

BNL-66552

MATERIALS RESEARCH SOCIETY CONFERENCE PROCEEDINGS

Proceedings of the 12th International Zeolite Conference

Conference held July 5-10, 1998
Baltimore, Maryland, U.S.A.

Editors:

M.M.J. Treacy

NEC Research Institute, Inc.
Princeton, New Jersey, U.S.A.

B.K. Marcus

Zeolyst International
Conshohocken, Pennsylvania, U.S.A.

J.E. Bisher

NEC Research Institute, Inc.
Princeton, New Jersey, U.S.A.

B. Higgins

Zeolyst Products & Chemicals, Inc.
Allentown, Pennsylvania, U.S.A.

OFFICIAL FILE COPY

BNL-66552

MATERIALS RESEARCH SOCIETY CONFERENCE PROCEEDINGS

Proceedings of the 12th International Zeolite Conference



Conference held July 5-10, 1998
Baltimore, Maryland, U.S.A.

Editors:

M.M.J. Treacy

NEC Research Institute, Inc.
Princeton, New Jersey, U.S.A.

B.K. Marcus

Zeolyst International
Conshohocken, Pennsylvania, U.S.A.

M.E. Bisher

NEC Research Institute, Inc.
Princeton, New Jersey, U.S.A.

J.B. Higgins

Zeolyst International Products & Chemicals, Inc.
Conshohocken, Pennsylvania, U.S.A.

OFFICIAL FILE COPY

transfer. This model is currently being investigated by taking into account the coupling of the molecular modes with those of a model zeolite framework (15).

CONCLUSIONS

The large changes observed in the ^{13}C NMR isotropic chemical shifts for $\text{CH}_3^{13}\text{CN}$ in H-MFI with temperature are the result of dynamical processes associated with the excitation of low-frequency, vibrational modes. We find no evidence for changes in the chemical structure of CH_3CN resulting from either partial or complete proton transfer.

ACKNOWLEDGEMENTS

This work was supported in part by the National Science Foundation Grant #CTS9713023. Helpful discussions with Dr. M. Allavena, H.L. Dai, and R.M. Hochstrasser are gratefully acknowledged.

REFERENCES

1. W.E. Farneth and R.J. Gorte, *Chemical Reviews* **95**, 615 (1995).
2. D.J. Parrillo, C. Lee, R.J. Gorte, D. White, and W.E. Farneth, *Journal of Physical Chemistry* **99**, 8745 (1995).
3. R.J. Gorte and David White, *Topics in Catalysis* **4**, 57 (1997).
4. J. Šepa, R.J. Gorte, David White, E. Kassab, and M. Allavena, *Chemical Physics Letters* **262**, 321 (1996).
5. J.F. Haw, M.B. Hall, A.E. Alvarado-Swaigood, E.J. Munson, Z. Lin, L.W. Beck, and T. Howard, *Journal of the American Chemical Society*, **116**, 7308 (1994).
6. A.G. Pelmenschikov, R.A. van Santen, J. Jänchen, and E. Meijer, *Journal of Physical Chemistry* **1993**, *97*, 11071.
7. C.-C. Lee, R.J. Gorte, and W.E. Farneth, *Journal of Physical Chemistry B* **101**, 3811 (1997).
8. J. Šepa, R.J. Gorte, B.H. Suits, and David White, *Chemical Physics Letters* **289**, 281 (1998).
9. J. Šepa, R.J. Gorte, B.H. Suits, and David White, *Chemical Physics Letters* **252**, 281 (1996).
10. J. Šepa, PhD Thesis, University of Pennsylvania (1998).
11. L. Kubelkova, J. Kotrla, J. Florian, *Journal of Physical Chemistry* **99**, 10285 (1995).
12. R.M. Shelby, C.B. Harris and P.A. Cornelius, *Journal of Chemical Physics* **70**, 34 (1979).
13. J.P. Culver, M. Li, L.G. Jahn, R.M. Hochstrasser and A.G. Yodh, *Laser Spectroscopy and Photochemistry on Metal Surfaces. Part I*, Edited by H.L. Dai and W. Ho, (World Scientific, Singapore, New Jersey, London, Hong Kong, 1995), pg. 542.
14. C.J. Jameson, *Chemical Reviews*, **91**, 1375 (1991).
15. M. Allavena, private communication.

