Analytical Characterization of Catalyst Structure and Product Distribution

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Objectives

Determination of reaction mechanisms in a catalytic reaction requires an understanding of the electronic and structural properties of the catalyst and catalyst support under reaction conditions and their relationship to product distribution. This information is essential in improving existing catalysts and designing new catalysts. To that end, our work under this task involves in-situ and ex-situ investigations of a number of catalysts using the techniques of x-ray diffraction (XRD), electron spin resonance (ESR) spectroscopy, SQUID magnetometry, and photoacoustic/FTIR spectroscopy. We are working with three research groups in CFFLS (Eyring et al at Utah, Wender et al at Pittsburgh, and Huffman et al at Kentucky) to obtain the relevant samples of catalysts and to coordinate our findings with their results of catalytic activity and product distributions. A brief summary of these results is given below, with details available in the cited publications.

Summary of the results

Catalysts for the production of diethyl carbonate:

Eyring et al at Utah are investigating the use of $CuCl_2/PdCl_2/AC$ (activated carbon) catalysts for the production of diethyl carbonate (DEC), an alternative to MTBE as a fuel additive. We have

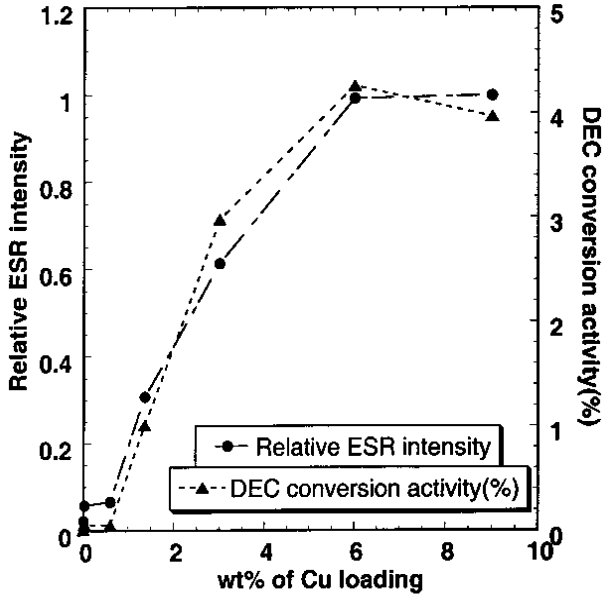

Fig. 1. Plot showing the variation of the ESR intensity of the Cu^{2+} surface species and the % DEC yield as a function of Cu loading.

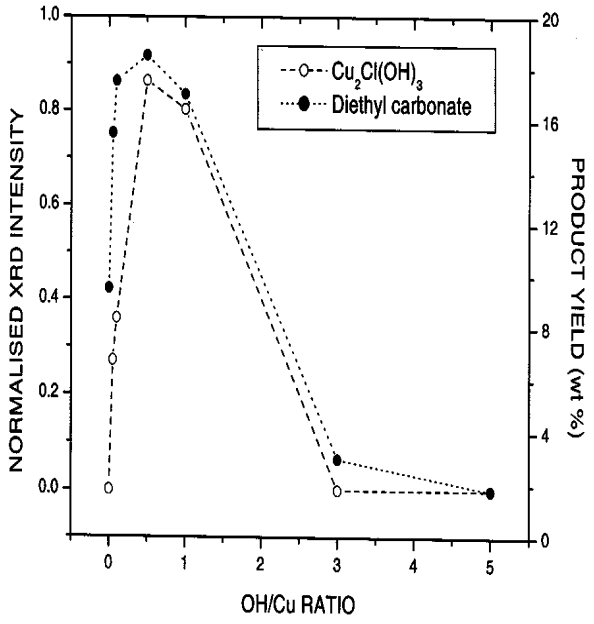

Fig. 2. Variations of the normalized XRD intensity of the paratacamite peak and the %DEC yield as a function of

investigated about 20 samples of these catalysts with different loadings of $CuCl_2$ and $PdCl_2$ and the catalysts pretreated with KOH, which have shown higher selectivity and yields for DEC. We have carried out room temperature XRD investigations and ESR spectroscopy at different temperatures (5 to 300K) on all these samples and coordinated our results with the % yield of DEC obtained by Eyring et al. Details of these results are planned to be published as two consecutive papers in the same journal [1,2]. The major conclusions from our studies [1] are summarized below.

