SiO_2/Al_2O_3 = 30$, PQ Co.) with 0.5 M NH_4NO_3 at 80°C.

As an example, catalyst No. 2 in table 1 was prepared as follows. A wetness solution was prepared by dissolving 0.017 mol of $Co(OAc)_2 \cdot 4H_2O$ and 0.012 mol of $Ca(NO_3)_2 \cdot 4H_2O$ in 100 ml of deionized water. This solution was added dropwise to 1.0 g of anhydrous NH_4ZSM-5 support. It consumed 1.00 ± 0.04 ml solution to fill only the pore volume of the support. The wetted sample was stored in a closed container saturated with water vapor for 7 days at room temperature. Then the sample was dried at 105 ± 5°C for 10 h and is denoted by 1.5(Co + Ca)/ZSM-5 in table 1, where 1.5 refers to 1 wt% Co and 0.5 wt% Ca in ZSM-5. Metal contents were determined by atomic absorption spectroscopy (Perkin-Elmer 2380 AAS).

The catalytic reaction was carried out in a quartz tubular reactor in a steady-state plug-flow mode. A tem-

Table 1
Selective catalytic reduction of NO with propane over various catalysts [a]

Catalyst No. [b]	Total metal loading in ZSM-5 [c] (wt%)	NO conversion (%) at						
		250°C	300°C	350°C	400°C	450°C	500°C	550°C
1	1.0 Co	2	5	9	20	55	75	63
2	1.5(Co + Ca)	2	8	24	63	84	70	55
3	1.5(Co + Sr)	2	8	19	50	88	79	62
4	1.8 Pd	1	6	7	6	3	2	4
5	1.0 Fe	7	14	17	15	12	9	7
6	1.0 Ni	3	6	8	11	14	12	11
7	0.91 Co [d]	1	3	5	9	29	76	75
8	1.1(Co + Ca) [e]	1	3	6	24	88	86	73
9	1.2(Co + Sr) [f]	1	2	7	73	86	76	63

[a] Reaction conditions: 900 vol ppm NO, 1000 vol ppm C_3H_8, and 2 vol% O_2 in He with GHSV = 30,000 h^{-1}.

[b] Catalysts Nos. 1–6 were prepared by the wetness method, and catalysts Nos. 7–9 were prepared by an ion-exchange method for comparison.

[c] When two cations are shown, Co is present as 1 wt% and the other is present as the remainder.

[d] Catalyst preparation: 2 g of NH_4ZSM-5 were mixed with 200 ml of 0.005 M cobalt acetate solution and stirred for 4 days at room temperature.

[e] Catalyst preparation: Ca/ZSM-5 was prepared by stirring 2 g of NH_4ZSM-5 and 200 ml of 0.1 M calcium acetate solution at 80°C for 12 h, and then 1.1(Co + Ca)/ZSM-5 was prepared by stirring 2 g of Ca/ZSM-5 and 200 ml of 0.1 M cobalt acetate solution at room temperature for 5 days.

[f] Catalyst preparation: Sr/ZSM-5 was prepared by stirring 2 g of NH_4ZSM-5 and 200 ml of 0.1 M strontium acetate solution at 80°C for 12 h, and then 1.2(Co + Sr)/ZSM-5 was prepared by stirring 2 g of Sr/ZSM-5 and 200 ml of 0.1 M cobalt acetate solution at room temperature for 5 days.

perature programmer was used with a K-type thermocouple installed in contact with the catalyst bed. Prior to the catalytic tests, the samples were calcined overnight with the temperature ramped at a rate 1°C/min and held at 550°C for 3 h in a flow of 20 vol% O_2 in He. The reactant gas mixture was obtained by blending four different gases (NO/He, C_3H_8/He, O_2 and He), so as to obtain 900 vol ppm NO, 1000 vol ppm propane, and 2 vol% oxygen in helium. Each gas flow was controlled by independent flow controllers. The gases (NO, O_2, and C_3H_8) were all $> 99.9\%$ purity and were blended with He ($> 99.99\%$ purity) to provide the desired gas mixture. For catalytic reaction studies, 0.23 g of catalyst was loaded into a flow reactor and exposed to the gas mixture at a flow rate of 230 ml/min. For a ZSM-5 density of 0.5 g/cm^3, this flow rate over 0.46 cm^3 catalyst corresponds to a gas hourly space velocity (GHSV) of 30,000 h^{-1}. An on-line gas chromatograph (HP 5890, series II) with a thermal conductivity detector in series with an on-line chemiluminescence NO_x-analyzer (Kimoto model 272), which separately measures NO and NO_2, were used for the analysis of the effluent gases. A 13X molecular sieve column was used in the gas chromatograph for separation of O_2, N_2, and C_3H_8.

