PROGRESS REPORT**Grant DE-FG02-90 ER14130, Second Period – 1/31/92 to 1/31/93****ALUMINUM COORDINATION AND ACTIVE SITES ON ALUMINAS,
Y ZEOLITES AND PILLARED SILICATES****P.I.: J. J. Fripiat****I. OVERALL PROGRESS**

During this second period of activity, major progresses have been made in the following directions.

1. In continuing our effort to characterize the nature of the aluminum species responsible for Lewis acidity in zeolites and in aluminas by nuclear magnetic resonance (NMR) the following new information was obtained.

a) The non-framework aluminas Al_{NF} characteristic MAS NMR spectra in zeolites is analogous to those of aluminas obtained from a precursor whose crystal growth is inhibited to such an extent that nano-sized particles are formed.¹ These particles contain aluminum in three kinds of coordination; (Al^{IV}) four-fold, (Al^{VI}) six-fold and (Al^V) five-fold coordinated species, the latter being the most abundant one.

b) Using proton-cross polarized ^{27}Al MAS NMR,² it has been shown that the three kinds of aluminum are present in relative proportions different from the bulk composition on the surface of alumina covered with chemisorbed water or in the non-framework alumina species in steamed or dealuminated zeolites. The proton magnetization transfer to aluminum is maximum for contact times much shorter in aluminas than in the alumina debris in zeolites, suggesting shorter Al-H distance in the former than in the later.

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c) Single pulse MAS NMR spectra obtained for thoroughly dehydrated samples (450°C), kept in sealed ampules, show that the symmetries of Al^{V} and Al^{VI} non-framework species in zeolites and of the Al^{V} species in aluminas are strongly affected by dehydration. The resulting increase in the quadrupolar coupling constant renders these species undetectable. The Al^{IV} coordination in aluminas or zeolite non-framework aluminas suffers to a lesser extent. The reversibility of the dehydration process upon chemisorbing water shed light on the surface activity.

2. While numerous techniques have been successful for scaling the acid strength of Brönsted sites, the situation is not satisfactory at all for the Lewis acid sites (L). The simultaneous use of EPR and NMR probes and of the dehydrochlorination of 1,1,1-trichloroethane (followed by FTIR) complement each other to some extent in scaling the acid strength of Lewis acid sites in steamed or dealuminated zeolites, and in aluminas with reference to the sulfated derivatives of ZrO_2 , HfO_2 , Al_2O_3 and TiO_2 hyperacids. As shown previously, the hyperfine splitting of the EPR spectrum of the aniline radical cation or of the O_2^- superoxide ion is a measurement of the electron acceptor site.³⁻⁵ Other researchers have suggested the shielding of the ^{31}P nucleus and, accordingly, the shift of its resonance line in chemisorbed trimethylphosphine (TMP) for detecting Brönsted and Lewis sites.^{6,7} The dehydrochlorination of 1,1,1-trichloroethane (TCE) is known to be catalyzed by Lewis acid or base.^{8,9} The results obtained with TMP and TCE on the aforementioned catalysts have been correlated to the scale obtained with the EPR probes. For TMP not only the shifts, but also the ^{31}P longitudinal relaxation times, T_1 , of the various TMP surface adducts have been measured. One salient feature is the multiexponential behavior of the ^{31}P magnetization

decay indicating that lines assigned to TMP:L and to TMP:H^+ are, in fact, indicative of several types of environments. The initial rate of dehydrochlorination of TCE is extremely sensitive to the strength of the Lewis acid sites and it follows quite nicely the scale obtained by the other techniques.

3. The study of *n*-butene isomerization have been extended to the new aluminas obtained from nano-sized precursors. With respect to the previous results, it appears that the most active catalysts are those activated at temperatures where the Al^{V} coordination shell becomes unstable (700 C). This observation correlates well with the activity obtained from the initial rate of dehydrochlorination of TCE (see item 2).

