JOURNAL OF CATALYSIS 155, 414–417 (1995)

NOTE

Ion-Exchanged Pillared Clays: A New Class of Catalysts for Selective Catalytic Reduction of NO by Hydrocarbons and by Ammonia

Selective catalytic reduction (SCR) of NO by NH_3 is presently performed with vanadia-based catalysts for flue gas applications (1). Hydrocarbons would be the preferred reducing agents over NH_3 because of the practical problems associated with the use of NH_3 (i.e., handling and slippage through the reactor). SCR of NO by hydrocarbons can also find important applications for lean-burn (i.e., O_2-rich) gasoline and diesel engines where the noble-metal three-way catalysts are not effective in the presence of excess oxygen (2, 3).

The first catalysts found to be active for SCR of NO by hydrocarbons in the presence of oxygen were Cu^{2+} ion-exchanged ZSM-5 and other zeolites, reported in 1990 by Iwamoto (4) and Held *et al.* (5) and in early patents cited in (6). Reports on a large number of catalysts for this reaction have appeared since 1990. The majority of these catalysts are ion-exchanged zeolites, including H^+ forms. Alumina and metal oxides supported on alumina have also been studied, but are less active. The early (1990–1992) literature on the subject, primarily by Japanese researchers, has been reviewed by Iwamoto and Mizuno (7) and will not be repeated here. The most active catalysts include: Cu–ZSM-5 (2, 4, 5, 8–14), Co–ZSM-5 and Co–Ferrierite (15–18), Ce–ZSM-5 (6, 19), and Cu–Zr–O and Cu–Ga–O (20, 21). Although Cu–ZSM-5 is the most active catalyst, it suffers from severe deactivation in engine tests, presumably due to H_2O and SO_2 (22–24). A comprehensive review and discussion on the reaction was made recently by Shelef (25).

Pillared interlayered clays (PILCs) have been studied extensively for a number of catalyzed reactions. We have found high activities of PILCs for SCR of NO by NH_3 (26, 28). Pillared clays have considerable Bronsted acidity (27, 28), and the protons can be exchanged with metal cations. The Bronsted acidity of TiO_2-PILC, in particular, remains high after heat treatment at temperatures as high as 400°C (27–29). In this note, we report first results on the activities of cation-exchanged pillared clays for SCR of NO by both hydrocarbon and NH_3.

TiO_2-pillared clay was prepared following the procedure of Sterte (29) as described in more detail elsewhere (29). The starting material was a purified montmorillonite (bentonite) powder from Fisher, with crystal sizes less than or equal to 2 μm. Titanium chloride ($TiCl_4$), also from Fisher, was used as the TiO_2 precursor. After pillaring (29), the resulting PILC was separated by vacuum filtration, and washed with distilled water until the filtrate water was free of chloride ions as determined by titration with $AgNO_3$. The PILC was then dried at 120°C for 10 h, and calcined at 400°C in air for 3 h.

The TiO_2-PILC was ion exchanged with copper nitrate solution following the conventional ion-exchange procedure. Copper nitrate was used as the source of Cu^{2+} ions. One g of TiO_2-PILC was added to 100 ml of 0.02 *M* copper nitrate aqueous solution. The mixture was stirred for 24 h at 70°C. The pH of the starting solution was adjusted to pH = 6.0 by adding proper amounts of ammonia solution. The ion-exchanged product was collected by filtration followed by washing with distilled water five times. The ion exchange procedure was repeated three times. Then the product was dried at 120°C followed by calcination at 400°C in air.

The SCR activity was measured with the same reactor system described elsewhere, and the same experimental details were followed (26, 28, 30). That the measured conversion was NO_x reduction to N_2 was confirmed by the NO_x mode of chemiluminescent analyzer and mass spectrometric analysis for N_2.

