

DOE/PC/93217-T8

QUARTERLY TECHNICAL PROGRESS REPORT

Superior Catalysts for Selective Catalytic Reduction of Nitric Oxide

July 1, 1995 - September 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 last quarter, we studied selective catalytic reduction (SCR) of NO with ethylene over Cu²⁺-exchanged pillared clay and the important effect of O₂ concentration. Also, the mechanism of the reaction was discussed. Details are discussed below.

Experimental Section:

The syntheses of the three catalysts are first described.

Synthesis of Cu²⁺-Exchanged Al₂O₃-Pillared Laponite. Al₂O₃-delaminated laponite used in the synthesis was obtained from Laporte Industries, Ltd. Prior to use, it was suspended as 1% (by weight) slurry and washed with dilute NH₄NO₃ solution to remove impurities and existing metal ions. After filtration, the residue was dried at 110°C in air. Then it was again suspended as 1% (by weight) slurry. 10 ml of 0.10M Cu(NO₃)₂ solution was added to 100 ml of the above slurry, with constant stirring. The acidity of the mixture was then adjusted to pH = 5.5 by using ammonium hydroxide and nitric acid solutions. The mixture was then kept at 50°C for 6 h. Subsequently, the residue was thoroughly washed with distilled water 5 times. The obtained solid sample was first dried at 110°C in air for 24 h, then crushed and sieved to collect the desired sized fractions. The samples were further heated to 400°C in air, and were kept at this temperature for 12 h. After these pretreatments, the samples were ready for further experiments. The BET N₂ surface area for the delaminated Al₂O₃ pillared laponite was 384 m²/g, and that of the Cu²⁺ ion-exchanged form was 360 m²/g.

Cu²⁺ Exchanged TiO₂-Pillared Bentonite Clay. Cu²⁺ exchanged TiO₂ pillared bentonite clays were prepared by ion exchange of TiO₂-pillared clays with copper nitrate solution following the conventional ion exchange procedure. TiO₂-pillared clay was

prepared from a purified montmorillonite (bentonite) powder (from Fisher, with crystal sizes less than or equal to 2 μm) and titanium chloride (TiCl_4 , also from Fisher) following the procedure of Sterte (1986). One gram of the obtained TiO_2 -pillared clay was added to 100 ml of 0.02 M copper nitrate 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 detailed procedure has been described in our previous paper (Yang and Li, 1995). The same pretreatment as that for the Cu^{2+} -exchanged Al_2O_3 -pillared laponite was made before the samples were ready for catalytic activity experiments.

Cu^{2+} -Exchanged ZSM-5. The Cu^{2+} -exchanged ZSM-5 was prepared by mixing the ZSM-5 sample (kindly supplied by Exxon Company) with an aqueous solution of cupric nitrate. The silica/alumina ratio in the ZSM-5 was 30. Before ion exchange, the ZSM-5 was washed in 0.01 M NaNO_3 solution. After washing, 2 g of ZSM-5 was added to 100 ml of 0.01 M cupric nitrate aqueous solution, with constant stirring for 12 h. The sample was collected after the resulting suspension was filtered, washed, and dried at 110°C. The detailed procedure was described by Sato et al. (1991). The same pretreatment was also made before the samples were ready for catalytic experiments.

Apparatus and Gases Used. The SCR activity measurements were carried out in a fixed-bed quartz reactor. The reaction temperature was controlled by an Omega (CN-2010) programmable temperature controller. The catalyst was supported on a fritted support. The typical reactant gas composition is as follows: NO = 1,000 ppm; 1,000 ppm of ethylene; 0% - 4% of oxygen; 500 ppm of

SO₂ (when used); 5% of water vapor (when used), and balance of N₂. The total flowrate was 250 cm³/min (ambient conditions). The catalyst size fraction was 80 - 100 US mesh, and 0.5 g was used in a typical experiment. The premixed gases (0.7% NO in N₂, 1.04% ethylene in N₂ and 1.0% SO₂ in N₂) were supplied by Matheson Company. The NO concentration was continuously monitored by a chemiluminescent NO/NO_x analyzer (Thermo Electron Corporation, Model 10). Details of the apparatus system for the SCR reaction have been described elsewhere (Yang et al., 1992).

Results and Discussion.

Comparison of Activities of Cu²⁺-Exchanged Delaminated Al₂O₃-Pillared Clays, Cu²⁺-Exchanged TiO₂-Pillared Clays and Cu²⁺-Exchanged ZSM-5. Cu²⁺-exchanged ZSM-5 is a most active and most extensively studied catalyst for hydrocarbon SCR. We have recently reported first results on Cu²⁺-exchanged TiO₂-pillared clays and showed that they are more active (by two to four times) than Cu²⁺-exchanged ZSM-5 (Yang and Li, 1995). Figure 1 compares the results of three catalysts for SCR with C₂H₄ in O₂ - the two mentioned above and Cu²⁺-exchanged Al₂O₃ delaminated pillared laponite clay. These three catalysts were compared under identical reaction conditions. The results showed that at temperatures higher than 350°C, Cu²⁺-exchanged delaminated Al₂O₃-pillared laponite clay was much more active than the two other catalysts. The catalytic behavior for the SCR reaction of Cu²⁺-exchanged delaminated Al₂O₃-pillared laponite is unique in two ways; the peak temperature is higher (at ~550°C) and the activities are higher at above 350°C. This unique behavior is related to its pore structure and its surface acidity. These two aspects (pore structure and surface acidity) are discussed separately below.

