Analytical Characterization of Catalyst Structure and Product Distribution

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I. INTRODUCTION

The objectives of our program are to characterize various catalysts used in the C-1 Chemistry reactions in order to determine their structural and electronic properties relevant to catalysis. The experimental techniques employed include x-ray diffraction (XRD), electron spin resonance (ESR) spectroscopy, magnetometry, thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). Some catalysts were synthesized in our laboratory (nanoparticles of CuO and Si-doped ferrihydrites, FHYD) while others were obtained from the research groups of Huffman et al (Kentucky), Wender et al (Pittsburgh) and Eyring et al (Utah). In this brief report, a summary of the major findings from this research carried out during the past one year is given. A more detailed account is available in the publications listed at the end of the report.

II. SUMMARY OF RESULTS

A. Structure, properties and roles of the different constituents in $Pt/WO_x/ZrO_2$ catalysts:

Platinum-promoted tungstated zirconia catalysts ($Pt_{0.5}/WO_x/ZrO_2$) have been used by Wender et al in the hydroisomerization of long-chain linear alkanes since they provide good stability and selectivity. However, a number of questions had remained unresolved which our recent studies have clarified. First, ZrO_2 exists in both the tetragonal and monoclinic forms. However, the exact role of the two phases was not clear. Our studies have shown that it is the tetragonal phase of ZrO_2 which supports the WO_x species and that WO_x is highly dispersed in the catalyst up to 600°C since no diffraction peaks due to crystalline WO_3 are observed (Fig. 1). Above 700°C, crystalline peaks due to WO_3 begin to appear, along with the conversion of tetragonal ZrO_2 to monoclinic ZrO_2 (Fig. 1). At 1000°C, WO_3 is crystallized and the tetragonal ZrO_2 is absent. These observations along with other supporting data reported in Publication #1 establishes the correlation of dispersed WO_x with tetragonal ZrO_2. These observations also show that the catalyst becomes unstable above 700°C.

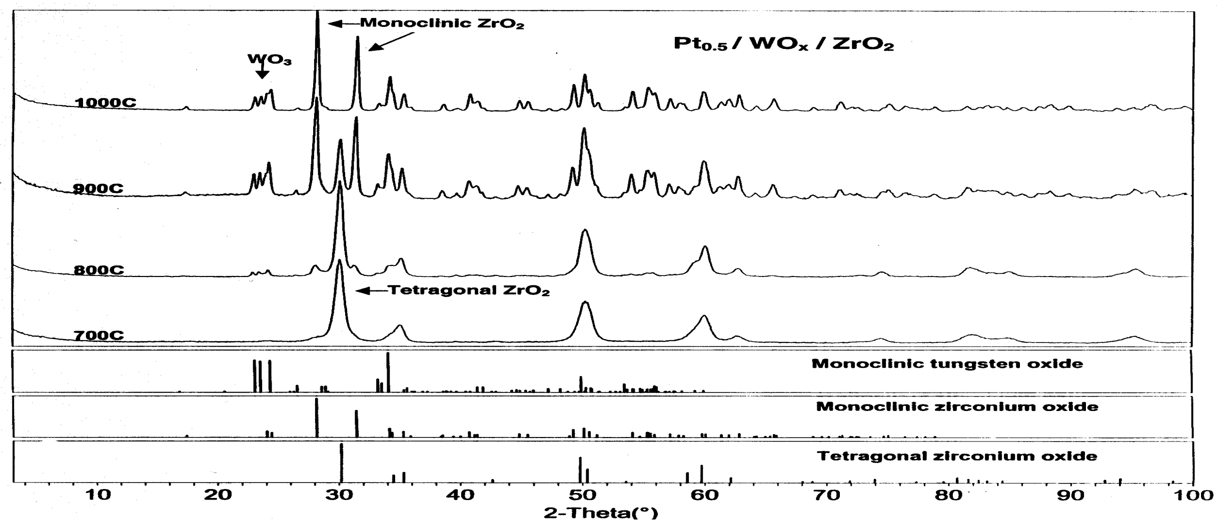

Fig. 1: Changes in X-ray diffractogram of $Pt/WO_3/ZrO_2$ upon annealing at different temperatures.

