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PROGRESS REPORT

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AlUMINUM COORDINATION AND ACTIVE SITES ON ALUMINAS, Y ZEOLITES AND PILLARED LAYERED SILICATES

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This report covers the activity of the laboratory over 15 months, from June 1, 1990 until August 31, 1991. Our work has been deployed in four directions, namely,

i) Study of the distribution of aluminum within three possible kinds of coordination shells: four-fold (IV), five-fold (V), and six-fold (VI), in aluminas and dealuminated zeolites by high-resolution solid state NMR or MAS NMR. Besides the classical one pulse spectra, nutation spectra have been studied.

ii) Study of the electron deficient sites by electron paramagnetic resonance (EPR) of probe molecules on aluminas and decationated zeolites. Electron deficient sites are considered as Lewis sites.

iii) Study of the model isomerization reaction 1 butene → 2 *cis* or *trans* butene on the aluminas characterized in i) and ii).

iiii) Synthesis of a silicate lattice in which silicon has been partially replaced by aluminum. The chosen silicate is that of the zeolitic (fibrous) sepiolite. It has been characterized as indicated in i) and ii).

As to August 31, 1991, the most significant results have been obtained for items i), ii) and iiii).

i) Distribution of aluminum within three coordination shells

Amorphous transition aluminas have been obtained from crystalline gibbsite or boehmite precursors, either unground or ground for variable periods of time in a ball mill. Grinding the precursors, and, thus, decreasing particle size or increasing the specific surface area creates significant amounts of Al^{V}, while the unground precursor has only Al^{VI}. Since the total intensity of the whole ^{27}Al spectrum does not change significantly upon grinding, Al^{V} is probably more abundant in the outer layers of the material. Upon thermal transformation of the precursors, Al^{IV} is formed. Unground materials are transformed into pseudo-spinels with $Al^{VI}/Al^{IV} \approx 2$ while ground materials keep fair amounts of Al^{V}. Aluminas obtained from ground boehmite have Al^{IV}, Al^{V} and Al^{VI} contents in the approximate ratio 1:1:2, while those obtained from gibbsite have less Al^{V}.

Dealuminated H mordenite (HM) and dealuminated H-faujasite (HY) after thermal treatment contains, beside the framework Al^{IV}, non-framework Al distributed among the same three kinds of coordination shells as those observed in aluminas. In fact, these ^{27}Al MAS spectra can be simulated by mixing the ^{27}Al spectrum of the non-dealuminated zeolite and the ^{27}Al spectrum of the alumina obtained from ground boehmite. Thus, the first significant result of this study is to show that small slabs of dehydroxylated boehmite-like materials, either isolated (alumina) or in the zeolite matrix are rich in Al^{V}. The main difference between both these situations is that in aluminas, Al^{V} disappears above 700°C, while in zeolite it is more stable. Probably at ~700°C, that is at the onset of δ alumina formation, sintering occurs in alumina, while it does not take place for small particles isolated from one another in the zeolite matrix. This observation reinforces the hypothesis that Al^V could be a near-surface species.

Nutation spectra show that in alumina and in dealuminated HM there is a broad distribution of ^{27}Al quadrupole coupling constant (QCC) for all kinds of coordination. Thus, a broad distribution of distortion of those coordination shells is likely.

ii) EPR molecular probes

This part of the project aims to detect surface electron acceptor sites. When exposed to aniline (A), HM produces the characteristic spectrum of the radical cation $A^{\ddagger}$. If, afterwards, O_2 is introduced, O_2^- is observed and its hyperfine splitting indicates that it interacts with Al ($I = \frac{5}{2}$). HM which has more non-framework Al (Al_{NF}) and more Al_{NF}^V is more active than dealuminated HY in this regard. We interpret this finding as an indication that A has transferred an electron to some distorted Al coordination shell, working as a Lewis site L ($\rightarrow L^-$) and that O_2 forms the adduct LO_2^-. On aluminas similar phenomena have been observed in using dimethylaniline (DMA) and O_2, but the hyperfine structure of LO_2^- is not clearly defined. Note that the ionization potential of A is 7.7 eV, while that of DMA is 7.1 eV. The Lewis sites on alumina would be less electron deficient than those on the zeolite Al_{NF}.