HYDROCHLOROFLUOROCARBON REACTIVITY AND STRUCTURAL CHARACTERIZATION OF ZINC EXCHANGED NAX

M.F. CIRAOLO*, P. NORBY*, J.C. HANSON[†], D.R. CORBIN[‡] and C.P. GREY*

*Chemistry Department, SUNY Stony Brook, Stony Brook, NY 11794-3400, USA;

cgrey@sbchem.sunysb.edu

[†]Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA;

[‡]DuPont CR&D, Wilmington, DE 19880-0262, USA;

ABSTRACT

Solid-state MAS NMR and synchrotron X-ray powder diffraction have been used to study the reactivity of fluorocarbons and to study the cation positions of Zn^{2+} -exchanged zeolite NAX. The structure of dehydrated ZnX was refined in the space group $\text{Fd}\bar{3}\text{m}$ and zinc cations were found in four different positions, all lying along the [111] direction. The residual sodium cations were located in the SII position in the supercages. Tetrahedral extra-framework aluminum were found (by ^{27}Al MAS NMR and diffraction) in the center of the sodalite cage. The reactivity of HCFC-124a ($\text{CF}_2\text{HCF}_2\text{Cl}$) over ZnX were studied with NMR and by temperature programmed desorption/mass spectrometry (TPD/MS). The unsaturated products of dehydrofluorination and dehydrochlorination reactions (CF_2CFCl and CF_2CF_2) were the TPD products, while saturated products such as HFC-125 ($\text{CF}_3\text{CF}_2\text{H}$) were the TPD products as observed by ^{19}F NMR.

INTRODUCTION

Basic zeolites have been proposed as materials for separating different mixtures of hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) produced in the synthesis of the environmentally-friendly replacements to the CFCs.¹ However, HCFCs are not stable in basic zeolites. For example, the conversion of CHClF_2 (HCFC-22) over zeolite 5A, was reported a number of years ago.² HCFCs will also undergo dehydrofluorination reactions at higher temperatures.³ We are studying the adsorption and reactivity of HCFC-124a ($\text{CF}_2\text{HCF}_2\text{Cl}$) on cation exchanged zeolites, with solid state NMR, powder diffraction and mass spectrometry, to study the interactions of the HCFCs with the extra-framework cations and framework oxygen sites. We relate this to the HCFC reactivity. We have chosen to study HCFC-124a since this molecule, in principle, undergo both dehydrofluorination and dehydrochlorination reactions. Dehydrofluorinations typically occur via a carbanion mechanism. In dehydrochlorinations may occur via (concerted) E2 or E1 mechanisms, the latter being

as the electrostatic field of the cation in the zeolite increases.⁴ Thus, in theory, the preference for dehydrofluorination versus dehydrochlorination may be related to the relative importance of the interactions with the basic oxygen atoms versus with the cations.

EXPERIMENTAL

Zeolite ZnX was prepared by ion-exchanging zeolite NaX (Aldrich Chemicals) with 0.1 M Zn(NO₃)₂ at a temperature of 60 °C over a period of 48 hours. Dehydration of the exchanged sample was carried out by ramping the temperature under vacuum to 450 °C over 12 hours then holding at 450 °C for an additional 24 hours. HCFC-124a (Dupont) loading levels were established by monitoring the drop in pressure, on exposure of the dehydrated sample to an HCFC atmosphere, with a calibrated vacuum line and an absolute-pressure gauge. ICP elemental analysis, (Galbraith) of the exchanged Zn-X sample gave a composition (weight %) of Na 1.13, Zn 11.76, Si 14.36, and Al 11.56, giving a composition for the unit cell of Na_{10.1}Zn_{36.8}Si_{104.3}Al_{87.7}O₃₈₄.