For $CuCl_2$/AC samples, we have identified two types of Cu^{2+} ESR signals: Cu^{2+} attached to AC support and clusters of $CuCl_2$ nanoparticles. A close correlation between the % yield of DEC and the intensity of the Cu^{2+} species is observed (Fig. 1), although the % yield of DEC is only about 4% with 6 to 9 wt % Cu loading. The addition of $PdCl_2$ increases this yield to about 10%. The pretreatment of $PdCl_2/CuCl_2$/AC catalysts with KOH increases the yield to about 18% for x=OH/Cu = 1. In our XRD experiments, we see the presence of paratacamite, $Cu_2Cl(OH)_3$, whose XRD intensity correlates well with the % yield of DEC(Fig. 2). For x > 1, the activity drops dramatically (Fig. 2), with the simultaneous conversion of paratacamite to calumetite, $Cu(OH, Cl)_2$. $2H_2O$. Thus paratacamite appears to be more efficient than $CuCl_2$ and certainly calumetite for regeneration of Pd(0) to $PdCl_2$ to continue the reaction. Details of our finding are given in Ref. 1 whereas the details of the preparation of the catalysts and production of DEC are given in the paper by Dunn/Eyring et al[2]

$Pt_{0.5}/WO_x/ZrO_2$(PWZ) catalysts for the hydroisomerization of long-chain linear alkanes:

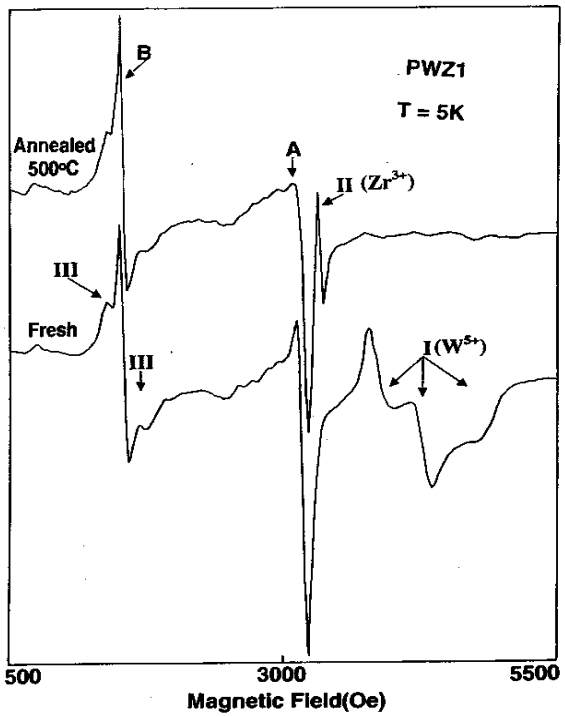

Fig. 3. ESR spectra of fresh and annealed PWZ catalyst showing the W^{5+} and Zr^{3+} signals.

Wender et al[3] at Pittsburgh have used these catalysts for the hydroisomerization of long chain linear alkanes since the PWZ catalysts provide good stability and selectivity. We have investigated the structural and electronic properties of the three constituents of the PWZ catalysts, viz Pt, WO_x and ZrO_2 using XRD, low temperature ESR spectroscopy, temperature variation of the magnetic susceptibility χ and thermogravimetric analysis (TGA). We have investigated the effects of preparation procedures, heat treatments to 1000C, tungsten loading and chemical reactions on the properties of the three constituents. Our results, a summary of which is given below, are detailed in two publications [4, 5]

ZrO_2 has two phases, monoclinic (m) and tetragonal (t). Our results show that with increasing WO_x loading, t-ZrO_2 phase is stabilized and under heat treatments, the gradual transformation of t-ZrO_2 to m-ZrO_2

above 700C is accompanied by crystallization of m-WO_3, which is not observable at lower annealing temperatures presumably due to its high dispersion and non-crystallinity. This leads us to propose that the dispersed WO_x species are associated with t-ZrO_2 only. From the magnitudes and the temperature variation of χ, we have inferred that Pt in fresh PWZ catalysts exists in oxidized form, α-PtO_2, Pt_3O_4 or their combination, depending upon their thermal history. These oxides are reduced to metallic Pt in the hydroisomerization reactions [4].

Additional important information on the PWZ catalysts has come from the recently reported ESR observation of the W^{5+} and Zr^{3+} states at low temperatures [5]. These signals are absent in samples without Pt suggesting that Pt has a role in changing the oxygen stoichiometry of WO_3 and ZrO_2 to generate the observed W^{5+} and Zr^{3+} states. In stoichiometric WO_3 and ZrO_2, the states W^{6+} and Zr^{2+} are diamagnetic and ESR silent. Also, studies on samples annealed at 500C showed possible electron transfer between the W^{5+} and Zr^{3+} states in which the concentration of one state increases at the expense of the other [5]. These studies have thus established electron transfer processes that are crucial in the catalytic activity of these catalysts.