The observation of LO_2^- formed from L^-, without the intervention of radiation induced defects, constitutes the next significant achievement of our work. What we do not know so far is the nature of the electron deficient Al coordination shell(s). On alumina we have observed that more Lewis sites were present on alumina with more Al^V, as is also the case on dealuminated zeolites, but this is circumstantial evidence and the link between both sets of observations remains to be established.

iii) Study of a model reaction

We have started to study the 1 butene isomerization on the different aluminas characterized in i). The results obtained so far indicate a large range of activity depending upon the preparation procedure, as grinding *vs.* non grinding and precalcination temperature. A large amount of experimental results is under study, but it too early to draw definite conclusions.

iiii) Synthesis and characterization of a novel silicate lattice

Fibrous mineral sepiolite $(Si_{12})Mg_8O_{30}(OH)_4(H_2O)_{32}$ has zeolitic channels with surface area in the order of 300 m^2g^{-1}. The surface is basic and it has been reported that it catalyzes the dehydration of ethanol into elthylene and that impregnation by Mn and V switches the selectivity in favor of 1.3 butadiene. We have succeeded in replacing about 0.5 Si (out of 12) by Al in the tetrahedral layer and in so doing we have observed that the solid becomes acid, the main sources of acidity being Lewis sites. Preliminary results show also that the aluminated sepiolite catalyzes the formation of 1.3 butadiene (with a selectivity of about 50%) from ethanol at ~300°C. An interesting aspect of these findings is in the fact that, opposite to zeolite, the substitution of Si^{IV} by Al^{IV} in sepiolite does not seem to increase the Brönsted acidity.

List of Publications

1. Fanren Chen, J. Davis and J. J. Fripiat. Aluminum Coordination and Lewis Acidity in Transition Aluminas, accepted by *J. of Catalysis*.
2. Fanren Chen and J. J. Fripiat, Formation of Radical Ion Pairs in Aniline Adsorption

on Zeolites, accepted by *J. Phys. Chem.*

3. J. B. d'Espinose and J. J. Fripiat, Aluminum Modified Sepiolite as Catalyst or Catalyst Support, Symposium on Catalyst Support, Division of Petroleum Chemistry, American Chemical Society, New York, August 25-30, 1991. Submitted to *Catalyst Today.*

Presentations

1. Paper (1) has been presented orally at the 12th North American Catalysis Conference in Lexington, KY in May 1991 by J. J. Fripiat.
1. Paper (2) has been presented as a poster at the same conference by F. R. Chen.
3. Paper (3) has been presented orally at the ACS meeting in New York by J. B. d'Espinose.

PLANS FOR UPCOMING YEAR

1) We intend to concentrate our NMR work on the detection of the surface species using the following techniques. The ^1H-^{27}Al cross-polarization at variable degrees of hydration of the surface should permit detection of the Al sites which interact with water and which are, therefore, most likely near the surface. The use of $P(CH_3)_3$ as Lewis base and the observation of the ^{31}P chemical shift at variable degrees of coverage could, as suggested by Lunsford, help in detecting $P(CH_3)_3$ chemisorbed on Lewis sites. We now have a MAS NMR probe allowing for the use of sealed tubes in which the sample can be studied at variable temperature with its adsorbed or chemisorbed molecules.

2) In the domain of the EPR, we will check new probe molecules. Benzene, for instance, seems to be interesting for dealuminated zeolites. The ideal situation would be

to have a range of probes with different ionization potentials enabling us to obtain a distribution of the Lewis sites with respect to the ionization potentials.

3) We have also set up a Thermal Program Desorption Instrument (TPD). TPD experiments with NH_3, $P(CH_3)_3$ and pyridine would complement the information obtained as described in item 2.

4) Particular attention will be given to the study of catalytic reactions carried out on well-defined samples of aluminas and zeolites. In addition to butene isomerization we will study the isomerization of methlycyclopentene. For zeolites we have not yet made our decision. Also, and pertaining to these considerations, we worry about the purity of the samples. For instance, traces of sodium in aluminas can kill part of the Lewis acid activity and affects the catalytic performances. We started preparing very pure aluminas with less than 50 ppm Na and we will compare them with those observed with "normal" chemical reagents.

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