Prior to catalytic measurements the analyzers were calibrated using standard gas mixtures. C_3H_8 conversion percent was calculated by the difference between C_3H_8 concentration in the reaction mixture before and after its passage through the reactor divided by the original concentration times 100. NO conversion efficiency was calculated similarly by using the NO_x analyzer.

3. Results and discussion

Table 1 shows comparative NO conversions in the range of 250–550°C for SCR of NO with propane over the various catalysts prepared by wetness and liquid state ion-exchange methods. Catalysts Nos. 1–3 containing cobalt, cobalt plus calcium or cobalt plus strontium prepared by the wetness method, show maximum catalytic activity of 75–88% NO conversion at 450–500°C. Catalysts Nos. 7–9 prepared by the liquid state ion-exchange method show similar activity. On the other hand, Pd-, Fe-, Ni-loaded catalysts (Nos. 4–6) show at most 17% NO conversion. From these results, it is clear that cobalt-containing catalysts are promising for SCR of NO by alkanes as suggested by Li and Armor [8].

It is noteworthy that at lower temperatures, for example at 350°C, the catalysts prepared by the wetness method are two to four times more efficient for NO conversion than the catalysts prepared by ion exchange. This could be a significant advantage if lower operating temperatures are required for practical or economic considerations.

According to our previous work [9], the distribution of Co^{2+} and cobalt oxide was determined for catalysts Nos. 1, 2, 3, 7, 8 and 9 by performing NO-TPD experiments and the results are shown in table 2. Also the total amounts of cobalt and alkaline earth metal were analyzed by atomic absorption spectroscopy. While there is no cobalt oxide in the ion-exchanged samples, there is some cobalt oxide in the wetness samples.

Stakheev et al. [10] reported that catalysts containing cobalt oxide exhibit activity for NO_2 formation. NO_2

Table 2
Composition of cobalt-containing ZSM-5 catalysts

Catalyst No.	Total metal loading in ZSM-5 (wt%)	Metal loading (wt%)		
		Co^{2+}	cobalt oxide	alkaline earth
1	1.0 Co	0.78	0.22	0
2	1.5 (Co + Ca)	0.42	0.58	0.5
3	1.5 (Co + Sr)	0.55	0.45	0.5
7	0.91 Co	0.91	0	0
8	1.1 (Co + Ca)	0.31	0	0.79
9	1.2 (Co + Sr)	0.45	0	0.75

formation improves the SCR activity, particularly in the lower temperature region. This is the main reason why wetness samples show higher activity than ion-exchanged samples at lower temperature.

The SCR activity of NO over Co/ZSM-5 is improved by the copresence of Ca or Sr at 450°C and below (see figure 1 and table 1, catalysts Nos. 1–3 and 7–9) for catalysts prepared by either the wetness method or liquid state ion exchange. In figure 1 the utility of propane for SCR over cobalt-containing catalysts prepared by the wetness method at various temperatures is displayed in terms of propane conversion. Propane is a selective reductant for NO, since the conversion trends for NO and propane are quite similar to each other up to the maximum NO conversion temperature of about 450°C, beyond which propane oxidizes almost completely. Modification of Co/ZSM-5 catalysts with Ca or Sr improves the SCR activities significantly. As shown in figure 1, for (Co + Ca)/ZSM-5 (catalyst No. 2), the NO conversion reaches 84% at 450°C. However, over Co/ZSM-5 (catalyst No. 1), the NO conversion is only 55% at 450°C. Also the maximum NO conversion over the Ca- or Sr-modified catalysts is shifted to lower temperature by about 50°C in comparison with Co/ZSM-5. The SCR catalytic activity is enhanced over a wide range of reaction temperature by the addition of Ca or Sr cocation into Co/ZSM-5. The reason for this cocation effect is not fully understood so far.

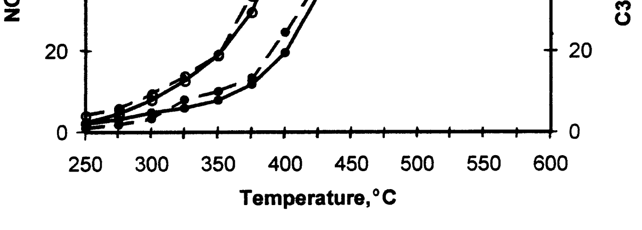

Figure 1. NO (——) and C_3H_8 (– – –) conversions during selective catalytic reduction over 1.0 Co/ZSM-5 (-●-) and 1.5(Ca + Co)/ZSM-5 (-○-), which are prepared by the wetness method. Reaction conditions: 900 ppm NO, 1000 ppm C_3H_8 and 2 vol% O_2 in helium with GHSV = 30,000 h^{-1}.