The SCR activities of the Cu^{2+} ion exchanged TiO_2 pillared clay have been measured at five temperatures: 200, 250, 300, 350, and 400°C. C_2H_4 was used as the reducing gas. Also, Ce_2O_3 was tested as a promoter. The effects of SO_2 and H_2O have also been tested. The experimental conditions were chosen to be the same as that reported in the literature for the Cu–ZSM-5 catalyst (7, 31), so a direct comparison could be made. The reaction conditions were as follows: NO = 1,000 ppm, O_2 = 2%, C_2H_4 = 250 ppm, N_2 = balance, total flowrate = 150 ml/min. and catalyst weight = 0.5 g.

The activities for SCR of NO by ethylene over Cu^{2+}-exchanged TiO_2-PILC are shown in Fig. 1. The results reported by Iwamoto *et al.* on Cu-ZSM-5 (7, 31) are also

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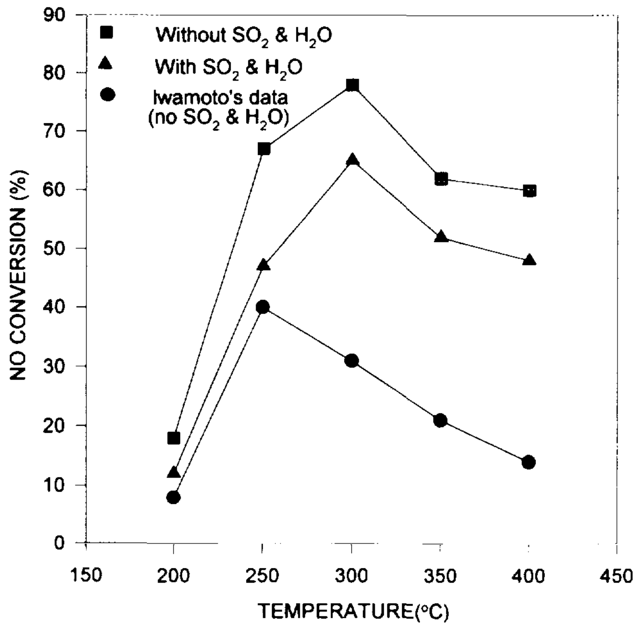

FIG. 1. NO conversion (to N_2) in the NO + O_2 + C_2H_4 reaction over Cu^{2+} ion exchanged TiO_2-pillared clay, with and without SO_2 (500 ppm) and H_2O (5% vol.). NO = 1,000 ppm, C_2H_4 = 250 ppm, O_2 = 2%, catalyst = 0.5 g, N_2 = balance, total flowrate = 150 cc/min. The data of Iwamoto *et al.* (7, 27) on Cu-ZSM-5 catalyst are included for a direct comparison. Identical experimental conditions were used.

shown in Fig. 1, for a direct comparison. Estimates of rate constants may be made from the conversion data based on two assumptions: The reaction is first-order (with respect to NO), and it is without diffusion limitation (which is not the case). The following rate constants (k) can thus be obtained following the integral analysis that we adopted previously (28): At 250°C: k(in $cm^3/g/s$) = 9.72 (A), 5.57 (B) and 4.47 (C); At 300°C: k = 14.56 (A), 10.09 (B) and 3.58 (C). Here (A) refers to Cu^{2+}-exchanged PILC without SO_2, (B) refers to that with SO_2 and H_2O, and (C) refers to Cu^{2+}–ZSM-5 without SO_2 and H_2O.

Figure 1 shows that the catalytic activity increased with increasing temperature, reaching a maximum of 79% NO conversion at 300°C, and then decreased at higher temperatures. It is clear that the Cu^{2+} exchanged TiO_2-PILC is substantially more active than the Cu–ZSM-5 catalyst. In the presence of H_2O (5%) and SO_2 (500 ppm), the activities of Cu^{2+}-exchanged TiO_2-PILC decreased, as expected. However, these decreased activities were still higher than that of Cu–ZSM-5 under SO_2/H_2O-free condition (Fig. 1).

