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QUARTERLY TECHNICAL PROGRESS REPORT

Superior Catalysts for Selective Catalytic Reduction of Nitric Oxides

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by

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SUMMARY

Work was done in three tasks during the first quarter. In Task 1, a new SCR reactor system has been built, complete with on-line GC and MS analyses. The GC is used to monitor the N_2 product so the $NO_x \rightarrow N_2$ conversion can be calculated. The MS is used to analyze the N_2O concentration. In addition, a wet analytical technique has been established for SO_3 analysis. The new SCR system and the SO_3 analytical technique have been subjected to shakedown tests with success. Along with the existing SCR reactor system, there are now two systems that are being run independently. In Task 2, a procedure for the synthesis of stable Fe_2O_3 pillared clay has been established. Inductive coupled plasma spectrometric analysis (ICP) has been used to analyze the chemical composition of the Fe_2O_3 pillared clay. Preliminary results for the SCR activities of the Fe_2O_3 pillared clay are obtained in Task 3. The results show that the activities are near that of the commercial V_2O_5/TiO_2 catalysts. However, the SO_2 -to- SO_3 conversion is substantially lower with the pillared clay catalyst, which could be an important advantage.

Task 1. SCR Reactor Construction and Upgrading

The SCR reactor system that was used in our laboratory for an EPRI program is now dedicated to this new program. The reactor system consists of a chemiluminescent NO/NO_x analyzer (Thermo Electron Corporation Model 10) and is shown in a schematic diagram in Figure 1. This reactor system does not have the capability for N₂O and SO₃ analyses. N₂O cannot be detected by chemiluminescent analyzer. The emission of both N₂O (which is very stable) and SO₃ from SCR has been of serious concern, especially for application to power plants using high sulfur American coals.

In order to upgrade the reactor system for N₂O and SO₃ analyses, and also to enable us to produce more experimental results, it was decided to build another SCR reactor system. The new SCR reactor system has an on-line quadrupole mass spectrometer for N₂O analysis while the SO₃ is collected and analyzed by using a wet analytical technique. Also on-line is a GC for N₂ product monitoring. The new reactor system is described below.

The tubular reactor is made of quartz heated by a coiled Nichrome wire. The reactor temperature is controlled by a programmable temperature controller (Omega CN-2010). The catalyst is supported on a fritted quartz support.

The simulated flue gas is made by mixing the gaseous reactants. The flow rates of the reactants are controlled by two sets of flow meters. Rotameters are used to control flows with high flow rates (i.e., He, NH₃/He, NO/He); mass flow meters are used for gases with low flow rates (SO₂ and O₂). The pre-mixed gases (0.8% NO in He and 0.8% NH₃ in He) are supplied by Cryogenic Supply. The 8% water vapor is generated by passing helium through a heated gas-washing bottle containing distilled water. All tubings leading to the reactor are heated tapes in order to prevent the deposition of ammonium sulfate. The effluent is analyzed by an on-line GC for N₂. From the N₂ concentration, the NO_x → N₂ conversion is known. A quadrupole mass spectrometer (UPI Model 1000) is also available to spot check the N₂O concentration in the product. (Attempts to analyze N₂O by GC with Porapak Q and R columns have failed, thus we have to resort to mass spectrometry.)

SO₃ Analysis. A wet analytical technique for measuring SO₃ concentration has been established. The procedure is described as follows. The effluent from the SCR reactor is bubbled through a BaCl₂ solution, where the SO₃ is captured quantitatively. The BaSO₄ forms a precipitate in the form of a white powder. The precipitate is collected on an ashless filter paper, which is then burned along with the precipitate in a crucible, so the amount of the precipitate can be accurately weighed. Heating of the effluent up to the point of collection is provided, so the formation of (NH₄)₂SO₄ in the lines is avoided. This technique has been tested successfully in our laboratory. A dummy catalyst was used in the control experiment. In a preliminary SCR run with the Fe₂O₃-pillared clay catalyst, an SO₂-to-SO₃ conversion of 0.5% was obtained, which is lower than those with the V₂O₅/TiO₂ catalysts reported in the literature. This is an encouraging result, since the SO₂ → SO₃ conversion is an important issue for the SCR reaction.