The second important question is the nature of electronic state of Pt. Since the catalysts contained only 0.5 wt.% of Pt, no information on the state of Pt could be determined from x-ray diffraction. However we used temperature-dependent magnetic measurements to show that in fresh $Pt/WO_x/ZrO_2$ catalysts, Pt exists in the form of Pt-oxospecies and that under the hydroisomerization conditions, these Pt-oxides are reduced to metallic Pt. Also, co-impregnation of tungsten and platinum to ZrO_2 support appears more favorable for the formation of Pt oxo-species. Details are given in Publication #1.

B. Structural and electronic properties of doped-ferrihydrite catalysts

Nanoparticles of ferrihydrites $(FeOOH)\cdot nH_2O$ with particle size of about 4 nm and ferrihydrites (FHYD) doped with Si, Al, Ni, Mo, Ir are under study by the Kentucky group (Huffman et al) in a number of C-1 Chemistry reactions. During the past year, we have made enormous progress in understanding the structural and electronic properties of the undoped and doped ferrihydrites, by employing the techniques of x-ray and neutron diffraction, magnetometry and ESR spectroscopy (Publications #2, 3, 4 and 5). Neutron diffraction studies showed that the two-line undoped FHYD order antiferromagnetically at $T_N \simeq 350$ K. The magnetic measurements show that each particle carries a magnetic moment $\mu_p \simeq 300\ \mu_B$, corresponding to 50 Fe^{3+} uncompensated ions, each with a magnetic moment of about 6 μ_B. Doping of FHYD with Si (viz. Si_x/FHYD), for x up to 0.5 have shown that μ_p decreases rapidly as x increases for initially dopings (Fig. 2). A detailed analysis on the magnetic properties of Si_x/FHYD for x = 0, 0.02, 0.05, 0.10, 0.15, 0.20, 0.26, 0.40 and 0.50 has been carried out (Publication #5) and the following picture has emerged from these studies.

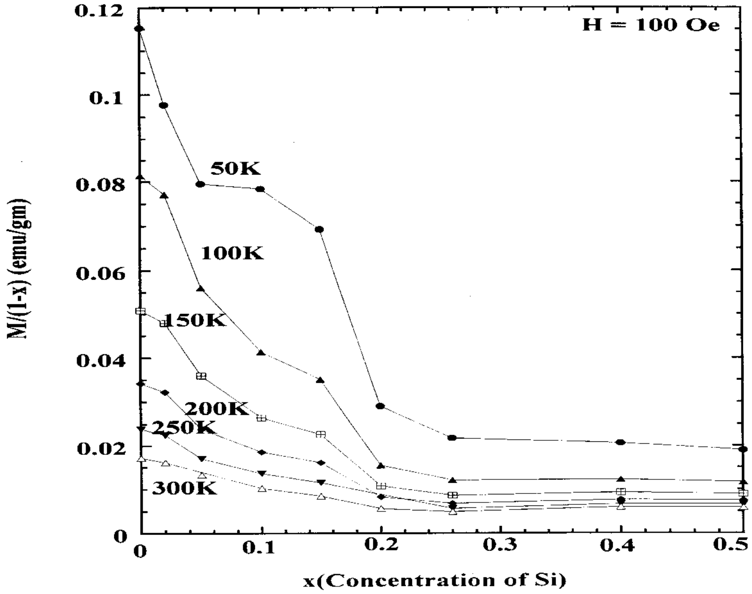

Fig. 2: Plot showing changes in the magnetization of Si_x/FHYD with x at different temperatures