Cerium is known to be a promoter for SCR by NH_3 (26). Ce_2O_3 (0.5% wt.) was doped into the Cu^{2+}–TiO_2-PILC catalyst by incipient wetness impregnation using Ce(III) nitrate hexahydrate solution. The impregnated sample was calcined in air at 400°C. Obviously, Ce(IV) was formed upon calcination and also during the reaction. The C_2H_4 SCR activities of the Ce-doped catalyst are shown in Fig. 2. The ceria dopant increased the C_2H_4 SCR activity at temperatures higher than 300°C, but decreased the activity at 250°C. The reason for the decrease is not known, although it could be related to poor dispersion (or sintering) of ceria at this temperature. Alternatively, it could be due to oligomerization of hydrocarbon that caused pore blocking. The effect of SO_2 + H_2O on the activity of the Ce-doped catalyst is also shown in Fig. 2, where a decrease but a still high activity was seen. The catalytic activities were fully recovered after SO_2 and H_2O were switched off. Thus, SO_2/H_2O did not alter (or poison) the active sites; rather, they probably occupied the sites reversibly.

A catalyst stability test was performed for the Ce-doped catalyst at 300°C in the presence of both SO_2 and H_2O. A decrease of approximately 3% in NO conversion was observed upon a 48-hour run. Further and more definitive experiments are underway. However, it is clear that this catalyst is far more stable than Cu–ZMS-5.

The higher activities of the Cu^{2+} exchanged pillared clay than the Cu^{2+} exchanged ZSM-5 can be attributed to at least two reasons. Firstly, the cation exchange capacities (CEC) of pillared clays are considerably higher than that of ZSM-5. A typical CEC value for pillared clays is 1 meq/g, which is about twice that of the ZSM-5 with a low Si/Al ratio (of 20). Secondly, the pore dimensions in the pillared clays are considerably larger than that in ZSM-5, and pore diffusion resistance is significant in the SCR reaction (3, 17). The pore size distributions in pillared

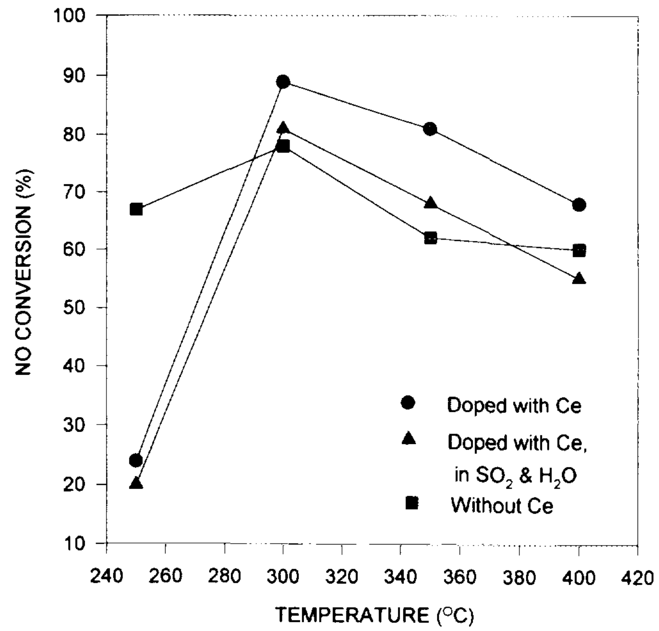

FIG. 2. Promoting effect of Ce on Cu^{2+} exchanged TiO_2 pillared clay in the C_2H_4 SCR reaction. Reaction conditions: NO = 1,000 ppm, C_2H_4 = 250 ppm, O_2 = 2%, catalyst = 0.5 g, total flowrate = 150 cc/min. Amount of dopant = 0.5% (wt.) Ce_2O_3.