Pore Structure of Delaminated Pillared Clay. Laponite is a synthetic hectorite with relatively small particle size (0.05 μm dimension), as compared with the size of natural hectorite or montmorillonite (2.0 μm dimension) (Olphen and Fripiat, 1979). The small particle size of laponite results in relatively more edge area than face area as compared to clays with larger sizes. Clays are known to flocculate in aqueous suspension by three different modes of association, i.e. edge-to-edge, edge-to-face, and face-to-face (Olphen, 1977). Clays exchanged with polyhydroxy metal cations also undergo association via these three modes.

The Al_2O_3 delaminated laponite was composed of micropores as well as a considerable amount of macropores, as shown by Pinnavaia et al. (1984). The edge-to-edge interactions of layers lead to the formation of macropores with dimensions larger than 3 nm. Some face-to-face aggregation also occurs that involves only 2-4 layers, which leads to the formation of micropores of dimensions 0.5-15 nm, as in laminated pillared clays. This short range stacking is not detected by x-ray diffraction, and thus a mixed laminated/delaminated structure is x-ray amorphous. The absence of distinct x-ray reflections in the XRD pattern of Cu^{2+} -exchanged Al_2O_3 -laponite (Figure 2A) indicated delamination of the sample.

In contrast, XRD of Cu^{2+} -exchanged TiO_2 -pillared clay (shown in Figure 2B) and Cu^{2+} -exchanged ZSM-5 (shown in Figure 2C) exhibit crystalline x-ray diffraction patterns. Both of these have only micropore structures (Yang and LI, 1995). Therefore, both macropores and micropores in Cu^{2+} -exchanged Al_2O_3 -delaminated laponite can readily allow hydrocarbon and nitric oxide molecules to reach the interior active sites. In addition, they have higher surface areas, that is, 384 m^2/g and 360 m^2/g for delaminated alumina-pillared laponite and its Cu^{2+} -exchanged form, respectively.

The peaking of NO conversion at a certain temperature for SCR is the result of two competing reactions; NO reduction by hydrocarbon, and oxidation of hydrocarbon that depletes the reductant. In addition, it is known that SCR reaction in molecular sieving catalysts is significantly limited by pore diffusion resistance (Cho, 1993; Li and Armor, 1994; Yang and Li, 1995). The diffusion rates of both reactant and product molecules may play a role in the overall rate. The temperature dependence is different for pore diffusion in macropores and in micropores. Diffusion in ZSM-5 (with channel dimension of the order of 5 Å) is an activated process, thus its temperature dependence is weaker than $\alpha T^{0.5}$ ($\alpha T^{0.5}$ being for Knudsen diffusion). Diffusion in macropores, as in the delaminated pillared clay, has a temperature dependence in the range αT to $T^{1.5}$. The stronger (or sharper) temperature dependence for diffusion in the delaminated clay will result in a higher peak temperature for the overall rate. The relationship is illustrated qualitatively in Figure 3. This is only a partial reason for the higher temperature peak for SCR in delaminated clay. Another possible reason, a chemical reason, is given in the discussion to follow.

Reaction Mechanism. Our data showed that Cu^{2+} -exchanged delaminated Al_2O_3 -pillared laponite is highly active. SCR activity was also measured for the Al_2O_3 -pillared laponite clay without Cu^{2+} exchange, and the sample with Cu^{2+} showed no activity. Cu^{2+} ions clearly play an important role in this reaction. Therefore, it is helpful to understand the location of Cu^{2+} ions in the Cu^{2+} -exchanged Al_2O_3 -pillared clay in order to gain insight into the reaction mechanism. The literature information on the actual location of metal ions in ion-exchanged pillared clays is scarce. It is generally thought that mobile metal ion species exist between the

clay layers to compensate the charges of the clay layers (Burch, 1988), and that the locations are different for different cations.

For cupric ion sites in the Cu^{2+} -exchanged alumina pillared clay, Kukkadapu and Kevan (1989), used ESR (Electron Spin Resonance) and ESEM (Electron Spin Echo Modulation) techniques to study the Cu^{2+} species and assigned the Cu^{2+} as a distorted octahedral species attached to the Al_{13} oligomeric pillar by displacement of water ligands. The basis of their assignment was that the observed ESR parameters were similar to that of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ chemisorbed on $-\text{Al}-\text{OH}$ groups of aluminum hydroxide, and most characteristic of distorted octahedral symmetric. Consequently, they indicated that Cu^{2+} ion was linked directly with four water molecules, two of which coordinated axially at a greater distance and the other two bonded equatorially at a shorter distance. The remaining two equatorial coordination positions were occupied by alumina pillar species.