For a particle of diameter $\simeq$ 40 Å, there are about 2500 Fe^{3+} spins out of which about 500 are in a surface shell of thickness $\simeq$ 1.5 Å. However, only about 50 ($\sqrt{2500} = 50$) Fe^{3+} spins on the surface are magnetically uncompensated which give the measured moment of 300 μ_B/particle. Since Si favors the tetrahedral bonding of the surface spins, initial doping by Si preferentially replaces the surface Fe^{3+} ions, leading to a dramatic decrease in the magnetization M (Fig. 2). When all the 500 surface Fe^{3+} are replaced by Si at x = 500/2500 = 0.2, additional doping by Si begins to replace the Fe^{3+} ions in the core of the nanoparticles, with the resulting increase in the amorphous nature of the particles. This is quite evident in the x-ray diffraction patterns where shift and broadening of the lines is observed for the higher x-values (Fig. 3).

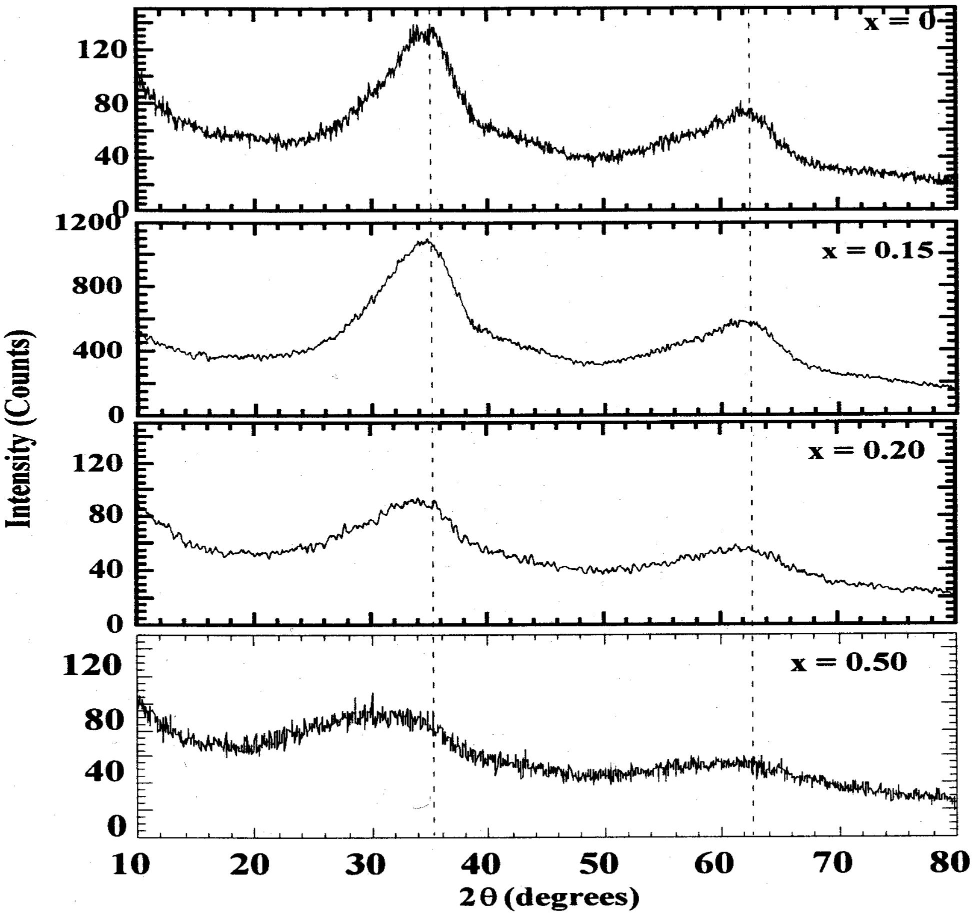

Fig. 3: X-ray diffractograms of Six/FHYD samples

Magnetic measurements on samples doped with 5% Ni, Mo, Ir and Al show that except for the case of Ni, magnetization M decreases upon doping with Mo, Ir and Al, similar to the case of Si doping. This is understandable since except for Ni all the other dopants are non-magnetic. For the Ni-doped FHYD, the magnetization increases. In ESR spectroscopy, the ESR line is broadened by different amounts by the different dopants (Fig. 4) except for Ni which narrows the line. For Si_x/FHYD, there is a strong correlation between the intensity of ESR line and the measured magnetization (Fig. 5). These results clearly show that the ESR line is due to the magnetically uncompensated surface Fe^{3+} ions. A detailed quantitative analysis is in progress upon completion of which a paper on this work will be submitted for publication (Publication #8).

