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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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Summary

In the last Quarterly Technical Progress Report (for January 1 - March 31, 1994), we reported the synthesis and (partial characterization) and SCR (Selective Catalytic Reduction of NO) activity for a delaminated Fe_2O_3 -pillared clay (Fe_2O_3 -PILC). The SCR activity for this PILC was substantially higher than that of the commercial-type $\text{V}_2\text{O}_5 + \text{WO}_3/\text{TiO}_2$ catalyst.

During the past quarter, we first completed the characterization of the delaminated Fe_2O_3 -PILC catalyst. Both physical characterization (micropore probing by adsorption and Mössbauer spectroscopy) and chemical characterization (by IR spectroscopy) were performed. Since the synthesis of this PILC sample was undertaken under a specific set of conditions and it is known that the PILC properties depend strongly on the synthesis conditions, we then proceeded to examine in a systematic manner the dependence of the catalytic properties of the PILC on its synthesis conditions. Four parameters in the synthesis were studied: Fe precursors, pH of the pillaring solution, concentration of the pillaring solution, and the starting clay. Finally, the effect of the Cr_2O_3 promoter on the SCR activity of the pillar clay was studied.

A. Characterization of the High-Activity, Delaminated Fe_2O_3 -PILC Catalyst

The detail synthesis procedure and the SCR activity of the delaminated PILC catalyst were reported in the last Quarterly Progress Report. A complete characterization was performed and the results are given below.

A1. Mössbauer Spectroscopic Analysis

Transmission Mössbauer spectra were measured using a constant acceleration mode Mössbauer spectrometer with ^{57}Co source at room temperature. The catalyst pellets were ground into a powder and was dispersed and mounted on scotch tape to provide a sample diameter of 25 mm. Spectra are reported relative to iron foil.

The Mössbauer spectra are shown in Figure 1. Upon examination of Fig. 1, it is apparent that there are contributions from a center doublet, surrounded by a sextuplet. First, the outside six peaks can be fit as a sextuplet. The two peaks in the center are fit as an equal area doublet.

The parameters from this initial fit are shown in Tables 1 and 2. Table 1 contains the sextuplet parameters and Table 2 contains the doublet parameters.

The literature on Mössbauer spectra of iron oxide pillared clays (1-5) show only a doublet, even though bulk iron oxides such as Fe_2O_3 and Fe_3O_4 , exhibit magnetic hyperfine splitting, giving six lines instead of two. This is the result of superparamagnetism; essentially the particles are too small to exhibit hyperfine splitting.

Now we discuss the magnetic components of the spectrum. First, similar systems yielding spectra similar to Fig. 1 are observed in the literature (6-8). There are differing values reported for similar systems shown in Table 1, and the variations are due to differences in particle size. For particles in a narrow size range, about 100-600Å, an average particle size can be estimated from the value of the hyperfine field. For the bulk Fe_2O_3 , the accepted value is around 515-518 kOe. As the particle size is reduced below 600Å, the value of hyperfine field gets smaller until the magnetically split component collapses into a doublet at about 130Å, due to superparamagnetism (9). Using only the data in Table 1, it is apparent that a value of the particle size in the delaminated clays is about 170Å. This result is consistent with that from XRD line broadening reported in our last Quarterly Progress Report.

A correlation between the average particle volume and the percent superparamagnetic contribution has been done for $\alpha\text{-Fe}_2\text{O}_3$ (8). The percent superparamagnetic in the case of Fig. 1 is 31.6%. There are 3 components of the delaminated PILC that contribute to this doublet: (1) the 3 wt % Fe_2O_3 impurity in the bentonite clay, (2) iron pillars, and (3) the superparamagnetic contribution from 170Å particles. Using the previously mentioned correlation, 170Å particles will give a 10% doublet contribution. Subtracting the contribution of the bulk particles leaves an estimated 22% Fe_2O_3 contribution from the iron pillars and 3% iron wt % clay impurity. This 3% wt % clay impurity is about 7% of the Fe_2O_3 in the sample, leaving about 15% of the iron in pillared form.