Variable-temperature ²⁷Al and ¹⁹F MAS NMR experiments were performed with a double resonance Chemagnetics probe, on a CMX-360 spectrometer. Chemical shifts for ²³Na, ²⁷Al and ¹⁹F are quoted relative to aq. sodium chloride, aq. aluminum sulfate and CCl₃F, respectively, as external standards.

X-ray synchrotron powder diffraction data were collected at the beamline X7B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), with a FUJI imaging plate (200 x 400 mm, spatial resolution 100 x 100 μm) mounted perpendicular to the incoming beam. Reactions were performed with a RXM-100 Multifunctional Catalyst Testing and Characterization Machine equipped with a MKS 100C Precision Quadrupole Mass Analyzer.

RESULTS

The room temperature structure of dehydrated ZnX has been refined in the cubic space group Fd3m and agreement factors of R_w = 2.22% and χ² = 5.34 were obtained. A total of 41.4 zinc and 8.6 sodium cations per unit cell were found (Table 1). Sodium cations were only located in the SII position in the supercell and ²³Na NMR demonstrated the lack of any SI sodium cations. The number of zinc cations is slightly higher than expected from the chemical analysis (37), while the number of sodium cations is lower. This is, most likely, due to the correlation between the occupancies of the Zn and Na SII positions, due to the overlap of the electron density, and is

reflected in the larger e.s.d.s for these sites. It is, therefore, difficult to refine the occupancies of these two sites independently. Zinc cations were located on a split, lower symmetry (32e), SI position, consistent with the previous report for ZnY.⁵ Attempts to model the electron density with a true SI position (16c), resulted in a very low occupancy for this site, and considerable residual electron density on the split position. A difference Fourier map revealed residual electron density at the center of the sodalite cage. This was attributed to extra-framework AlO₄⁻ species, which have been previously reported in Zeolite A and dealuminated X.⁶ A resonance at 92 ppm is observed in the ²⁷Al MAS NMR of dehydrated ZnX, consistent with this species.⁷ The positions of the different refined cation positions are shown in Figure 1.

Atom	Position	Occupancy
Zn	SI (32e)	5.7(2)
Zn	SI' (32e)	16.8(3)
Zn	SII' (32e)	12.7(4)
Zn	SII (32e)	6.2(6)
Na	SII (32e)	8.6(16)
Al	(8a)	1.62(2)
O	(32e)	5.41(35)

Table 1. Occupancies, per unit cell, for the refined cation positions and extra-framework AlO₄⁻ ion. Standard deviations for the occupancies are given in parentheses.

Reactions of HCFC-124a (CF₃HCF₂Cl) adsorbed on ZnX were studied with ¹⁹F and ²⁷Al variable temperature MAS NMR. Reactivity of the HCFC-124a was observed with ¹⁹F MAS NMR after heating the sample for only 3 minutes at 150 °C. Two additional resonances were detected at -141 and -89 ppm which were assigned to HFC-125 (CF₃CF₂H). After longer treatment of the sample at 150 °C (up to 1 hour), a number of smaller resonances were observed between -80 and -95 ppm, which are assigned to the CF₃ groups in HCFC-124 (CF₃CFHCl), HFC-123 (CF₃CHCl₂) and HFC-116 (CF₃CF₃). A much broader, less intense resonance at ca. -126 ppm is observed. The linewidth, and the sidebands observed for this resonance, indicate that it does not come from a gaseous species, and it is assigned to either a longer chain saturated fluoro- or chlorofluorocarbon, or a silicon fluoride species. When the sample is ramped to 225 °C (for 20 mins), this resonance disappears and small broad peak at -168 ppm with associated spinning sidebands is observed. Simultaneously, a noticeable change in the ²⁷Al NMR spectrum is observed: the resonance from the extra-framework AlO₄⁻ species at 92 ppm disappears, and a

broad peak from an octahedral aluminum species at -0.8 ppm begins to appear. After 45 minutes at this temperature, the intensity of this resonance has increased, presumably as the framework aluminum atoms are attacked and more Al-F species are produced.