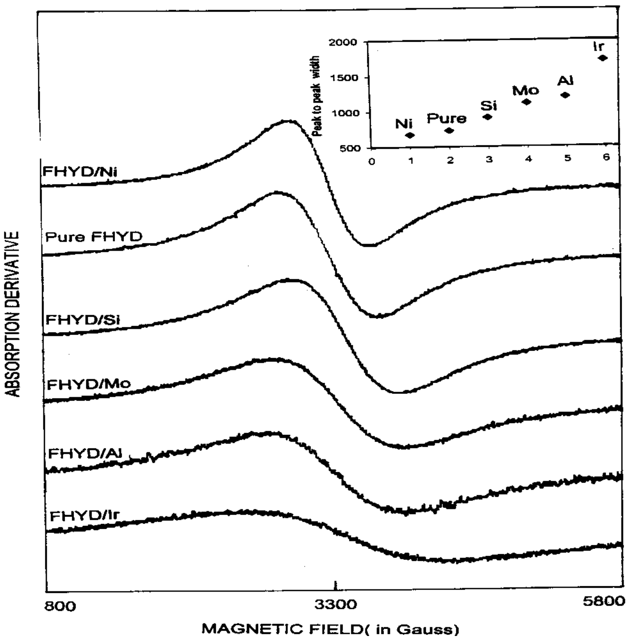

Fig. 4: Plot showing the effect of different dopants on the ESR spectrum of FHYD at 300K

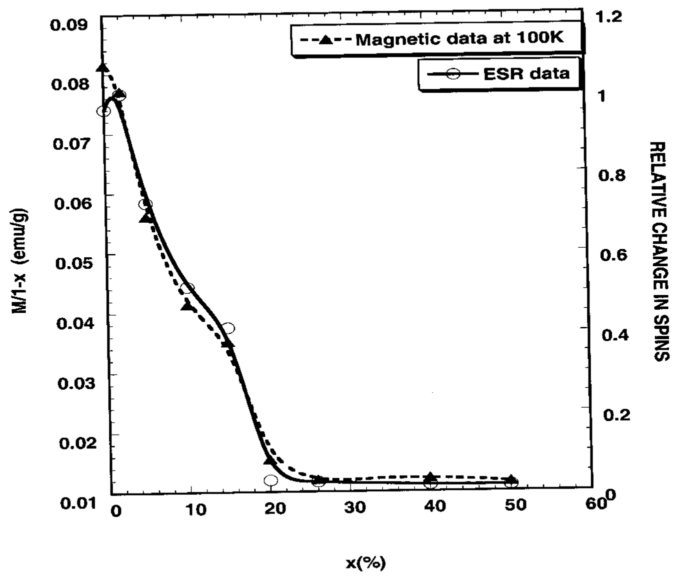

Fig. 5: Plot showing the correlation between ESR line intensity and magnetization of Si_X/FHYD

The above results have important implications for the catalytic properties of the doped FHYD nanoparticles. It is noted that catalysis usually involves unpaired electrons of a catalyst and the ESR signal and the magnetization are a measure of the density of the unpaired electrons. Therefore the changes observed in the ESR signal and magnetization upon doping provides a probe for the catalytic properties. Some of the samples investigated here were obtained from Huffman et al whereas most of the Si and Al doped FHYD were prepared in our laboratory. In the near future, we expect to receive some samples from Huffman et al which have been exposed to catalytic reactions. These samples will be similarly investigated to provide further insights into various catalytic processes. The results obtained so far show that the magnetically uncompensated surface spins for Fe^{3+} are likely to play the most important role in catalysis and that with appropriate dopants, the electronic and structural properties of FHYD can be manipulated.