3. Doped ferrihydrites and other nanoparticle systems:

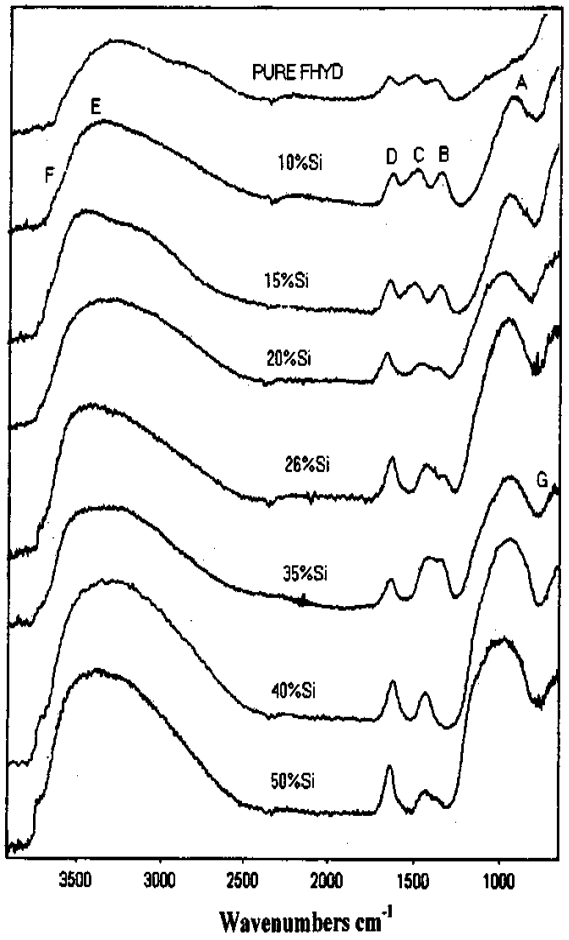

Fig. 4. PAS spectra of FHYD illustrating the effect of Si doping.

Nanoparticles of ferrihydrites, $FeOOH.nH_2O$, doped with Si, Al, Ni, Mo, Ir and transition metals supported on alumina are being tested by Huffman et al as catalysts for reforming reactions. We have made considerable progress in understanding the structural and electronic properties of these ferrihydrites (FHYD), as detailed in several publications [6 – 11]. A

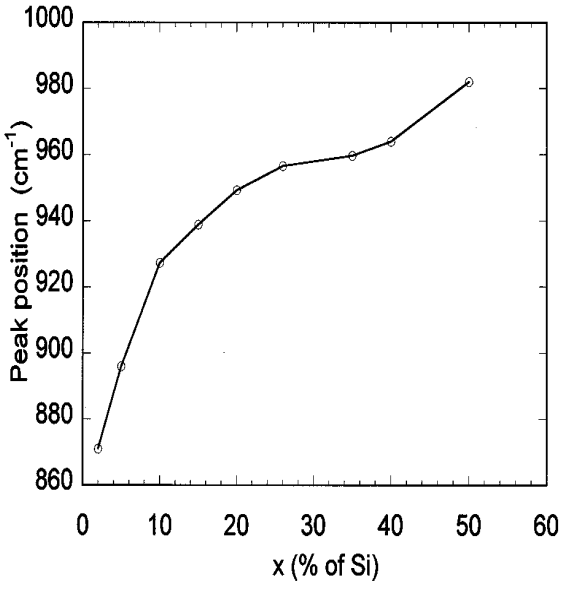

Fig. 5. Plot showing the shift of the peak A in Fig. 4 with Si doping.

major result is that Fe^{3+} spins on the surface of FHYD are nearly free and available for participation in catalytic reactions. Doping with Si, Al, Ni, Mo, and Ir affects both magnetic and structural properties (Fig. 4 and Fig. 5), but by different levels [8, 9, 11]. In the PAS/FTIR studies of the doped FHYD, the appearance of a new band A near 900 cm^{-1} (Fig. 4) and its shift with % of Si (Fig. 5) is assigned to Fe-O-Si species. Other changes observed with Si doping viz. the decrease in magnetization and increase in the ESR linewidth can also be explained if Si replaces Fe [9]. It is known that doping with Si also increases the useful stability range of FHYD from 200^{o}C to 400^{o}C, without seriously affecting its catalytic properties.