A similar conclusion was reported recently by Bergaoui et al. (1995) by using adsorption isotherm and EPR techniques to study Cu^{2+} ion sites on both wet and dry Cu^{2+} alumina pillared saponite. They confirmed that Cu^{2+} was directly bonded to surface (Al-O) groups on alumina pillars similar to Cu^{2+} chemisorbed on bulk alumina phases, and that there was no mobile ion-exchanged $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ present in the interlayer region.

Note that all these studies were performed at temperatures below 200°C . The Cu^{2+} -exchanged pillared laponite clays in our SCR reaction system were subjected to higher temperatures. The Cu^{2+} -exchanged alumina pillared laponite will undergo further dehydration and dehydroxylation at higher temperatures (than 200°C) and change its coordination state (Kukkadapu and Kevan, 1988). However, based

on their results, it is likely that the Cu^{2+} species in our SCR reaction system was directly bonded to alumina pillars as $\text{Cu}^{2+}\text{-O-Al}^{3+}$ on the catalyst rather than existing as a mobile species. We use the term "ion exchanged" to describe the catalyst due to the procedure by which the sample was prepared. Such a structure is favorable for dispersion of Cu^{2+} ions in Cu^{2+} -exchanged alumina pillared laponite. Furthermore, the high SCR activity was likely the result of such Cu^{2+} species that combined with the acidity of the pillared clay, as discussed below.

It is known that pillared clays have both Lewis and Brønsted acidities (He et al., 1988). The acidity of Cu^{2+} -exchanged alumina pillared laponite is shown by IR spectra of chemisorbed NH_3 , Figure 4. The IR spectra were measured for a self-supporting pellet of the sample after ammonia adsorption at 25°C , followed by helium purge at increasing temperatures. The strong absorption bands at 1640 cm^{-1} can be assigned to the bending mode of ammonia molecules coordinated on Lewis acid sites, whereas the band at 1455 cm^{-1} is the characteristic absorption due to ammonium ions on Brønsted acid sites (Kung and Kung (1985)). The intensities of both 1640 cm^{-1} and 1455 cm^{-1} bands decreased as temperature was increased. When the temperature was increased to 410°C , the intensity of the 1455 cm^{-1} band nearly vanished and that of 1640 cm^{-1} band remained strong. This result indicates that Lewis acid sites were dominant in the Cu^{2+} -exchanged alumina pillared laponite at high temperatures. The result is in line with that of Yamanaka et al. (1988) and Min et al. (1988).

Based on the understanding of the structure and the acidity of the Cu^{2+} -exchanged delaminated Al_2O_3 -pillared laponite, it is clear that the support acidity and the metal ion (Cu^{2+}) redox property both play a significant role in the SCR reaction mechanism. It is

proposed that ethylene chemisorbs on the Lewis acid sites on the Cu^{2+} -exchanged alumina pillared laponite. The ethylene is activated and forms oxygenated species in the presence of oxygen, since it is known that alkenes complex with alumina by Al^{3+} - O^{2-} ionic pairs as identified by IR spectroscopy (Gordymova and Davydov, cited in Davydov, 1990). At the same time, NO adsorbs on the Cu^{2+} ion sites which are bonded to the alumina pillars. The obtained oxygenated hydrocarbon intermediates and the adjacent chemisorbed NO further react to form nitrogen-containing hydrocarbon-oxygenated intermediates on the conjugated Al-O-Cu sites. These intermediates further decompose into nitrogen and carbon dioxide. The activity of the oxygenated hydrocarbon intermediate is related to the acidity, and the Cu^{2+} ion redox property is responsible for the activity of the adsorbed NO. Both the acidity and the Cu^{2+} ion redox property are important for the overall activity. Since Cu^{2+} ions are anchored on the alumina pillars in the Cu^{2+} -exchanged alumina pillared laponite, these two factors combine well to yield the high SCR activity. The structure of Cu^{2+} anchored on the alumina pillars are likely the Lewis acid sites that are needed for the reaction (Shelef, 1995). The importance of the support in the SCR reaction has been noted by Cho (1995) and Shelef (1995).

Now we return to the experimental data. Increasing the reaction temperature resulted in a slight decrease in Lewis acidity. The Lewis acidity still remained high enough at the SCR reaction temperatures as shown in Figure 4. Meanwhile, increasing temperature also increased the activity of the oxygenated hydrocarbon intermediates on the Lewis sites. Thus, at high temperatures the oxygenated hydrocarbon intermediates readily reacted with the chemisorbed NO species on adjacent Cu^{2+} ion sites. Oxygen was necessary (as will be discussed shortly) in the reaction. However, significant ethylene oxidation occurred on the surface at

still higher temperatures that decreased the SCR rates, as already discussed.

Effect of O₂ on SCR Activity Over Cu²⁺ Ion Exchanged Al₂O₃-Pillared Laponite. It is known that oxygen is important in SCR reactions both by hydrocarbon (e.g. over Cu²⁺ ZSM-5, Iwamoto, 1990) and by NH₃ (i.e., over V₂O₅/TiO₂, Bosch and Janssen, 1988). The effect of O₂ on SCR by C₂H₄ over Cu²⁺-exchanged Al₂O₃-pillared laponite was studied, and the results are shown in Figure 5. Figure 5 shows NO conversion as a function of oxygen concentration over Cu²⁺-exchanged Al₂O₃-pillared laponite at various temperatures. In the absence of oxygen, no or little activity was seen, as shown in Figure 5. At all reaction temperatures studied, NO conversion increased significantly with oxygen concentration, up to 2% O₂, followed by a slight decrease at 4% O₂.

