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QUARTERLY TECHNICAL PROGRESS REPORT

Superior Catalysts for Selective Catalytic Reduction of Nitric Oxide

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by

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Brief Summary

During the past quarter, progress has been made in four tasks as summarized below:

Task 1. A delaminated Fe_2O_3 pillared clay was synthesized and carefully characterized. The chemical composition was measured by ICP atomic emission spectrometry. The structural changes in the clay as well as the iron oxide particle sizes were characterized by X-ray diffraction techniques.

Task 2. The Selective Catalytic Reduction (SCR, i.e., NO reduction with NH_3) activities of the delaminated pillared clay were tested and compared with four other most active SCR catalysts: a commercial $\text{V}_2\text{O}_5 + \text{WO}_3/\text{TiO}_2$ catalyst, a Fe_2O_3 -pillared clay, and two supported Fe_2O_3 catalysts (on Al_2O_3 and TiO_2). The delaminated Fe_2O_3 pillared clay exhibited the highest SCR activities. Catalyst stability test showed that the delaminated sample was also stable.

Task 3. To further increase the SCR activity of the delaminated pillared clay, Cr_2O_3 was doped as a promoter by incipient wetness.

Task 4. Deactivation effects of SO_2 and H_2O on the SCR activities of the delaminated Fe_2O_3 pillared clay were studied, and compared with other SCR catalysts. The delaminated clay catalyst showed the least deactivation.

Task 1. Iron Oxide Pillared Clay Synthesis

(1) Synthesis of Delaminated Pillared Clay

The clay suspension solution was prepared by dispersing 10 grams of bentonite (Fisher Scientific, purified grade) in 1 liter distilled water. Our chemical analysis showed that the bentonite from Fisher was mostly Na^+ montmorillonite. The pillaring agent was prepared by hydrolysis of 3 liters of 0.2 M $\text{Fe}(\text{NO}_3)_3$, and anhydrous sodium carbonate was added to the vigorously stirred $\text{Fe}(\text{NO}_3)_3$ solution to adjust the pH value of the solution. CO_2 evolution occurred during hydrolysis. The resulting solution was aged for 24 hours at room temperature prior to use. The ratio of base to iron was equal to 2, i.e., $\text{OH}^-/\text{Fe} = 2$, and the final pH value of the solution was 1.8. The aqueous clay suspension was dropwise added to the polyoxoiron cation solution through a funnel. The cation exchange capacity of the bentonite was 103 meq/100g. The ratio of Fe/clay was approximately 60 (mmole of Fe)/m.e.q. of clay). The pillaring/delaminating (ion-exchange) reaction took place at room temperature. It was found that the nature of the pillared clay product depended on the reaction condition. Pillared clay resulted from short (e.g., below 3 hrs.) reaction times whereas delaminated pillared clay formed after long reaction times (e.g., over 12 hrs.). (The delamination process in this reaction is under further study.) Both Fe_2O_3 -PILC and delaminated Fe_2O_3 -PILC were prepared and were subsequently subjected to SCR activity tests. After the reaction, the suspension solution was kept still to separate the top portion of the clear solution. The pillared/delaminated clay was separated by vacuum filtration of the suspension solution. The collected solid sample was redispersed and washed in distilled water. The final sample was collected after repeatedly dispersion/washing/filtration for three times. The collected solid samples were first dried at 120°C for 24 hours, then crashed and sieved to collect the desired fractions. The samples were further heated to 400°C at a rate of $2^\circ\text{C}/\text{min.}$ in a tabular reactor and were kept at the temperature for a period of at least 12 hours. After these pretreatments, the samples were ready for further experiments.

(2) Chemical Composition Analysis

The chemical composition of the delaminated pillared clay was analyzed by inductively coupled plasma (ICP) atomic emission spectrometer (Thermo Jarrel Ash 61 ICAP). A fusion-dissolution method was used for sample preparation. The clay sample (0.1 gram) was fused with a mixture (0.6 gram total) of lithium metaborate and lithium tetraborate (at a weight ratio of 1:2) in a graphite crucible at 1000°C for about one hour. After slowly cooling to room temperature, the fluxed bead was dissolved in 250 ml hot 2% HNO₃ solution. When the fluxed bead dissolved completely, the solution was filtered to remove graphite fiber impurity that came from the crucible. The bentonite sample was analyzed by the same procedure.