We have synthesized other nanoparticle systems such as CuO [12], Mn_5O_8 [13], $CoFe_2O_4$ and NiO by sol-gel and electrochemical methods for potential applications. The nanoparticles of CuO were found to have some catalytic activity by the Utah group [2]. In 6.6nm CuO particles, we have observed anomalous hysteresis loops at room temperature, a detailed paper on which is now ready for submission. Besides their catalytic potential, nanoparticles of CuO and NiO may have applications in the emerging field of spintronics.

Students

During 2000, two graduate students completed their M. S. theses: Paromita Roy on "Magnetic properties of Si-doped ferrihydrite nanoparticles" and Heidi Magnone on "Synthesis and characterization of metal oxide nanoparticles". Another student, Monica Constantinescu, is expected to complete her M. S. thesis in the next few months.

Future Plans

The implications of our recent ESR results in the PWZ catalysts [5] will be investigated for developing a suitable reaction mechanism in consultation with Dr. Wender. For the $PdCl_2/CuCl_2$/AC catalysts, the results are being organized in a manuscript and this paper will be submitted for publication in the near future. At the CFFLS meeting in August 2001, we will consult with the Utah group to plan followup experiments to improve the yield for DEC. For ferrihydrites, our recent breakthrough for the analysis of the magnetic data [10] will now allow us to complete our analysis of the magnetic data on doped ferrihydrites [13]. This work will be written up for publication in the next few months, in collaboration with Huffman et al [11]. Analysis of the structural data from FTIR and XRD on doped ferrihydrites (Fig. 4 and 5) is also near completion [14].

Cited publications

1. A. Punnoose, M. S. Seehra, B. C. Dunn and E. M. Eyring, "X-ray diffraction and ESR investigations of $PdCl_2/CuCl_2$/activated carbon catalysts used in the synthesis of diethyl carbonate" (to be submitted)

2. B. C. Dunn, E. M. Eyring et al " Production of diethyl carbonate from ethanol and CO over a heterogeneous catalyst" (to be submitted).

3. S. Zhang, Y. Zhang, J. W. Tierney, and I. Wender, "Hydroisomerization of normal hexadecane with platinum-promoted tungstate-modified zirconia catalysts". Appl. Catal. A, 4930, 1-17 (1999).

4. A. Punnoose, M. S. Seehra and I. Wender, "Structure, properties and roles of the different constituents in $Pt/WO_x/ZrO_2$ catalysts" to be published in Fuel Processing Technology.

5. A. Punnoose and M. S. Seehra, "ESR observation of W^{5+} and Zr^{3+} states in $Pt/WO_x/ZrO_2$ catalysts" submitted for publication to Catalysis Letters.

6. M. S. Seehra, V. S. Babu, A. Manivannan and J. W. Lynn, "Neutron scattering and magnetic studies in ferrihydrite nanoparticles" Phys. Rev. B 61, 3513-3518 (2000).

7. M. S. Seehra, P. Roy and A. Manivannan, "Hysteresis loop shifts in magnetic field cooled FeOOH nanoparticles", Mater. Res. Soc. Symp. Proc., 58, 511-516 (2000).

8. M. S. Seehra, V. S. Babu, P. Roy and A. Manivannan, in Cluster and Nanocluster Interfaces edited by Jena, Khanna and Rao (World Scientific Publishing Co., 2000) pp. 229 – 234.

9. M. S. Seehra, A. Punnoose, P. Roy, and A. Manivannan, "Effect of Si doping on the ESR properties of ferrihydrite nanoparticles", IEEE Transaction on Magnetics (in press).

10. M. S. Seehra and A. Punnoose, "Deviations from the Curie law variation of magnetic susceptibility in antiferromagnetic nanoparticles", Phys. Rev. B (in press).

11. A. Punnoose, M. S. Seehra, N. Shah and G. P. Huffman, "Magnetic properties of ferrihydrite nanoparticles doped with Ni, Mo and Ir", presented at the Eleventh Conference on Computational Research on Materials, Morgantown, 2001(to be submitted for publication).

12. A. Punnoose, H. Magnone, M. S. Seehra and J. Bonevich, "From bulk to nanoscale magnetism and exchange bias in CuO nanoparticles", Phys. Rev. B (to be submitted).

13. A. Punnoose, H. Magnone and M. S. Seehra, "Synthesis and antiferromagnetism of Mn_5O_s", IEEE Transaction on Magnetics (in press).

14. M. S. Seehra, A. Manivannan, A. Raman, A. Punnoose and P. Roy, "Structural properties of ferrihydrite nanoparticles determined by x-ray diffraction and FTIR spectroscopy", presented at the Eleventh Conference on Computational Research on Materials, Morgantown, 2001(to be submitted for publication).