Figure 5 also shows the fact of shifting peak temperature for the reaction with O₂ concentration. For example, the temperature for the peak activity at 2% O₂ was 550°C, whereas it shifted to 450°C at 4% O₂. This was the direct result of C₂H₄ oxidation that was more severe at 4% O₂. Similar O₂ effects were reported recently by Cho (1995) using transient techniques for SCR of NO by ethylene over Cu-ZSM-5. The O₂ effect is clearly important in applications for design for optimal operation.

Figure Captions:

Figure 1. SCR activity over (A) Cu^{2+} -exchanged delaminated Al_2O_3 -pillared laponite, (B) Cu^{2+} -exchanged TiO_2 -pillared bentonite, and (C) Cu^{2+} -exchanged ZSM-5. $\text{NO} = 1,000$ ppm, $\text{C}_2\text{H}_4 = 1,000$ ppm, $\text{O}_2 = 2\%$, catalyst = 0.5 g, $\text{N}_2 = \text{balance}$, total flowrate = 250 cc/min.

Figure 2. XRD spectra at room temperature of (A) Cu^{2+} -ion exchanged Al_2O_3 -pillared laponite (B) Cu^{2+} -ion exchanged TiO_2 -pillared bentonite (C) Cu^{2+} -exchanged ZSM-5.

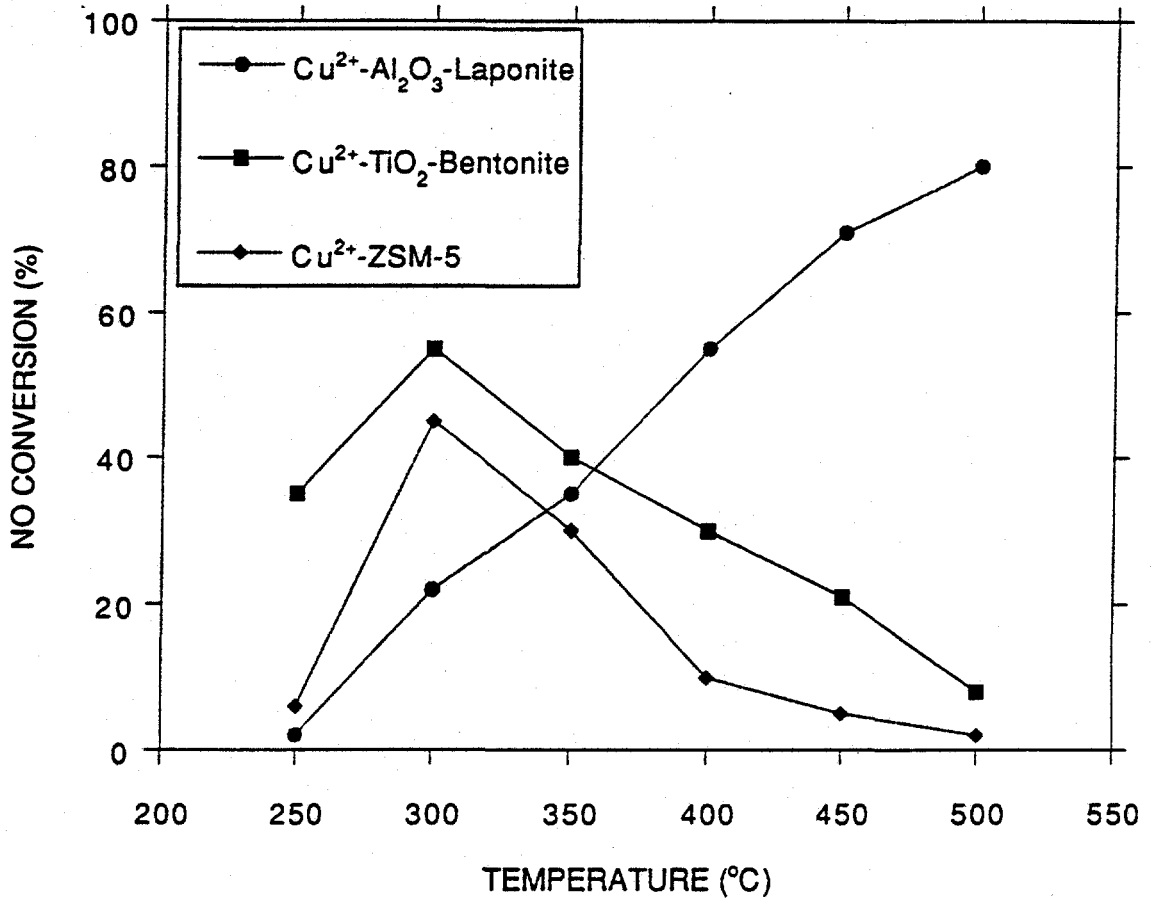
Figure 3. Temperature peak in NO conversion is the result of chemical rate and pore diffusion rate (both increase with T) and hydrocarbon oxidation (to decrease NO conversion at high T). Pore diffusion in macropores in delaminated pillared clay has a higher T dependence than that in micropores in laminated pillared clay, hence resulting in a higher peak temperature for NO conversion.