The ICP results are shown in Table 1. The water contents in Table 1 were obtained separately by thermo-gravimetric analysis (TGA) by heating in helium to 400°C. ICP results of montmorillonite and Fe₂O₃-PILC have been reported in last Quarterly Report. They are included here for comparison.

Table 1 shows that after ion exchange/pillaring reaction, the contents of the cations, Na⁺, K⁺, Ca⁺⁺ and Mg⁺⁺, decreased. However, the most significant change in the synthesized samples was the iron oxide content, which increased from 3.66% to up to 30.61%. The iron oxide pillared clay contained about 10% iron oxide. The extra amount of iron oxide in delaminated/pillared clay was doped on the surface.

(3) X-Ray Diffraction Characterization

X-ray diffraction patterns were obtained using powder samples in a Stoe transmission powder diffractometer with CuK α radiation. Normally, the data were collected in 2 minutes. For samples with weak signals or being amorphous, the data collection time was extended to at least 6 minutes.

XRD was also used to determine the Fe₂O₃ particle size. The particle size measurement was based on X-ray line broadening using a method described by Klug and Alexander (1). Silicon was used as a standard for calibration of half-height line width.

Table 1. Chemical Compositions (% by wt.) of Clay and Pillared Clays

	Montmorillonite	Delaminated Fe₂O₃-PILC	Fe₂O₃-PILC
SiO ₂	60.32	44.36	59.19
Al ₂ O ₃	19.14	13.93	19.63
Fe ₂ O ₃	3.66	30.61	9.55
TiO ₂	0.16	0.15	0.18
CaO	1.41	0.55	0.47
MgO	2.35	1.56	2.06
Na ₂ O	2.88	0.59	0.65
K ₂ O	0.51	0.33	0.34
H ₂ O	8.50	3.54	3.06
Total	98.93	95.61	95.13

(3A) Structural Analysis by X-Ray Diffraction

X-ray diffraction (powder) patterns of the starting clay (bentonite) are shown in Figure 1. Pattern A was recorded without pre-treatment. Pattern B was recorded after the sample was calcined at 300°C for two hours. The decrease of d_{001} spacing from 12.1 to 9.85 Å was due to dehydration of the interlayer hydrates.

XRD patterns of smectite clays generally show basal diffraction 001 and two dimensional diffraction hk only (2,3). Other hkl diffractions are usually not observed. The random or unoriented clay sample only show a strong 001 diffraction; the hk diffractions are also strong but diffusive (Figure 1). The characteristics of the hk diffractions is that the peak terminates steeply at the low-angle side but falls off gradually at the high-angle side. The hk reflections are characteristic of the type of the clay mineral, whereas the (001) basal reflection is characteristic of the conditions, i.e., interlayer water, cations, etc.

Other major peaks in Fig. 1 are assigned as follows (4). The peaks at 2θ of 19.6° ($d = 4.49$ Å) and 34.9° ($d = 2.57$ Å) are assigned to the two dimensional diffraction, hk , reflections. These non-basal hk two-dimensional reflections arise from the diffraction of the random stacking of layers. Each observed hk reflection is the summation of several hk index pairs. The diffraction at 19.6° ($d = 4.49$ Å) is the summation of hk indices of (02) and (11) , and the diffraction at 34.9° ($d = 2.57$ Å) is the summation of hk indices of (13) and (20) . The two-dimensional hk reflections are strongest in unoriented crystals. The peak at $2\theta = 26.5^\circ$ ($d = 3.36$ Å) is the diffraction of (101) from quartz impurity.

The XRD patterns of the synthesized clay catalysts are shown in Fig. 2. In the Fe_2O_3 -pillared clay sample, the d_{001} spacing was 26.4 Å, and the two-dimensional hk reflections remained. For the delaminated sample, no reflections were observed in the 2θ range 3 - 45° . The disappearance of the regular basal spacing of clay and the distinct lines corresponding to larger interlayer spacing (i.e., $2\theta < 5^\circ$) was also observed by Burch and Warburton (5) in their preparation of Fe_2O_3 pillared clay. Pillared clays that exhibit no (001) reflection have been referred to as "delaminated clay" (6,7) in the literature.

Figure 1. XRD patterns of bentonite (CuK α source). A: No pretreatment;
B: Calcined at 300°C for 2 hours.

Relative Intensity, A.U.

Figure 2. XRD patterns (CuK α source) of bentonite (A); Fe₂O₃-pillared clay (B); and delaminated pillared clay (C).