To maximize the resolution of the central two doublets, another Mössbauer spectrum was taken by adjusting the velocity range to +/- 4 mm/sec from +/- 10 mm/sec and recalibrating the

mössbauer with sodium nitroprusside. In this case, the data from the sextuplet in Fig. 1 was entered as an invariant into mössbauer fitting procedure. Thus, only the fitting of the equal area doublet was carried out. Results from this fitting yielded no significant improvements of the doublet fit. Table 3 contains a comparison of the doublet parameters with published iron pillared clay mössbauer results. The literature data on pillared clays are devoid of hyperfine splitting. The large variations in parameters are clearly seen in Table 3. Although it is known (1-5) that the major contribution to Doublet II is from iron oxide pillars, iron impurities in the clay also make a contribution.

Summarizing the Mössbauer characterization results, the structure of the delaminated sample can be described as "house-of-cards," and a schematic representation of the structure is shown in Fig. 2. This picture is also consistent with our XRD results reported in the last Quarterly Progress Report, as well as the micropore probing results to be given below.

A2. Micropore Size Distribution by Molecular Probing

The existence of micropores and the micropore size distribution in the delaminated clay sample were further studied by sorption of probe molecules at subcritical temperatures. Under subcritical conditions, micropore filling takes place and the micropore volumes can be calculated.

Thermogravimetric analysis (TGA) was employed to measure the weight gains, by sorption of molecules with known dimensions. Pore volumes for different pore dimensions were measured in this manner.

Three probe molecules were used, with their kinetic diameters given below: N₂ (3.6 Å), n-hexane (4.9 Å) and 1,3,5 trimethyl benzene (8.6 Å). The cumulative pore volumes were calculated from the equilibrium sorption amount assuming the adsorbate as liquid. The equilibrium sorption amounts of n-hexane and trimethyl benzene were measured at room temperature by TGA. The N₂ sorption was measured at 77K with the Quantasorb Analyzer. The results are shown in Fig. 3. For the N₂ sorption, the α_s method was used to obtain the micropore volume (10). From the data shown in Fig. 3, it is seen that a significant amount of

micropores with dimensions smaller than 9 Å existed in the delaminated sample. For the Fe₂O₃-pillared clay, the cumulative pore volume by N₂ sorption was 0.19 cm³/g, compared to 0.13 cm³/g for the delaminated clay. From this result, it is clear that the delaminated sample contained pillared clay fragments, thus it should be properly referred to as delaminated pillared clay.

A3. In Situ FT-IR Characterization

To examine the surface acidity and to identify the Brønsted and Lewis acid sites of the delaminated/pillared clay, FT-IR spectra of adsorbed ammonia were measured. The IR spectra were measured with a Nicolet Impact 400 FT-IR spectrometer. The samples were pressed into self-supporting disks. The typical weight of the prepared disks was 60-70 mg, which was equivalent to 12-14 mg/cm². The *in situ* IR spectra of NH₃ adsorbed on pillared/delaminated clays were recorded by using an IR cell that allowed the sample to be treated at high temperatures under vacuum or in different gases. The samples were pretreated at 300°C *in vacuo* for 2 hours prior to adsorption. The spectra of adsorbed ammonia at room temperature are shown in Fig. 4.

Figure 4 shows the effects of water vapor on the absorption bands at 1636.7, 1458 and 1595.1 cm⁻¹. The peak at 1636.7 cm⁻¹ is attributed to the bending vibration of surface hydroxyl groups (11). The negative absorption band in spectra (a) and (b) were due to the consumption of surface hydroxyl groups by ammonia adsorption, since all spectra were ratioed against that of the sample before NH₃ exposure. Similar negative peaks were also observed when ammonia was adsorbed on V₂O₅/SiO₂ (12). The strong peak at 1458 cm⁻¹ was due to ammonia adsorbed on Brønsted acid sites (13). The weak peak at 1595.1 cm⁻¹ was likely due to ammonia coordinatively adsorbed on the catalyst surface, i.e., on Lewis acid sites.

Figure 4 shows that the IR band at 1637 cm⁻¹ changed from a negative one to a position one, after about 3 minutes of exposure to 2% H₂O. It is interesting to note that the peak intensity at 1458 cm⁻¹ actually increased in the first few minutes upon H₂O exposure. Concurrently, the weak band at 1595 cm⁻¹ gradually decreased and eventually disappeared. This suggests that,

with the addition of water vapor, the Lewis acid sites were converted to Brønsted acid sites and the coordinatively adsorbed ammonia was transformed into ammonium ions on the surface.