Figure 4. FT - IR spectra of ammonia absorption at 25°C on Cu^{2+} -exchanged alumina-pillared laponite followed by helium purge at (A) 25°C, (B) 200°C, (C) 300°C, (D) 350°C, (E) 410°C.

Figure 5. Oxygen effect on SCR activity over Cu^{2+} -ion exchanged Al_2O_3 -pillared laponite. Reaction conditions: $\text{NO} = 1,000$ ppm, $\text{C}_2\text{H}_4 = 1,000$ ppm, $\text{O}_2 = 0\%-4\%$, catalyst = 0.5 g, $\text{N}_2 = \text{balance}$, total flowrate = 250 cc/min.

Figure 6. Poisoning effect of H_2O and SO_2 on Cu^{2+} -exchanged Al_2O_3 -pillared laponite for the SCR of NO by ethylene. Reaction conditions: $\text{NO} = 1,000$ ppm, $\text{C}_2\text{H}_4 = 1000$ ppm, $\text{O}_2 = 2\%$, $\text{SO}_2 = 500$ ppm (when used), $\text{H}_2\text{O} = 5\%$ (when used), $\text{N}_2 = \text{balance}$, catalyst = 0.5 g and total flowrate = 250 cc/min.

Figure 1. SCR Activity Over Cu^{2+} -Ion Exchanged Al_2O_3 Pillared Laponite



U²¹ exchanged alumina pillared layer

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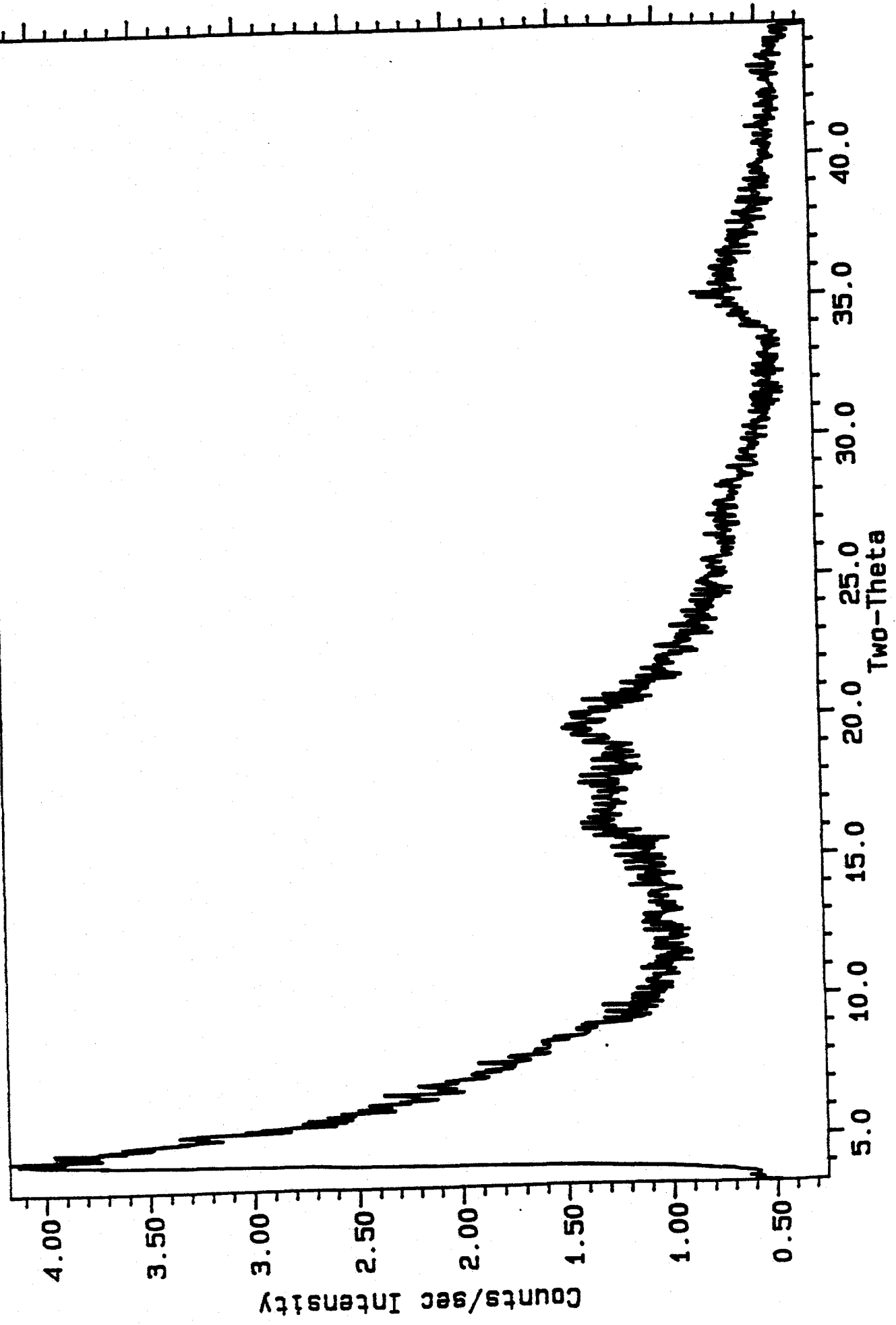


