

DOE/PC/93217--T7

QUARTERLY TECHNICAL PROGRESS REPORT

Superior Catalysts for Selective Catalytic Reduction of Nitric Oxide

April 1, 1995 - June 30, 1995

by

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Submitted to

Pittsburgh Energy Technology Center
U.S. Department of Energy
Under Contract DE-FG22-93PC932217

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During the past quarter, we continued our effort on synthesizing new pillared clay catalysts for the selective catalytic reduction (SCR) of NO. We continued the work on SCR of NO by NH₃. We also explored the possibility of using pillared clays (or ion-exchanged pillared clays) for SCR of NO by hydrocarbons. The latter is more desired as explained below. Selective catalytic reduction of NO by NH₃ is presently performed with vanadia-based catalysts for flue gas applications (1). Hydrocarbons would be the preferred reducing agents over NH₃ because of the practical problems associated with the use of NH₃ (i.e., handling and slippage through the reactor). SCR of NO by hydrocarbons can also find important applications for lean-burn (i.e., O₂-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 Cu²⁺ 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 H₂O and SO₂ (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 PILC's for SCR of NO by NH₃ (26,27). Pillared clays have considerable Brönsted acidity (27,28), and the protons can be exchanged with metal cations. The Brönsted acidity of TiO₂-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 NH₃.

EXPERIMENTAL

TiO₂-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 (TiCl₄), also from Fisher, was used as the TiO₂ 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 AgNO₃. The PILC was then dried at 120°C for 10 h, and calcined at 400°C in air for 3 h.

The TiO₂-PILC was ion exchanged with copper nitrate solution following the conventional ion-exchange procedure. Copper nitrate was used as the source of Cu²⁺ ions. One g of TiO₂-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 5 times. This ion exchange procedure was repeated 3 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 N₂ was confirmed by the NO_x mode of chemiluminescent analyzer and mass spectrometric analysis for N₂.

RESULTS AND DISCUSSION

SCR by C₂H₄

The SCR activities of the Cu²⁺ ion exchanged TiO₂ pillared clay have been measured at five temperatures: 200, 250, 300, 350, and 400°C. C₂H₄ 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: $\text{NO} = 1,000$ ppm, $\text{O}_2 = 2\%$, $\text{C}_2\text{H}_4 = 250$ ppm, $\text{N}_2 = \text{balance}$, 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 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 $\text{cm}^3/\text{g/s}$) = 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 $\text{SO}_2/\text{H}_2\text{O}$ 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. The effect of $\text{SO}_2 + \text{H}_2\text{O}$ 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, $\text{SO}_2/\text{H}_2\text{O}$ 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 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).

SCR by NH_3

Fe^{3+} ion-exchanged TiO_2 -PILC was prepared by the same ion exchange procedure for Cu^{2+} exchange, except $\text{Fe}(\text{NO}_3)_3$ solution was used in place of $\text{Cu}(\text{NO}_3)_2$. A commercial-type catalyst, $\text{WO}_3 + \text{V}_2\text{O}_5/\text{TiO}_2$ (34), was used for direct comparison. The results are shown in Fig. 3.

The activity of the $\text{WO}_3 + \text{V}_2\text{O}_5/\text{TiO}_2$ catalyst was high at temperatures up to 400°C , and $\text{H}_2\text{O} + \text{SO}_2$ 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

SO₂ and H₂O significantly increased the activity, which reached about 98% NO conversion at near 500°C. This was an unexpected result. The effects of SO₂ + H₂O are more or less negative for all known SCR-NH₃ catalysts. However, the negative effects are at temperatures below 400°C. The effect of SO₂ alone (without H₂O) can be a positive one (depending on the catalyst), since it increases the Brønsted acidity which is responsible for the reaction (30,35). A possible reason for the increase in activity by H₂O + SO₂ is an increase in the Brønsted acidity on the catalyst in the high temperature range (450-550°C), although the mechanism is obviously different from those proposed for the NH₃ SCR on V₂O₅/TiO₂ (35-37).

Further work on SCR over other cation exchanged pillared clays is in progress in our laboratory. Other hydrocarbons including CH₄ 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.