Publications #7 and 8 on the properties of nanophase carbons provide important insights for catalysis since these carbons are often used as catalyst supports.

III. WORK IN PROGRESS

Other catalyst systems currently under investigation include $CuCl_2/PdCl_2$/carbon obtained from Eyring et al (Utah), and a number of Fe and Mo catalysts supported on Al_2O_3 obtained from Huffman et al (Kentucky). In addition, we have recently synthesized CuO nanoparticles in the size range of 6 to 30 nm as potential catalysts. X-ray diffraction studies on all these catalysts have been completed which have provided information on the crystalline components and their crystallite size. Magnetic and ESR studies are now in progress which are expected to be completed during the coming year. For the $CuCl_2/PdCl_2$/carbon catalyst, x-ray diffraction shows very high dispersion of $CuCl_2/PdCl_2$ on the carbon support. Magnetic and ESR measurements provide evidence of unpaired spins on Cu, with evidence for nanoparticle magnetism. More details on these results will be provided in future reports.

IV. PERSONNEL

Graduate assistant Paromita Roy completed her M.S. thesis in May, 2000 on the “Magnetic properties of Si-doped ferrihydrite nanoparticles”. A new student, Heidi Magnone, has joined the group recently. She has successfully synthesized the CuO nanoparticles with assistance from Dr. Alex Punnoose. Dr. Punnoose joined the group in October 1999 and he has the major responsibility for the experimental studies in this program. Dr. A. Manivannan, Research Assistant Professor, has made contributions in magnetic studies in the early stages of the Program and in the measurements of the particle sizes by TEM (Transmission Electron Microscopy). The TEM measurements were carried out at NIOSH (National Institute of Safety and Health) in Morgantown, with the kind assistance of Diana Schwegler-Barry. Others collaborators on the publications listed below include J. W. Lynn of NIST, a former research associate V. S. Babu, and Professor N. C. Giles at WVU, Prof. Wender at Pittsburgh and Professor Huffman at Kentucky.

V. PUBLICATIONS & PRESENTATIONS

1. Structure, properties and roles of the different constituents in $Pt/WO_x/ZrO_2$ catalysts, A. Punnoose, M. S. Seehra and I. Wender, Journal of Catalysis (submitted).
2. Neutron scattering and magnetic studies of ferrihydrite nanoparticles, M. S. Seehra, V. S. Babu, A. Manivannan and J. W. Lynn, Physical Review B 61, 3513-3518 (2000).
3. Hysteresis loop shifts in magnetic field cooled FeOOH nanoparticles, M. S. Seehra, P. Roy and A. Manivannan, Proc. Materials Research Soc. June 2000 (in press).
4. Influence of chemisorption on the magnetism of interacting ferrihydrite nanoparticles, M. S. Seehra, V. S. Babu, P. Roy and A. Manivannan, Cluster and Nanostructure Interfaces World Scientific, June 2000 (in press).
5. Effects of Si doping on the magnetism of ferrihydrite nanoparticles, P. Roy, A. Manivannan and M. S. Seehra, Physical Review B (submitted).
6. Interaction of oxygen with nanophase carbons investigated by electron spin resonance spectroscopy, A. Manivannan, A. Punnoose, and M. S. Seehra, Proc. Materials Research Soc., June 2000 (in press).
7. Microstructure, dangling bonds and impurities in activated carbons, A. Manivannan, M. Chirila, N. C. Giles and M. S. Seehra, Carbon 37, 1741-1747 (1999).
8. Correlation of ESR parameters and magnetization in doped ferrihydrite nanoparticles, A. Punnoose, M. S. Seehra and G. P. Huffman (manuscript near completion).
9. Synthesis and magnetic properties of CuO nanoparticles, A. Punnoose, H. Magnone and M. S. Seehra, paper presented at the 10th Annual Conference on Computational & Structural Materials, hosted by West Virginia University; manuscript for publication under preparation.