For clays and their variants, the surface acidity and the type of acid sites (Brønsted or Lewis sites) are dependent on the extent of hydration-dehydration. The FT-IR spectrum of ammonia adsorbed on the delaminated/pillared clay at 150°C is shown in Fig. 5. A very strong and sharp peak at 1453 cm^{-1} was observed. The difference with the spectra taken at room temperature was that there was no negative band at around 1630 cm^{-1} . This was due to dehydration at 150°C which eliminated the adsorbed water molecules.

The I.R. results showed that the delaminated/pillared clay was abundant in Brønsted acid sites on the surface. As shown in our previous work (14-16) Brønsted acid sites on V_2O_5 and other oxides are the active sites for selective catalytic reduction of NH_3 with NO . The high catalytic activity for SCR of this clay catalyst may be correlated with its strong Brønsted acidity.

Figure 6 shows the IR spectra of ammonia adsorbed on montmorillonite and the delaminated/pillared clay on the same intensity scale. Ammonia adsorbed on montmorillonite also gave an absorption band at around 1450 cm^{-1} , but its relative intensity was low. It is known that there are only Lewis acid sites on Fe_2O_3 (17,18). The origin of the strong Brønsted acid sites in this clay catalyst was probably the result of the interactions between Fe_2O_3 and the clay. Further studies of these interactions are in progress.

B. Effects of Synthesis Conditions on the PILC Catalyst - Search for the Best Catalyst

The most important step in the synthesis of metal oxide pillared/delaminated clay is ion-exchange. Poly- or oligometric hydroxy metal cations are exchanged with the interlayer cations of clay, and then these hydroxy-metal cations are decomposed into oxide pillars between the silicate layers by heat treatment.

The hydrolysis conditions to form oligomers from the pillaring solution and the intercalation conditions to substitute the oligomers for the small cations between the clay layers are very important to the final PILC.

In this task, the experimental results on the preparation and catalytic properties for SCR reaction of the iron-oxide pillared/delaminated clay are obtained. This study emphasizes on the influence of the preparation conditions on the catalytic activities for the SCR reaction of NO with NH_3 .

B1. Effects of Different Precursors on SCR Activity

Different salts at different pH values were used in the ion exchange step, and the results are summarized below.

Sample	Pillaring Solution			S.A. m^2/g	XRD	Conversion of NO
	Salt	Aging (hr)	pH			
611	FeCl_3	21	1.7	71	--	44%
612	$\text{Fe}(\text{NO}_3)_3$	21	1.7	150	Amorphous	95.0%
613	$(\text{Fe}_3\text{Ac}_7\text{OH} \cdot 2\text{H}_2)\text{NO}_3$	21	3.2	137	Amorphous	73.0%

*All samples were prepared from pillaring solutions formed by hydrolysis of Fe^{3+} salt solutions (0.2 M) at the room temperature, using Na_2CO_3 as the base for pH adjustment. The solution/clay ratio was 60 mmol Fe^{3+}/g bentonite.

*The BET N_2 surface areas were measured after outgassing for 1 hr at 200°C in He.

*All samples tested in SCR reaction were precalcined at 400°C in air.

*SCR conditions: $\text{NO} = \text{NH}_3 = 1,000$ ppm, $\text{O}_2 = 2\text{-}4\%$, $\text{N}_2 = \text{balance}$, total flow rate = 500 ml/min., Catalyst weight = 0.4 g, Temperature = 350°C .

It is clear that the nitrate precursor yields the best catalyst.

B2. Effects of pH of the Pillaring Solution on the SCR Activity

The effects of the pH value in the ion exchange step on the SCR activity of the final PILC are summarized below. Only pH value was varied. The SCR activity was tested at 350°C .

Ion Exchange Condition

Sample	pH	Aging (h)	Reaction (h)	NO Conversion
621	1.40	16	6	70.5%
622	1.70	16	6	88.5%
623	1.80	16	6	64.0%

*All samples are prepared as follows:

Add a slurry containing 1.0 g Bentonite and 100 ml distilled water into a 0.2 M 300 ml $\text{Fe}(\text{NO}_3)_3$ solution under constant stirring. Change the pH value of the pillaring solution by adding different amounts of Na_2CO_3 .

*All PILC samples were pretreated at 400°C (in air) before SCR reaction.

The results above show that the SCR activity is sensitive to the pH value, and that pH = 1.7 yields the best catalyst.