The XRD analysis showed that the delaminated sample not only lost its (001) diffraction, but also the two-dimensional diffraction peaks at d-pacings equal to 4.49 Å and 2.57 Å, i.e., the clay lost its two dimensional characteristic diffractions. As discussed by Occelli et al. (8), the delaminated clay does not preclude the possibility of short range ordering in the interlayer direction. Also the absence of the two dimensional reflections does not mean that there was no short range two dimensional structure in the clay. Rather, the large two dimensional structure could have been fragmented into small pieces giving a semi-amorphous form. These small pieces would be the basic units in the structure referred to as "house-of-cards," which have shown to be superior over the normal pillared clays in many aspects (7,8,9,10,11).

(3B) Fe₂O₃ Particle Size by XRD Line Brodening

The chemical composition analysis indicated that there were Fe₂O₃ particles in addition to the fragmented Fe₂O₃-pillared clay. The Fe₂O₃ particle size has been analyzed by XRD and plans are underway for Mössbauer analysis.

As discussed, the X-ray diffraction patterns for the clay structure disappeared. However, the weak and broadened peaks at 2θ of 33.36° (d = 2.686 Å) and 35.79° (d = 2.520 Å) became discernible by extending the data collection time to 400 seconds, as shown in Fig. 3. These two peaks were reflections by the (104) and (110) faces, respectively, of hematite (12).

From the line broadening, the particle size can be calculated with the following formula (1).

$$L = K\lambda / \beta \cos \theta$$

Where L is the mean dimension of the crystallites, K is Scherrer constant and for spheres, K = 0.893 (β_{1/2}), λ is the wavelength of CuKα which is 1.5418 Å, β is the breadth (line width at half height, β_{1/2}) of pure diffraction profile on 2θ scale in radians, and θ is the diffraction angle.

The value of β was calculated by the following procedure (1): By using the breadths of silicon standard (b₀) and catalyst sample (B₀) from their XRD profiles and finding the Kα doublet separation of Cu radiation from the literature, the corrected breadths of silicon standard

Figure 3. XRD of the delaminated/pillared clay. The broad and weak peaks at 33.43° and 35.79° are reflections of (104) and (110) faces of hematite.

(b) and catalyst sample (B) were obtained. With the ratio of b/B and β values was found from the curves for correction integral breadths of Debye-Scherrer lines for instrumental broadening. The value of β was found to be 0.6163. Therefore, the average α -Fe₂O₃ particle size was 170 Å.

Task 2. SCR Activity and Stability

(1) Activity for Selective Catalytic Reduction of NO by NH₃

The NO SCR activities for the delaminated Fe₂O₃-pillared clay were measured under conditions both with and without SO₂/H₂O. The results are shown in Figs. 4 and 5. Three other high-activity catalysts were also included for comparison: V₂O₅ + WO₃/TiO₂, Fe₂O₃/Al₂O₃ and Fe₂O₃/TiO₂. The delaminated pillared clay showed clear superiority over the other catalysts.

The V₂O₅ + WO₃/TiO₂ contained 8.2% WO₃ and 4.8% V₂O₅. This is a catalyst being commercially used (13,14) and its SCR activity was the same as a US commercial catalyst tested in our laboratory. This catalyst was SO₂ resistant. However, the delaminated pillared clay exhibited higher activities under conditions both with and without SO₂/H₂O. The NO conversions at 400°C for this catalyst reached 98.8% (without SO₂/H₂O) and 98.7% (with SO₂/H₂O). Its activity was decreased considerably at lower temperatures.

Supported Fe₂O₃ catalysts were among the most active catalysts for the NO SCR reaction (15). The data by Wong and Nobe were also included for comparison,, Fig. 4. Wong and Nobe only studied the reaction without SO₂ and H₂O, and their reactant gas composition was the same as that used in this study. Their catalyst amount was 14 g and the gas flowrate was 300 lNTP/hr. So a conversion, based on first-order reaction (15) and plug flow reactor, was needed for our comparison. The conversions shown in Fig. 4 were with this conversion. It is seen that the supported Fe₂O₃ catalysts show lower activities than Fe₂O₃-pillared clay, as well as the other catalysts. It was noted by Wong and Nobe that there was pore diffusion limitation in their reactions, and effectiveness factors ranging from 16% to 95% were indicated. By including the effectiveness factors, however, the NO conversion for the delaminated pillared clay was still higher than the supported Fe₂O₃ catalysts.