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FIGURE CAPTIONS

- Fig. 1.** NO conversion (to N₂) in the NO + O₂ + C₂H₄ reaction over Cu²⁺ ion exchanged TiO₂-pillared clay, with and without SO₂ (500 ppm) and H₂O (5% vol.). NO = 1,000 ppm, C₂H₄ = 250 ppm, O₂ = 2%, catalyst = 0.5 g, N₂ = 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.
- Fig. 2.** Promoting effect of Ce on Cu²⁺ exchanged TiO₂ pillared clay in the C₂H₄ SCR reaction. Reaction conditions: NO = 1,000 ppm, C₂H₄ = 250 ppm, O₂ = 2%, catalyst = 0.5 g, total flowrate = 150 cc/min. Amount of dopant = 0.5% (wt.) Ce₂O₃.
- Fig. 3.** Comparison of activities for SCR by NH₃ between WO₃ + V₂O₅/TiO₂ and Fe³⁺-exchanged TiO₂ pillared clay. Reaction conditions: NO = NH₃ = 1,000 ppm, O₂ = 3%, SO₂ = 1,000 (when used), H₂O = 5% (when used) and N₂ = balance. Total flowrate = 500 ml/min. Catalyst amount = 0.4 g.

Figure 1

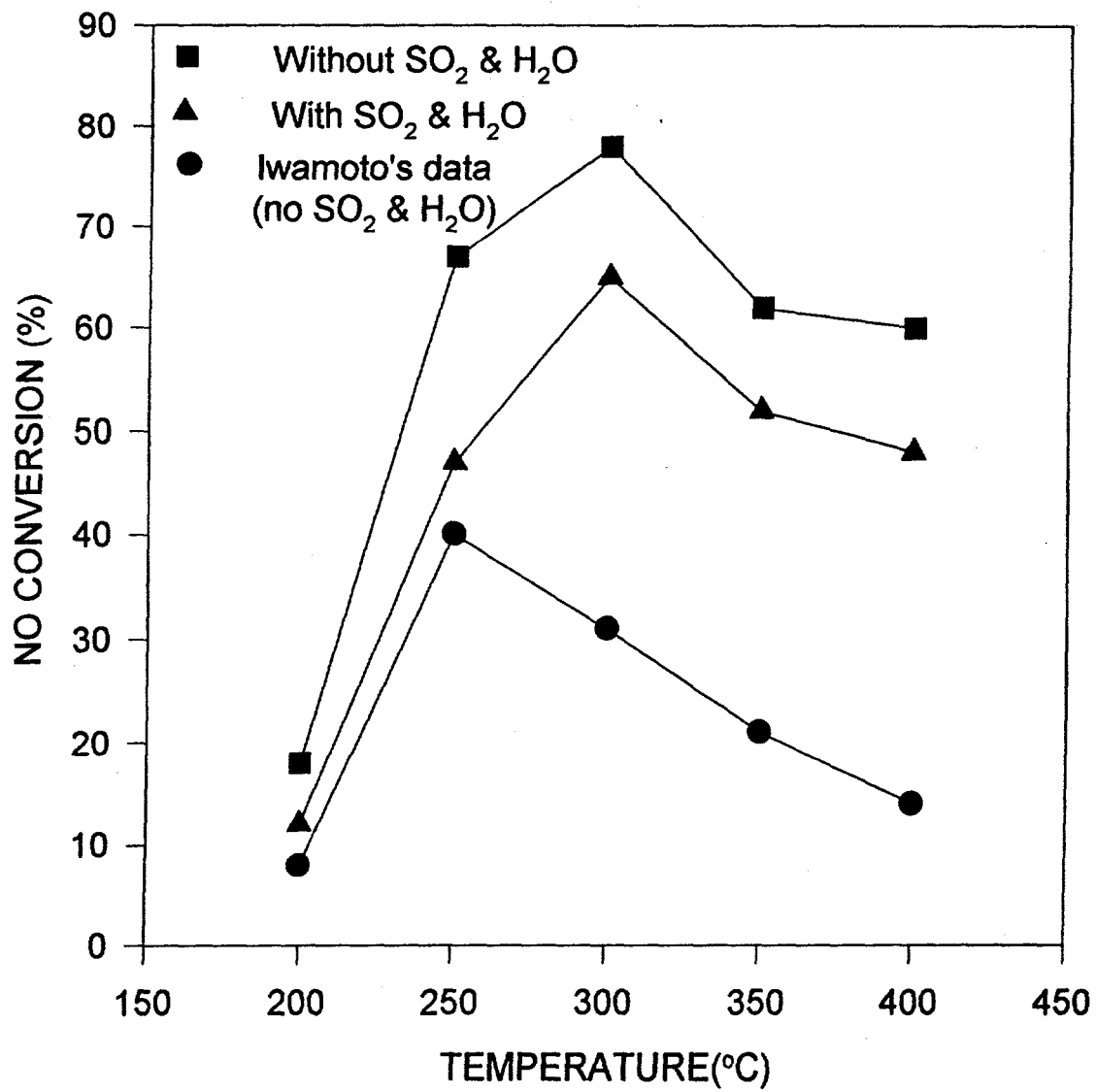
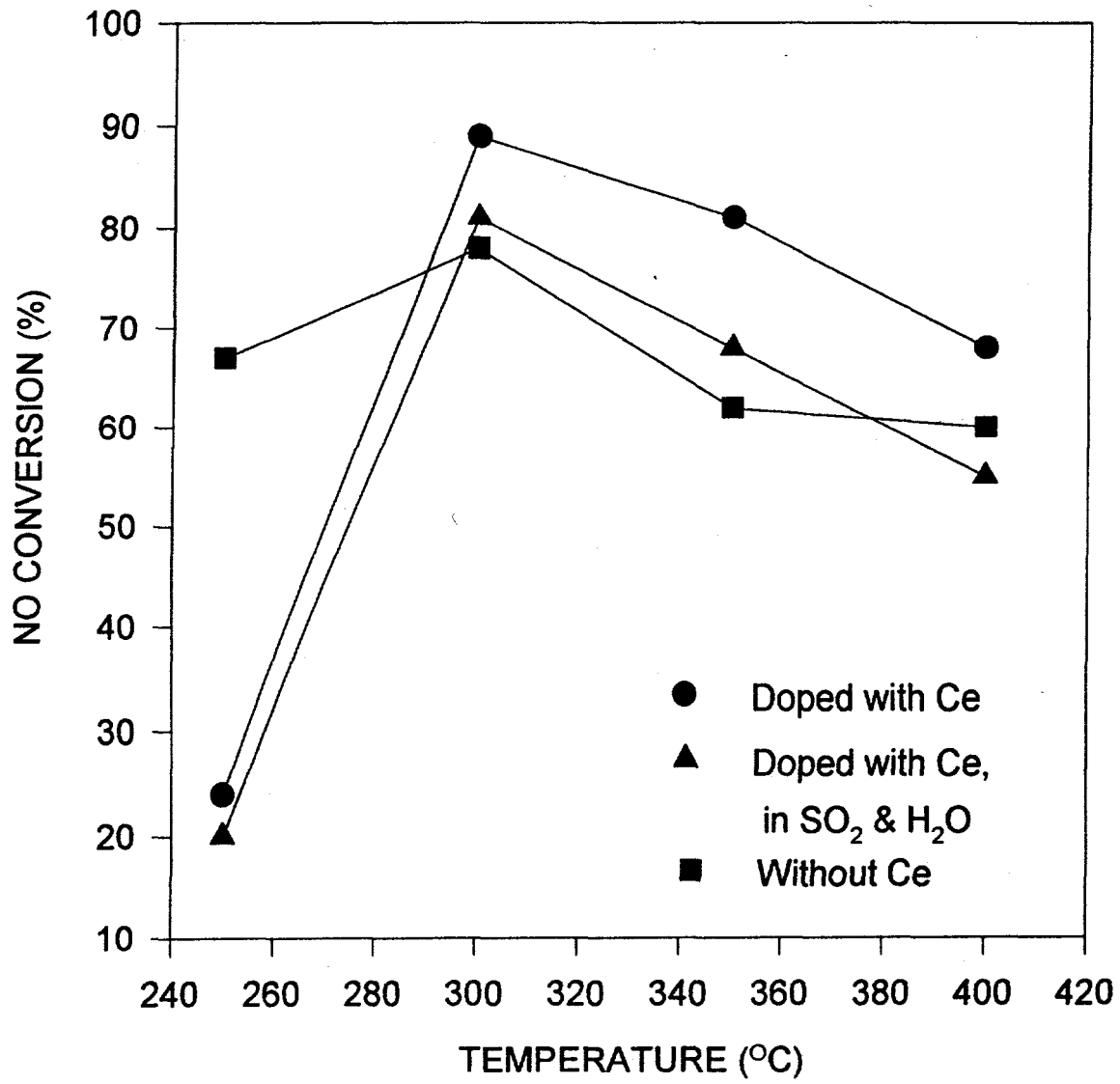