Zhu et al. [11] reported that NO adsorbs mainly on Co^{2+} and forms Co^{2+}–$(NO)_2$ and Co^{2+}–(NO) species. It is well known that there are three or four cationic sites in the ZSM-5 framework [12]. We do not know the specific location of the cationic site of Co^{2+} for NO adsorption in ZSM-5. However, the NO-TPD experimental results indicate at least three different adsorption sites for wetness and ion-exchanged samples.

Figure 2 shows typical NO-TPD curves for wetness and ion-exchanged samples for Co/ZSM-5 and (Co+Ca)/ZSM-5. The NO-TPD profiles differ which is probably due to a different distribution of adsorption sites and chemical compositions of the catalysts. While samples only containing cobalt show a relatively narrow TPD profile, the samples containing cobalt and alkaline earth metals have a broader TPD profile. For ion-exchanged 0.91 Co/ZSM-5, figure 2A curve a shows NO desorption at 140 and 170°C. For wetness sample 1.0 Co/ZSM-5, figure 2B curve a shows NO desorption at 100 and 200°C. On the other hand, ion-exchanged 1.1(Co + Ca)/ZSM-5 in figure 2A curve b shows NO desorption at 100, 200 (shoulder), 230, and 440°C while for wetness sample 1.5(Co + Ca)/ZSM-54, figure 2B curve b shows NO desorption at 100, 150 (shoulder), 180, and 400°C. The introduction of alkaline earth metal into Co/ZSM-5 creates new active sites for NO reduction. Since the loading of Ca or Sr is less than 1 wt%, their positions are not definitively characterized, but we suppose that they have a 2+ oxidation state.

We have also investigated the oxygen dependence of NO_x conversion for 1.5(Co + Ca)/ZSM-5 (catalyst No. 2) and 1.1(Co + Ca)/ZSM-5 (Catalyst No. 8). The NO_x conversion decreases when the oxygen content increases, which is quite general. The O_2 dependence of NO_x conversion is compared for O_2 concentrations of 2 and 8% as shown in figure 3.

For 1.5(Co + Ca)/ZSM-5 (figure 3B) with 8% O_2,

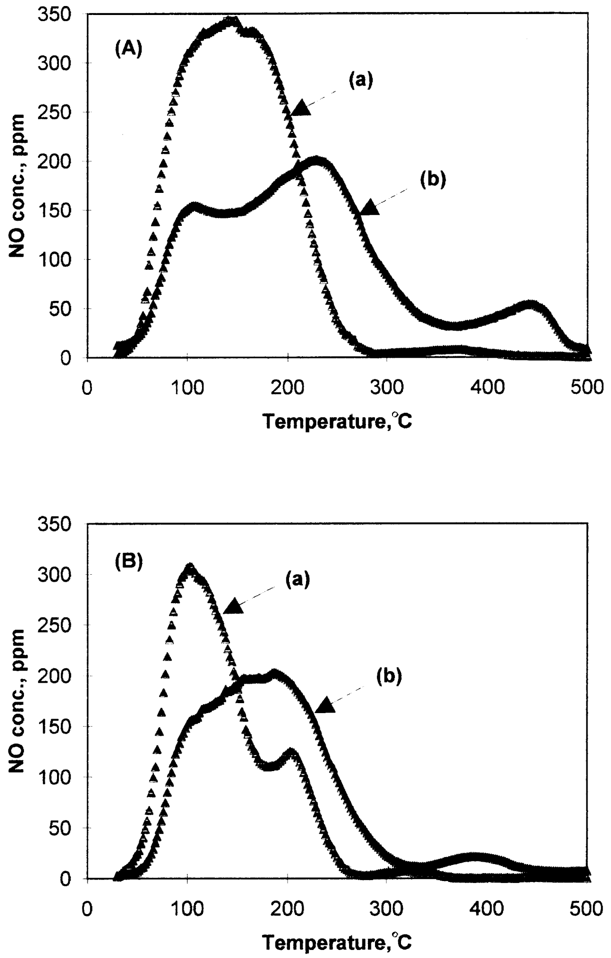

Figure 2. (A) NO-TPD curves of (a) 0.91Co/ZSM-5 and (b) 1.1(Co + Ca)/ZSM-5 which were prepared by ion exchange. (B) NO-TPD curves of (a) 1.0Co/ZSM-5 and (b) 1.5(Co + Ca)/ZSM-5 which were prepared by the wetness method.