Figure 4. Selective catalytic reduction of NO with NH_3 on different catalysts. Reaction conditions: $NO = NH_3 = 1,000$ ppm, $O_2 = 2\%$, N_2 balance, total flow rate = 500 ml/min., catalyst weight = 0.4 gram. A: delaminated pillared clay, B: $V_2O_5 + WO_3/TiO_2$, C: Fe_2O_3 -pillared clay, D: Fe_2O_3/Al_2O_3 and E: Fe_2O_3/TiO_2 .

Figure 5. Selective catalytic reduction of NO with NH_3 on different catalysts. Reaction conditions are the same as in Fig. 4 except H_2O (8%) and SO_2 (500 ppm) are added. A: delaminated pillared clay, B: $\text{V}_2\text{O}_5 + \text{WO}_3/\text{TiO}_2$ and C: Fe_2O_3 -pillared clay.

(2) Catalyst Stability

The stability of iron oxide pillared clays have been studied by a number of researchers. It was reported that sulfite-pillared clay was stable at elevated temperatures and pressures and iron oxide pillared clay was stable under reducing conditions even at a temperature as high as 500°C. However, unstable iron oxide pillared clays have also been observed. SEM/EDS analysis (16) showed that the iron oxide pillars migrated to the edge of the clay when the pillared clay was exposed to air at ambient temperature for three months. Prompted by these reports, the delaminated pillared clay was subjected to a longevity test under the SCR conditions. As shown in Table 2, the NO conversion stayed in the range 83-86% when SO₂ and H₂O were switched on, and the conversion was stable at 95-99% without SO₂ and H₂O. No deactivation was shown after four days. The delaminated clay is therefore stable under the SCR reaction conditions.

Task 3 Preparation of Promoted Catalysts

To further improve the catalyst activity, Cr₂O₃ was added as a promoter to the delaminated Fe₂O₃-PILC catalyst.

A series of catalysts doped with different Cr₂O₃ amounts were prepared by the incipient wetness impregnation technique. Chromium acetate aqueous solution was used as precursor for Cr₂O₃. After the impregnation, the catalysts were dried at room temperature first, then in an oven at 110°C for 16 hours in air. The final catalysts were obtained by calcination at 350°C for 4 hours to decompose the acetate. The following catalysts have been prepared:

1.25%Cr₂O₃/delaminated Fe₂O₃-PILC

2.5%Cr₂O₃/delaminated Fe₂O₃-PILC

5.0%Cr₂O₃/delaminated Fe₂O₃-PILC

The SCR catalysts activities of these catalysts will be studied during the next reporting quarter.

Table 2. Longevity Test of SCR Activity for the Delaminated Fe₂O₃ Pillared Clay

Time (Hr)	2*	3	24	48	96	97*
NO Conversion (%)	97.5	84.0	83.0	85.0	84.5	98.8

Reaction conditions: NO = NH₃ = 1,000 ppm, O₂ = 2%, SO₂ = 1,000 ppm (when used),
H₂O = 8% (when used), total flowrate = 500 ml/min, catalyst = 0.4 g, 400°C.

*Reaction without water vapor and SO₂.

Task 4 Poison Resistance Study

To understand the poison resistance of the delaminated Fe_2O_3 -PILC, the catalyst was tested under both without $\text{SO}_2/\text{H}_2\text{O}$ and with $\text{SO}_2/\text{H}_2\text{O}$ conditions at temperatures from 250°C to 400°C . The results of SCR activities with SO_2 and H_2O are shown in Fig. 5. For the delaminated pillared clay, the activities are compared for conditions with and without $\text{H}_2\text{O}/\text{SO}_2$, Fig. 6. Figure 6 shows that at lower temperatures ($< 300^\circ\text{C}$), $\text{SO}_2/\text{H}_2\text{O}$ exhibited a deactivation effect on the SCR activity, this deactivation effect decreases as the reaction temperature approaches the normal SCR reaction temperature (i.e., 400°C). At 400°C , the negative effect of $\text{SO}_2/\text{H}_2\text{O}$ almost totally disappeared.

Further study on the poisoning effects will be conducted.

Figure 6. Selective catalytic reduction of NO with NH₃ on delaminated Fe₂O₃ pillared clay. Reaction conditions are the same as in Fig. 4.

A: Without SO₂ and H₂O vapor addition. B: With SO₂ (500 ppm) and H₂O (8%) addition.

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