B3. Effects of Concentration of the Pillaring Solution on SCR Activity

In this series of experiments, we used $\text{Fe}(\text{NO}_3)_3$ as the precursor, and fixed pH at 1.7 (as they were the optimal values from B-1 and B-2), and only changed the concentration. The results are summarized below. (The SCR conditions were the same as in B-1.)

Pillaring Conditions

Sample	$\text{Fe}(\text{NO}_3)_3$ (M)	mmol Fe^{3+} /g bentonite	S.A. (m^2/g)	NO Conversion
631	0.4	120	148	84.0%
632	0.2	60	167	96.0%
633	0.1	30	132	88.2%

All samples were prepared from pillaring solutions formed by hydrolysis of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at room temperature, using Na_2CO_3 as the base, pH = 1.70. Pillaring time = 96 h. The optimum conditions were those for sample No. 632.

B1. Effect of Clay Type on PILC

The bentonite sample used for the synthesis of PILC was a purified form of the natural clay (supplied by Fisher). A commercially available clay was obtained from Laporte, Inc. (Kindly donated by Dr. Gordon Patterson, Laporte Labs, Gonzales, TX). This clay was a synthetic type with well defined structure and properties, with the trade name of Laponite. The chemical structure of Laponite is similar to bentonite. However, the crystal diameter/thickness aspect ratio of Laponite is smaller than bentonite. As a result, it is easier to form delaminated PILC from Laponite. In this work, we use Laponite as the starting clay and compared the resulting PILC with that from bentonite.

Trinuclear acetato hydroxy-iron (III) intrate, $[\text{Fe}_3(\text{OCO CH}_3)_7\text{OH} \cdot 2\text{H}_2\text{O}]\text{NO}_3$, was used as the iron cation precursor. It was prepared following the procedure described by Yamanaka et al (5). 80.8g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 50 ml of ethyl alcohol and was subsequently reacted with 140 ml of anhydrous acetic acid. The solution was then cooled in an ice bath. The resulting precipitate was separated and used in the pillaring procedure.

A 0.04 mol/l aqueous solution of the trinuclear acetato hydroxy-iron (III) nitrate was added to a 1% Laponite aqueous slurry under constant stirring. The concentration ratio of the mixture was 3.0 mmol iron per gram of Laponite. The mixture was at pH = 3.2 after reacting for 4h at 35°C. The resulting material was separated by centrifuge and was washed with distilled water 3 times to remove the excess iron ions. It was then dried in air at the room temperature and calcined at 350°C for 6 h.

The XRD pattern showed no peaks, as shown in Figure 7. The BET N_2 surface area was 243 m^2/g . The NO conversion for SCR was 71% 350°C. The SCR condition was the same as above. It is clear that Laponite (under these conditions) was not as good as bentonite.

B5. Promoting Effect of Cr_2O_3 on SCR Activity

The results are shown in Figure 8. A strong promoting effect at 300°C (by doping 2.5% Cr_2O_3 in the delaminated PILC) was seen. However, a negative effect was seen at higher temperatures. Further studies are underway on promoters for SCR.

References

1. Doff, D.H., Gangas, N.H.J., Allan, J.E.M., and Coey, J.M.D., Clay Minerals, **23**, 367 (1988).
2. Martin-luengo, M.A., Martin-scarvalho, H., Ladriere, J., and Grange, P., Clay Minerals, **24**, 495 (1989).
3. Occelli, M.L., Stencel, J.M., and Suib, S.L., J. Mol. Catal., **64**, 221 (1991).
4. Lee, W.Y., Tatarchuk, B.J., and Raythatha, R.H., J. Catal., **115**, 159 (1989).
5. Yamanaka, S., and Hattori, M., "Iron Oxide Pillared Clay," in Pillared Clays, Ed. by R. Burch, Catalysis Today, **2**, 261 (1988).
6. Lund, C.R.F., and Dumesic, J.A., J. Phys. Chem., **85**, 3175 (1981).
7. Hobson, M.C., and Gager, H.M., J. Catal., **16**, 254 (1970).
8. Kundig, W. and Bommel, H., Phys. Rev., **142**, 327 (1966).
9. Yoshioka, T., Koezuzkz, J., Ikoma, H., J. Catal., **16**, 264 (1970).
10. Gregg, S.J. and Sing, K.S.W., "Adsorption, Surface Area and Porosity," Academic Press, London, 2nd Ed., 1982.
11. Little, L.H., "Infrared Spectra of Adsorbed Species," Academic Press, London, 1966.
12. Rajadhyaksha, R.A., and Knözinger, H., Appl. Catal., **51**, 81 (1989).
13. Kung, M.C. and Kung, H.H., Catal. Rev.-Sci. Eng., **27**, 425 (1985).
14. Chen, J.P. and Yang, R.T., J. Catal., **125**, 411 (1990).
15. Yang, R.T., Chen, J.P., Kikkinides, E.S., Cheng, L.S., and Cichanowicz, J.E., Ind. Eng. Chem. Res., **31**, 1440 (1992).
16. Chen, J.P., and R.T. Yang, J. Catal., **139**, 277 (1993).
17. Rochester, C.H., and Topham, S.A., J. Chem. Soc. Faraday Trans. I, **75**, 1259 (1979).
18. Peri, J.B., J. Phys. Chem., **69**, 220 (1965).