Figure 2



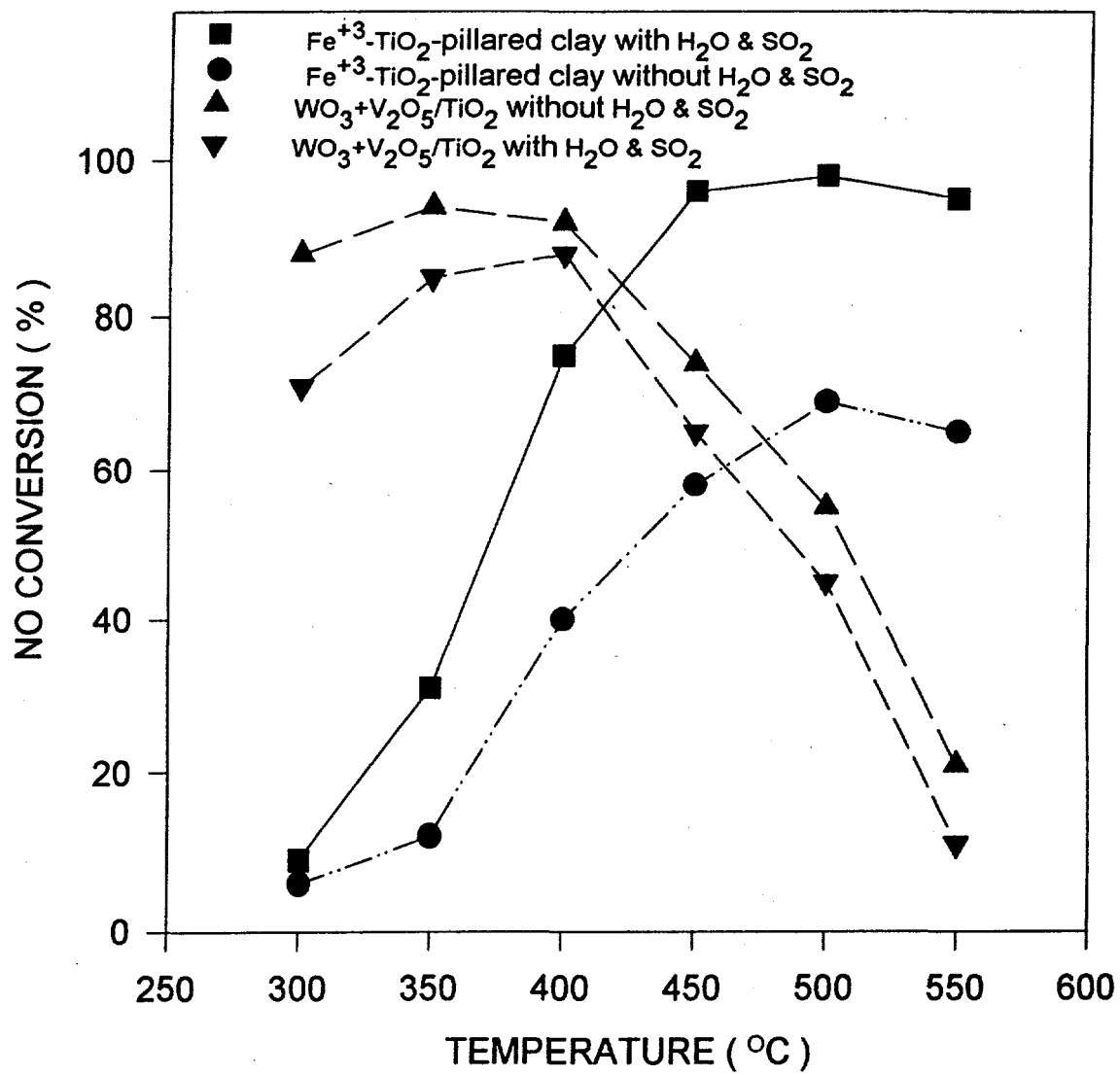


Fig. 3