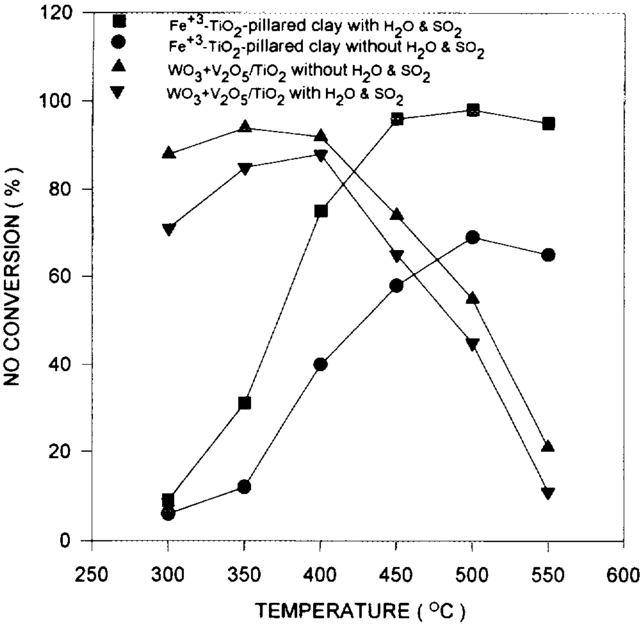

FIG. 3. Comparison of activities for SCR by NH_3 between WO_3 + V_2O_5/TiO_2 and Fe^{3+}-exchanged TiO_2 pillared clay. Reaction conditions: NO = NH_3 = 1,000 ppm, O_2 = 3%, SO_2 = 1,000 (when used), H_2O = 5% (when used) and N_2 = balance. Total flowrate = 500 ml/min. Catalyst amount = 0.4 g.

clays are typically in the range 5–15 Å (32, 33), compared to the channel dimensions of the order of 5 Å in ZSM-5. Moreover, it is possible that there exists a more favorable chemical environment (for redox) for the Cu^{2+} ion in the pillared clay than in the structure of zeolite, and this may also be the reason for the H_2O resistance of the pillared clay catalyst. The residual Brönsted acidity also helps activate the hydrocarbon for the reaction (25).

Fe^{3+} ion-exchanged TiO_2-PILC was prepared by the same ion exchange procedure for Cu^{2+} exchange, except $Fe(NO_3)_3$ solution was used in place of $Cu(NO_3)_2$. A commercial-type catalyst, WO_3 + V_2O_5/TiO_2 (34), was used for direct comparison. The results are shown in Fig. 3.

The activity of the WO_3 + V_2O_5/TiO_2 catalyst was high at temperatures up to 400°C, and H_2O + SO_2 decreased the activity; both are well known results. The Fe^{3+} exchanged TiO_2-PILC showed significant catalytic activities only at temperatures above 400°C. The addition of SO_2 and H_2O significantly increased the activity, which reached about 98% NO conversion at near 500°C. This was an unexpected result. The effects of SO_2 + H_2O are more or less negative for all known SCR-NH_3 catalysts. However, the negative effects are at temperatures below 400°C. The effect of SO_2 alone (without H_2O) can be a positive one (depending on the catalyst), since it increases the Bronsted acidity which is responsible for the reaction (30, 35). A possible reason for the increase in activity by H_2O + SO_2 is an increase in the Bronsted acidity on the catalyst in the high temperature range (450–550°C), although the mechanism is obviously different from those proposed for the NH_3 SCR on V_2O_5/TiO_2 (35–37).

Further work on SCR over other cation exchanged pillared clays is in progress in our laboratory. Other hydrocarbons including CH_4 are being studied as the reducing agents. The mechanism of the reaction on this new class of catalysts, in particular for hydrocarbon SCR, is also being studied.

ACKNOWLEDGMENT

This work was supported by Department of Energy under DE-FG22-93PC93217.

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Received January 27, 1995; revised May 9, 1995

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