Another model reaction is presently studied for zeolites. It has been generally suggested that xylene isomerization proceeds through ring protonation and the 1,2 shift of one methyl group, and that the disproportionation passes through a diarylmethane type intermediate.^{10,11} Indeed, this type of intermediate has been observed in the case of toluene disproportionation on H-mordenite.¹² However, there is still uncertainty about the type of acid sites (Lewis or Brønsted) that are involved in the disproportionation.

In our work, the transformation of *o*-xylene was carried out in a recirculation reactor on a series of H-mordenite samples containing different amounts of Lewis or Brønsted acid sites and the effect of H_2 and NO on the transformation was also investigated. The reaction was performed at $\sim 150^\circ\text{C}$. The H-mordenite samples were prepared by calcining and outgassing a partially dealuminated H-mordenite ($\text{Si/Al} = \sim 20$) at 500, 600, 700 and 800°C . Upon increasing the calcination temperature, the amount of non-framework Al and Lewis acid sites increased, which were demonstrated, respectively, by ^{27}Al MAS NMR and EPR with

NO as molecule probe. This should also imply that the amount of Brønsted acid sites decreased accordingly. Our results show that, relatively, the disproportionation was favored at the detriment of isomerization upon increasing the calcination temperature, since the ratio of the rate of isomerization over that of disproportionation decreased constantly. Both H₂ and NO in the reaction mixture inhibited specifically the disproportionation without affecting the isomerization. The inhibition effect was more pronounced when the concentration in H₂ or NO was higher. Based on the effect due to the presence of H₂, Guisnet *et al.*¹¹ suggested that the disproportionation is initiated with the abstraction of a hydride ion from a methyl group by a Brønsted acid center, forming a carbocation and one molecule of H₂, since the addition of H₂ in the gas phase would inhibit the formation of H₂ from the reaction, thus, affecting the disproportionation. However, this assumption can not account for the effect due to the presence of NO, which is known to interact with Lewis acid sites.¹³ NO can compete with xylene for the available Lewis acid centers and, thus, reduce the rate of disproportionation. These results confirm the Brønsted acid catalyzed nature of xylene isomerization and suggest strongly that Lewis acid sites of H-zeolites play an important role, if not essential, in the disproportionation of xylene.

4. A great deal of efforts have been devoted to understanding the mechanistic aspects of the cracking of saturated hydrocarbons.^{14,15} Although it is usually believed that a carbenium ion intermediate is essential to the cracking, it is still controversial as to how this intermediate is formed. Olefinic impurities which can be easily protonated, hydride abstraction by a Lewis acid site and direct protonation of the alkane σ bonds passing through a penta-coordinated carbocation, have been proposed. Recently, much emphasis has been put on the direct

protonation pathway.^{14,15}

The transformation of *tert*-hydrogen containing saturated hydrocarbons such as methylcyclohexane (MCH) and 3- and 2-methylpentanes (MP) was investigated by EPR at different temperatures on an H-mordenite.

The transformation of MCH at room temperature on H-mordenite was very slow. A weak EPR signal was detected about three days after adsorption. Upon heating, the signal developed significantly and a well-defined EPR spectrum was obtained after heating at 60°C for 2 h. The hyperfine structure remained unchanged until about 135°C and the spin density reached about 10^{16} spins/g. The analysis of the spectrum showed that the signal corresponds to a neutral radical formed by abstracting a hydrogen atom from the *tert*-carbon atom of MCH, indicating that the cleavage of the *tert*-C-H bond of MCH can take place even at room temperature on H-mordenite. At temperatures higher than 160°C, the aforementioned signal disappeared completely and at the same time another spectrum with different hyperfine structure appeared, the intensity of which increased until 200°C. This spectrum is due to the formation of olefinic species. A stable neutral radical was also observed at 100°C in adsorption of 3-MP. The subsequent transformation were similar to those observed in the case of MCH, i.e. from the neutral radical to olefinic and then to aromatic species. The formation of organic radicals is believed to take place on zeolite Lewis acid sites.^{16,17}