Fig 2 A

Siemens Analytical X-Ray Instruments Inc. chen53

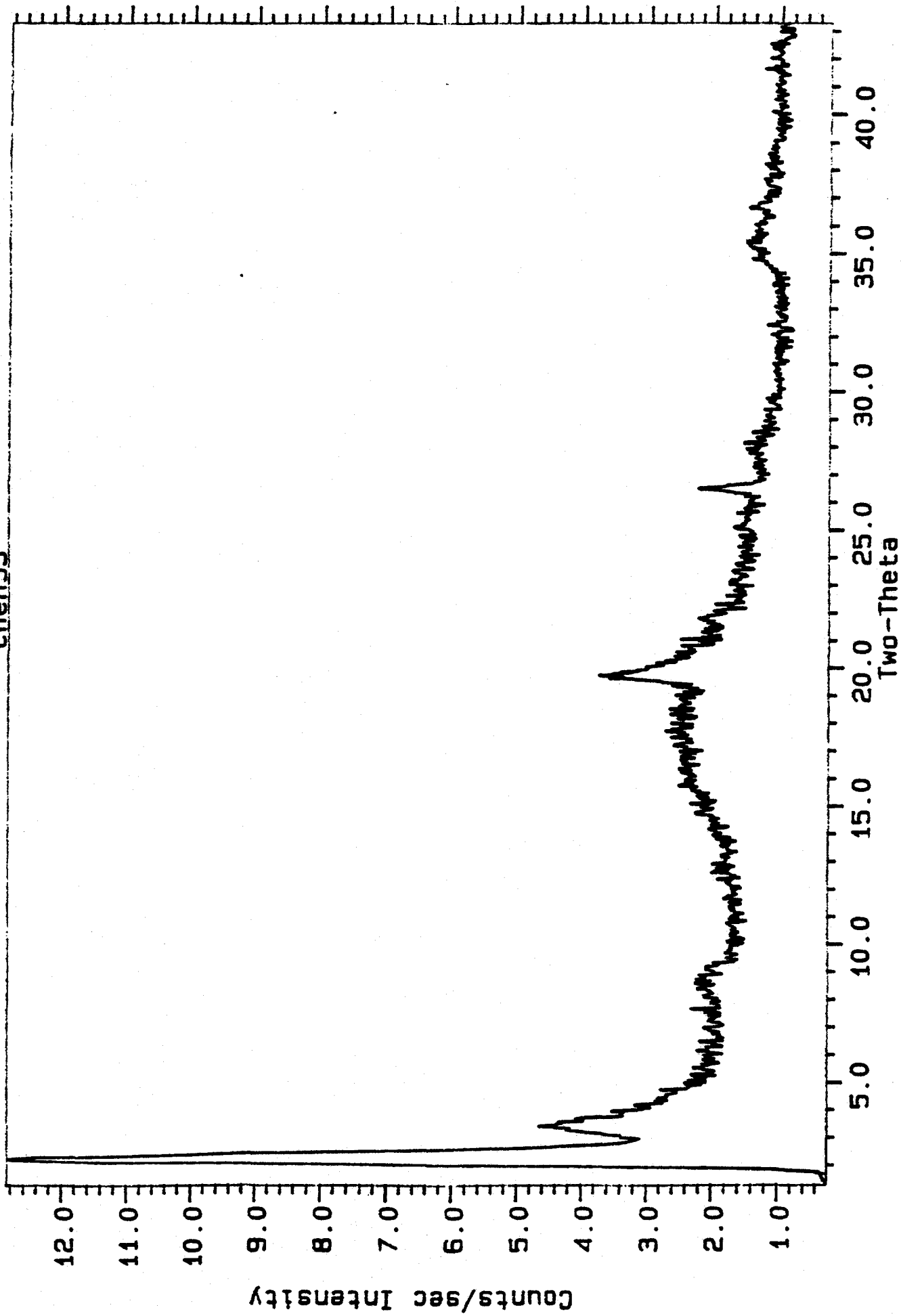