Table 1. Magnetically Split Component: The Sextuplet

Hyperfine Field (kOe)	Isomer Shift (mm/sec)	Identified Species	Reference
501	0.351	Fe ₂ O ₃	this work
496	-	158 Å particles Fe ₂ O ₃ /SiO ₂	7
516	-	650 Å particles Fe ₃ O ₄ /SiO ₂	7
503	0.38	180 Å particles Fe ₂ O ₃ /SiO ₂	8
518	0.39	bulk α -Fe ₂ O ₃	8

Table 2. Superparamagnetic Component: the Doublet

Isomer Shift (mm/s)	Quadrupole Splitting (mm/s)	% Superpara- magnetic	Identified Species	Reference
0.304	0.738	31.6	Fe ₂ O ₃	This work
0.328	0.811	63	α -Fe ₂ O ₃ /SiO ₂	6
0.60	0.68	45	158 Å particles Fe ₂ O ₃ /SiO ₂	7
0.56	0.71	70	650 Å particles Fe ₂ O ₃ /SiO ₂	7
0.38	0.44	-	180 Å particles Fe ₂ O ₃ /SiO ₂	8
-	-	0	bulk α -Fe ₂ O ₃	8
0.63	0.73	100	7% wt α -Fe ₂ O ₃ /SiO ₂	59

Table 3. The Doublets Parameters: Comparison with Iron Pillared Clays

Doublet 1: Isomer Shift mm/s	Doublet 1: Quadrupole Splitting mm/s	Doublet 1: % Relative Area	Doublet 2: Isomer Shift mm/s	Doublet 2: Quadrupole Splitting mm/s	Doublet 2: % Relative Area	Reference
-	-	-	.304	.738	31.6	This work
0.30	1.29	29	0.33	0.74	68	1
0.33	0.93	49	0.34	0.54	51	2
0.34	1.14	62	0.35	0.70	38	3
-	-	-	0.37	0.76	100	4
0.42	1.41	17	0.38	0.72	83	5

Fig. 1 Mössbauer spectrum of delaminated/pillared clay in the range of ± 10 mm/sec, shown relative to iron foil.

Fig. 2 Schematic representation of the delaminated/pillared clay containing iron oxide particles.

Figure 3 Cumulative micropore volume as a function of pore dimension measured by micropore filling with probe molecules ($\text{N}_2 = 3.6 \text{ \AA}$, n-hexane = $4.9 \text{ \AA}$ and 1,3,5-trimethyl benzene = $8.6 \text{ \AA}$).

Fig. 4 FT-IR spectra of ammonia adsorbed on delaminated Fe₂O₃ pillared clay (a). (b)-(f) are after exposure to 2% H₂O, at one-minute successive time intervals. All spectra are taken at room temperature, and ratioed against the sample before NH₃ exposure (but after calcination).

Fig. 5 FT-IR spectra of ammonia adsorbed on delaminated/pillared clay at 150°C.

Fig. 6 FT-IR spectra of ammonia adsorbed on montmorillonite (top) and delaminated/pillared clay at room temperature.

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Fig. 7. XRD of Delaminated Fe_2O_3 Pillared Laponite

Fig. 8 Effect of Cr₂O₃ doping on the SCR activity of Fe₂O₃ PILC (Sample 613). Open Circles: Delaminated PILC Sample 613. Dots: With 2.5% Cr₂O₃ doped in Sample 613. The SCR reaction conditions are given in Section B1.

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