5. We reported last year¹⁸ that we have been able to substitute Si by Al in the framework of sepiolite, a magnesium silicate having zeolitic channels with cross-section $\sim(10 \times 4) \text{ \AA}^{19}$ and mesopores with diameter around 100 Å. Consequently, the lattice acquires a negative charge which can be balanced, for instance, by VO^{2+} . The transformation of ethanol into

butadiene on this dual-function catalyst appears to result from a Prins reaction between acetaldehyde (formed on the redox sites) and ethylene resulting from dehydration of ethanol on Lewis sites.

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II. LIST OF PUBLICATIONS

1. F. R. Chen, J. G Davis, and J. J. Fripiat, *J. Catal.* **133**, 263-278 (1992).
2. F. R. Chen and J. J. Fripiat, *J. Phys. Chem.* **96**, 819-823 (1992).
3. F. R. Chen, S. Weng, W. Zhang, X. Guo, and J. J. Fripiat, *J. Chem. Soc. Faraday Trans.* **88**, 887-890 (1992).
4. J. B. d'Espinose and J. J. Fripiat, *Catalysis Today* **14**, 125-140 (1992).
5. H. Yong, D. Coster, F. R. Chen, J. G. Davis, and J. J. Fripiat, *Proc. 13th Intern. Congress of Catalysis*, Budapest, July 1992, Preprints, p. 1.
6. Y. Hong, F. R. Chen, and J. J. Fripiat, "Structural and Textural Factors Influencing the Rate of Butene Isomerization on Aluminas," submitted to *Catalysis Letters*.
7. D. J. Coster, A. Bendada, F. R. Chen, and J. J. Fripiat, "Relationship Between the Scaling of the Acid Strength of Lewis Sites by EPR and NMR Probes," submitted to *J. of Catalysis*.
8. F. R. Chen and J. J. Fripiat, "Electron-accepting Strength of Aluminum Species in H-Zeolites," *Proc. 10th International Conference on Zeolites*, Montreal, Canada, July 1992, accepted.

III. PRESENTATIONS

1. Paper 6 was presented orally at the 10th International Conference on Catalysis in Budapest by J. J. Fripiat, July 1992.
2. Paper 8 was presented as a poster at the 9th International Conference on Zeolites in Montreal, Canada by F. R. Chen, June 1992.
3. A poster entitled "Dealumination of Y Zeolites by Chemical Treatments," by D. P. Siantar, W. S. Millman and J. J. Fripiat was presented by D. P. Siantar, at the 9th International Conference on Zeolites, Montreal, Canada, June 1992.
4. A summary of the work performed under this grant (up to February 1992) was presented by J. J. Fripiat at the 8th DOE/BES Heterogenous Catalysis and Surface Chemists Meeting, Santa Monica, CA, March 1992.

IV. PLAN FOR UPCOMING YEARS

1. We plan to focus our attention on the detection of Al surface species using proton Al cross-polarization on materials dehydrated or dehydroxylated in the temperature range between 500-700 C and exposed to known doses of NH_3 and H_2O .
2. Variable temperature studies of the ^{31}P resonance in trimethylphosphine and the measurement of the ^{31}P longitudinal relaxation at variable temperatures should help understand the nature of the TMPH^+ adduct on acid catalyst and its interference with nearby Lewis sites.
3. The TPD instrument is finally working and the technique of NH_3 TPD will be an additional tool for scaling acid strength.
4. Infrared studies of chemisorbed CO, NO, CO_2 and H_2 on the catalysts on which the model reactions are performed will be an additional tool which would help understanding of i) the

nature of the basic and acid sites and ii) poisoning effect (as that of NO reported in item 3).

In brief, during this year we will prepare ourselves for the next stage of our study, namely, i) the study of the synergy between Brönsted and Lewis acid sites and ii) the study of the balance between acid and basic sites.

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