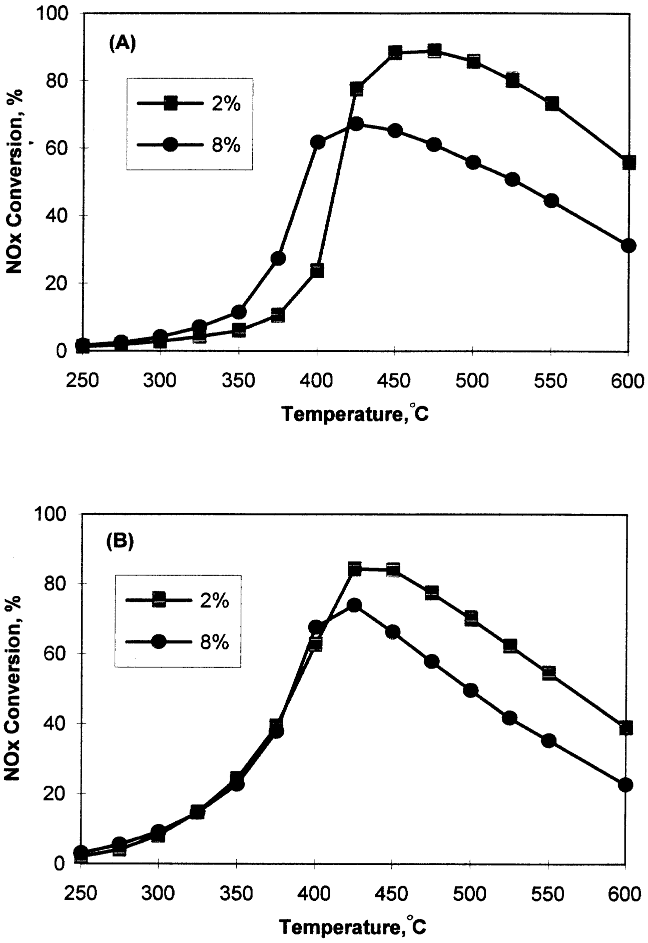

Figure 3. Effect of oxygen concentration in the feed on NO_x conversion over (A) 1.1(Co + Ca)/ZSM-5 and (B) 1.5(Co + Ca)/ZSM-5 which were prepared by ion exchange and the wetness method, respectively. Reaction conditions: 900 ppm NO, 1000 ppm C_3H_8, and 2 and 8 vol% O_2 in helium with GHSV = 30,000 h^{-1}.

there is no serious decrease in NO reduction to 400°C. However, at 400°C and greater NO_x conversion is reduced by about 20%. On the other hand, the O_2 dependence for 1.1(Co + Ca)/ZSM-5 (figure 3A) is different. With 8% O_2 at temperatures to 400°C NO_x conversion increases by about 40%, however, at temperatures higher than 420°C NO_x conversion decreases by about 30%. These experimental results indicate that the relative amount of metal loaded onto the catalyst is important for its catalytic properties and that cobalt oxide seems to be necessary for NO reduction by hydrocarbons in the presence of excess oxygen.

Zeolites are widely used as catalyst supports with metal ions incorporated by ion exchange [13]. However, the experimental procedure of cation exchange into zeolites is somewhat cumbersome and time consuming. A zeolite is suspended into a large volume of aqueous solution. Usually the volume ratio of aqueous solution to a zeolite support is about 50–100, which seems far from economic. This suspended mixture is mixed thoroughly by stirring or shaking for a certain period. After ion exchange, the solid and liquid must be separated by filtering and washing. To prepare a catalyst containing two different cations, the ion-exchange procedure is normally carried out separately for each ion since competitive ion exchange occurs in a single solution.

d'Itri et al. [14] prepared Cu-ZSM-5 by wet impregnation which is similar to our wetness method. In wet impregnation, 10 g of ZSM-5 is suspended into 250 ml of aqueous solution and the suspended water is removed by a rotary evaporator at 303 K.

In contrast, the wetness method seems shorter and more convenient. A catalyst can be prepared by using only a minimum amount of aqueous solution to fill the pore volume of the zeolite support [15,16], and then leaving it in a closed container which is saturated with water vapor at ambient temperature for a desired period. Also, the wetness method allows two different cations to be incorporated simultaneously since the total liquid volume of the solution is absorbed into the zeolite.

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