Task 2. Iron Oxide Pillared Clay Synthesis

The general procedure for preparing pillared clays is described below:

- (1) A clay sample is suspended in distilled water;
- (2) A polymeric (or oligomeric) cation complex is prepared by dissolving a metal salt in distilled water. If necessary, a base is added into the solution to promote the hydrolysis. The solution is aged at a selected temperature for a period of time;
- (3) By mixing the clay suspension and the polyoxometallic complex solution, the ion exchange reaction takes place;
- (4) After a certain period of ion exchange at a given temperature, the clay sample is collected by filtration or centrifuge, followed by heating (e.g., to 400°C) to decompose the polyoxometallic complex into oxide which forms pillars.

Fe₂O₃ pillared interlayer clay (Fe₂O₃-PILC) can be prepared by ion exchange of smectite (especially montmorillonite) with iron cation containing compounds, such as solution of

any of the iron salts $\text{Fe}(\text{NO}_3)_3$, FeCl_3 , $\text{Fe}(\text{ClO}_4)_3$, $\text{Fe}_2(\text{C}_2\text{O}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$ and iron organometallic compounds.

It has been reported in the literature that the most stable Fe_2O_3 -PILC is prepared by intercalating with an aqueous solution of trinuclear acetato hydroxyl-iron(III) nitrate, $[\text{Fe}_3(\text{OCOCH}_3)_7\text{OH}\cdot 2\text{N}_2\text{ONO}_3]$. Therefore, the above iron acetate was chosen as a first candidate for Fe_2O_3 -PILC preparation.

A. Preparation of Trinuclear Acetato Hydroxyl-Iron(III) Nitrate

One hundred grams of iron nitrate, $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (Strem Chemical, Inc.) was dissolved in 50 ml ethanol (Fisher Scientific Co.). The solution was stirred until iron nitrate was completely dissolved. 140 ml of anhydrous acetic acid (99.9%, J.T. Baker Inc.) was added to the stirred solution. A very dark solution was observed as soon as the acetic acid solution was added. The solution was stirred 5 more minutes and then was kept in an ice bath for precipitation. The resulting precipitation or crystalline (trinuclear acetato hydroxyl-iron nitrate) was collected by vacuum filtration or heated on a hot plate to evaporate ethanol and NHO_3 .

The collected precipitate was used as the pillaring agent without further purification.

B. Preparation of Fe_2O_3 -PILC

The collected trinuclear acetato hydroxyl-iron(III) nitrate crystal was dissolved in two liters distilled water. 20 grams of bentonite (Fisher Scientific) was added into the stirred solution. After reacting (ion exchanging) for at least four hours, the suspension solution was kept still to separate clay from the solution. The prepared sample was first dried at 120°C for 24 hours, the crashed and sieved to collect the desired fractions. The sample was further heated to 400°C at a rate of $2^\circ\text{C}/\text{min}$. in a tabular reactor and was kept at the temperature for a period of at least 12 hours.

C. Chemical Composition Analysis

To precisely and accurately analyze the chemical constitutions of the clay and the prepared pillared clay, inductive coupled plasma spectrometric analysis (ICP) was performed in this work. (This was done in the Chemistry Department.) The sample must be first dissolved into a solution. Because of the existence of sodium in the clay sample, instead of using the standard procedure whereby the sample mineral is fused with Na_2CO_3 followed by dissolving in water, a now more widely used method is adopted where the clay is fused with lithium borates followed by dissolution. It is found that this is an excellent technique for bringing silicates into solution for ICP or atomic absorption analysis. The chemical compositions of the clay and the pillared clay were analyzed by using a model Thermo Jarrel Ash 61 ICAP analyzer. The clay sample (0.1000 gram) was mixed with 0.600 g total of lithium metaborate and lithium tetraborate (1:2 ratio and fused) in 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% HNO_3 solution. When the fluxed bead completely dissolved, the solution was filtered to remove graphite fiber impurity that came from the crucible.