Fig. 2 B

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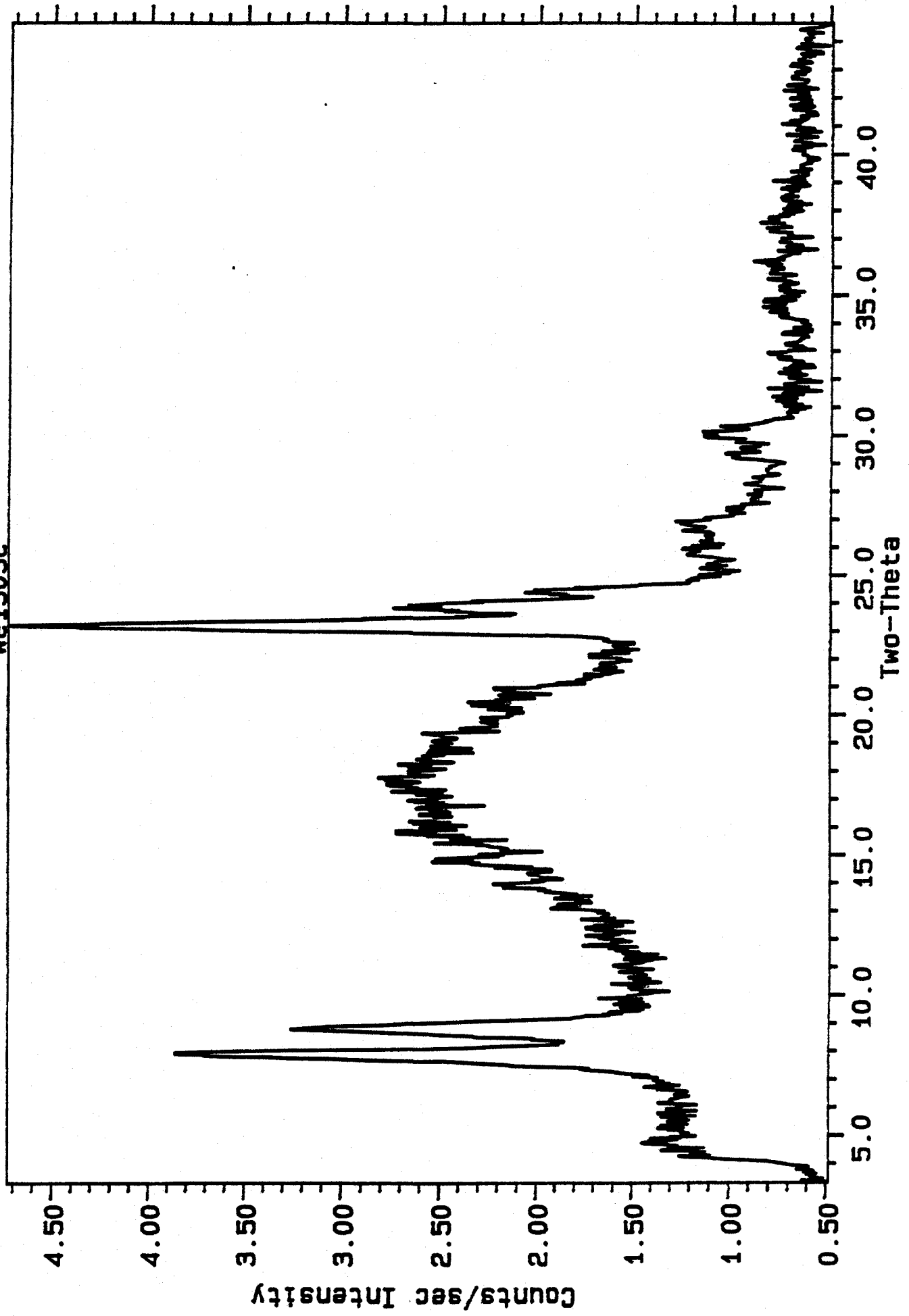