The ICP analysis results are shown in Table 1. The water contents in Table 1 were analyzed separately by thermo-gravimetric analysis (TGA) by heating the samples in helium to 400°C and measuring the weight loss.

Table 1 shows that after ion exchange/pillaring reaction, the compositions of the cations, Na^+ , K^+ , Ca^{2+} and Mg^{2+} all decreased. However, the most significant change in the synthesized sample was the increase in the iron oxide content from 3.66% to about 10%.

Task 3. SCR Activity of Fe_2O_3 -PILC

The SCR activity of Fe_2O_3 -PILC was measured via NO_x conversion expressed by

$$\text{NO Conversion} = X = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}}$$

The rate constant was calculated assuming plug flow reactor. The catalyst activity was expressed by a first order rate constant (k) with respect to NO,

$$\text{Rate} = -\frac{1}{W} \frac{d[\text{NO}]}{dt} = k[\text{NO}]^1[\text{NH}_3]^0$$

where W is the weight of the catalyst. Assuming plug flow, the rate constant (k) can be calculated by:

$$k = \frac{F_0}{[\text{NO}_0]W} \ln(1 - X)$$

where F_0 is the inlet molar flow rate of NO, $[\text{NO}]_0$ is the inlet molar concentration of NO, and x is the fractional NO conversion.

SCR rates on the Fe_2O_3 -PILC catalyst were measured at 4 temperatures and under the following conditions:

- With H_2O and SO_2 (indicated by + H_2O , + SO_2)
- With H_2O and without SO_2 (indicated by + H_2O , - SO_2)
- Without H_2O and SO_2 (indicated by - H_2O , - SO_2)

In order to obtain accurate reading from the NO_x chemiluminescent analyzer, the NO_x conversion was kept low by using a very high space velocity. (Here the space velocity is expressed by gas hourly space velocity, i.e., number of reactor volumes of reactant gas at the ambient conditions processed per hour.) The experimental results are shown in Figures 2 and 3. The space velocity was $30,000 \text{ hr}^{-1}$, which was a very high space velocity. The rate constant at 400°C was 22.5 ml/g/s under $\text{SO}_2/\text{H}_2\text{O}$ free conditions (Figure 3). This rate constant was quite high; the rate constant for the commercial $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ catalyst is about 40 ml/g/s . It is quite encouraging that the first Fe_2O_3 -PILC sample showed this level of activity. However, like the commercial catalyst, H_2O has a negative effect while the effect of SO_2 is small. The lack of SO_2 effect is encouraging.

Table 1. ICP Chemical Composition Analyses for Clay and Pillared Clay (Weight %)

	Montmorillonite	Fe₂O₃-PILC
SiO₂	60.32	59.19
Al₂O₃	19.14	19.63
Fe₂O₃	3.66	9.55
TiO₂	0.16	0.18
CaO	1.41	0.47
MgO	2.35	2.06
Na₂O	2.88	0.65
K₂O	0.51	0.34
H₂O	8.50	3.06
Total	98.93	95.13

Figure 1. Schematic diagram of experimental SCR reactor: (A) chemiluminescent NO/NO_x analyzer for Reactor 1 or GC/MS analyses for Reactor 2; (B) NH_3 scrubber; (C) water vapor generator; (D) SCR reactor; (E) temperature program controller.

Figure 2. NO conversion on Fe₂O₃-PILC. Reaction conditions: NO = NH₃ = 1,000 ppm, SO₂ = 1,000 ppm, O₂ = 2%, H₂O = 8% (when used), N₂ = balance, total flow rate = 500 ml/min., catalyst = 0.4 gram.

Figure 3. First order rate constant of NO conversion on Fe_2O_3 -PILC. Reaction conditions: $\text{NO} = \text{NH}_3 = 1,000$ ppm, $\text{SO}_2 = 1,000$ ppm, $\text{O}_2 = 2\%$, $\text{H}_2\text{O} = 8\%$ (when used), $\text{N}_2 = \text{balance}$, total flow rate = 500 ml/min., catalyst = 0.4 gram.

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