Fig 2c

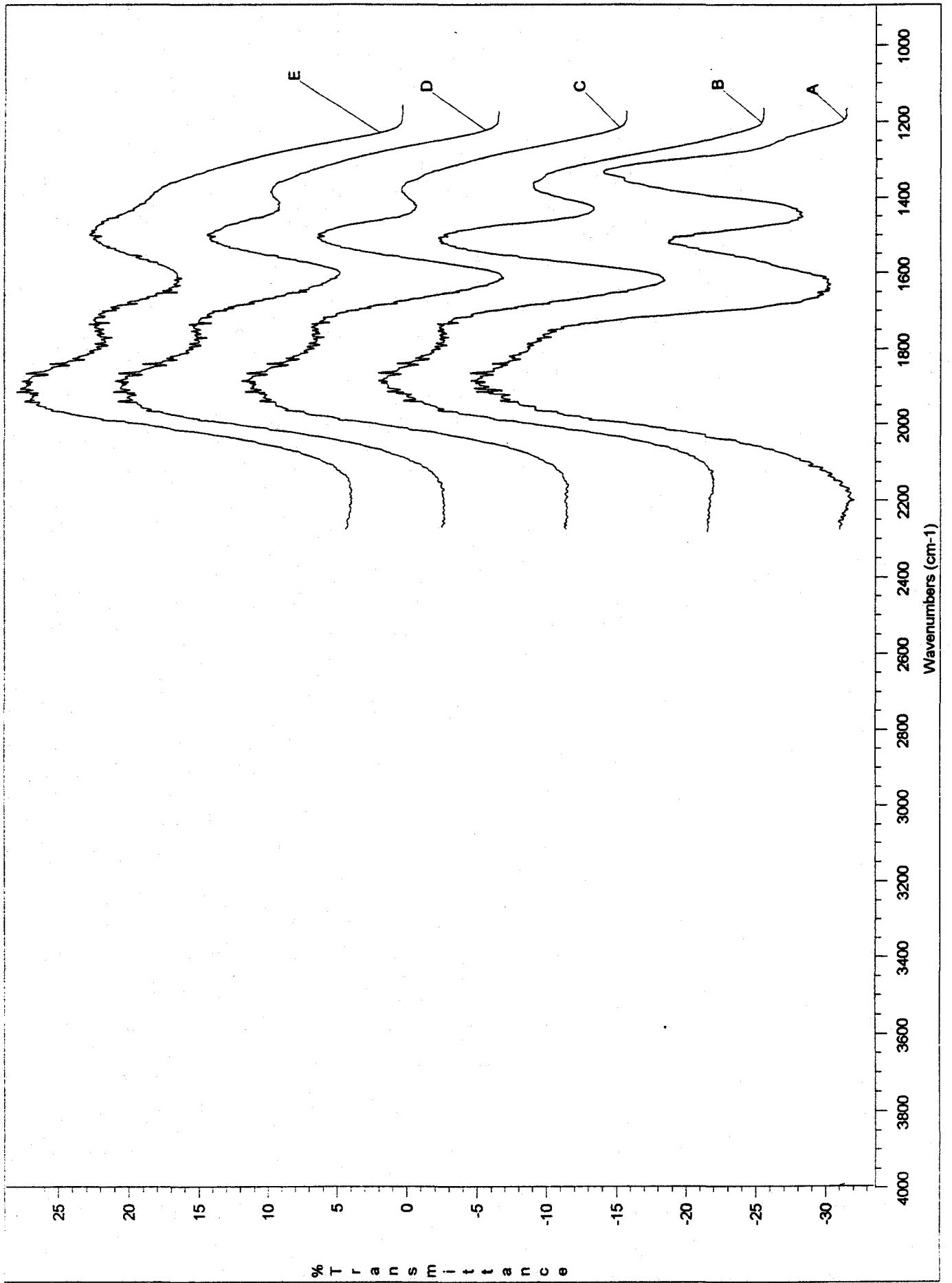


Figure 4. O₂ Effect On SCR Activity Over Cu²⁺-Ion Exchanged Al₂O₃ Pillared Laponite

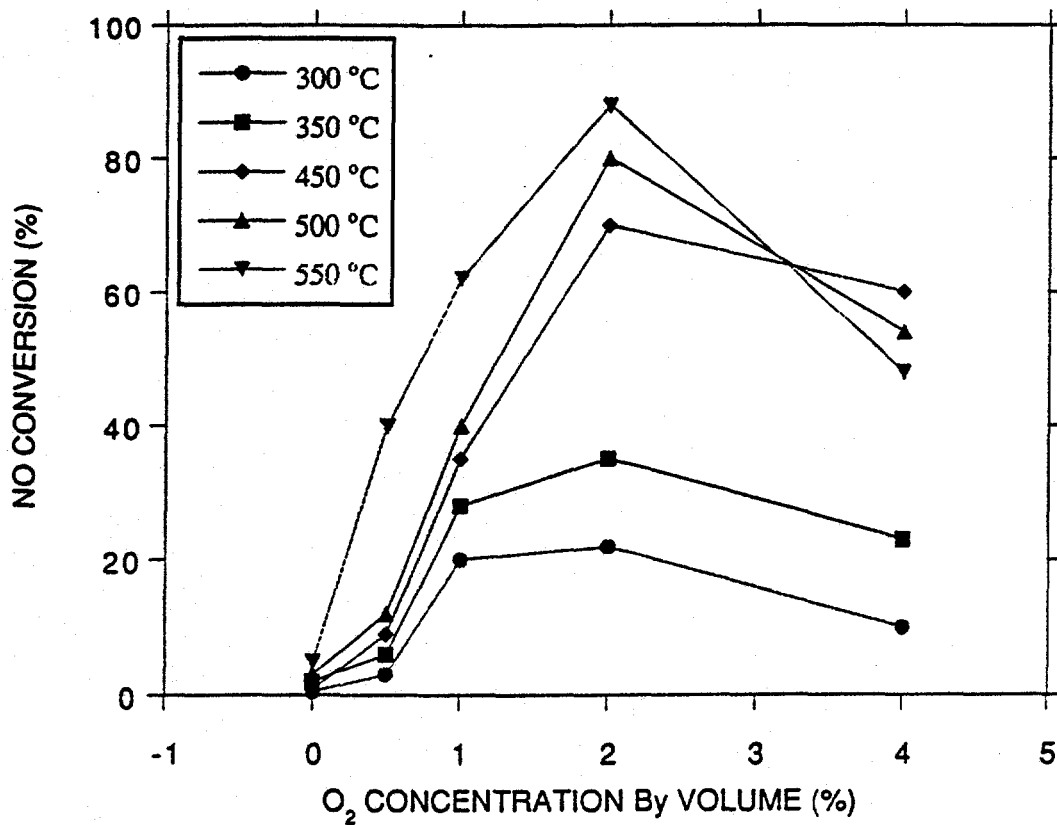


Figure 5, The Poisoning Effect of H₂O And SO₂