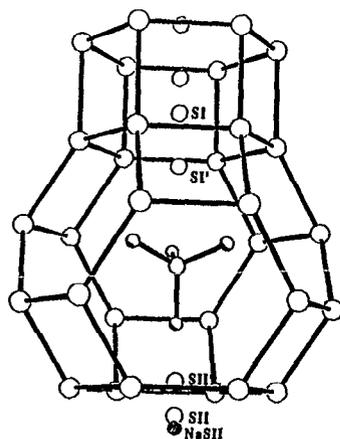


Figure 1. A view of a sodalite cage and connected double six-ring, showing the zinc (SI, SI', SII and SII) and sodium (NaSII) positions, and the AlO_4 extra-framework species in the center of the sodalite cage.

Products from TPD studies of samples of excess HFC-124a-loaded ZnX were studied with mass spectroscopy. As the temperature was ramped above 50°C , the dehydrochlorination and dehydrochlorination products (HFC-1114 (CF_2CF_2) and HCFC-1113 (CF_2CFCl), respectively) were observed in approximately equal amounts as the most abundant products. HCFC-124a was not observed and thus must completely react before desorption. Some HCl was observed, but no HF was seen, the latter presumably attacking the zeolite framework, at the temperatures required for desorption. Only very small concentrations of saturated products were detected.

DISCUSSION

Rietveld refinement of bare partially zinc-exchanged NaX has shown that there are both zinc and sodium cations in the supercages available for gas binding after the sample has been dehydrated. The zinc position lies only 0.53 \AA above the plane formed by the 3 O2 atoms in the

supercage, so will be less exposed to gas sorbates than the sodium cations which lie 1.1 \AA above the O2 plane. Clearly, further ion-exchange is required to remove these sodium cations. The products in an open reaction system (TPD/MS) differed considerably from those detected in the closed reaction vessel (NMR). No unsaturated products were observed with NMR, the major product being HFC-125. Both dehydrofluorination and dehydrochlorination reactions are clearly occurring, as the products from these reactions were observed by MS. The saturated products are proposed to result from the addition of HF or HCl to the unsaturated products. Thus, HFC-125 is formed from the addition of HF to CF_2CF_2 , the product of the dehydrochlorination reaction, the driving force presumably being the formation of the thermodynamically-stable CF_3 group. However, fluorine and chlorine substitution reactions cannot be ruled out. Coking is also observed in the sealed systems, which may account for the loss of some of the products of the dehydrohalogenation reactions. Although HCFC-124a dehydrohalogenation reactions were observed at 150°C , attack of the extra-framework AlO_4 species by HF did not occur until higher temperatures. Rapid attack of the framework and further dealumination was observed at 225°C .

ACKNOWLEDGMENTS

Support from the following grants is gratefully acknowledged: DE-FG02-96ER14681, CHE-9405436 and DE-AC02-93CH10084. CPG is a DuPont Young Professor and a Cottrell Scholar of the Research Corporation.

REFERENCES

- (1) D.R. Corbin and B.A. Mahler, World Patent, W.O. 94/02440(3 February 1994).
- (2) P. Cannon, J. Am. Chem. Soc. **80**, 1766 (1958).
- (3) C.P. Grey and D.R. Corbin, J. Phys. Chem. **99**, 16821 (1995).
- (4) W. Klading and H. Noller, J. Catal. **29**, 385 (1997).
- (5) A.P. Wilkinson, A.K. Cheetham, S.C. Tang and W.J. Reppart, J. Chem. Soc. Chem. Commun., 1485 (1992).
- (6) J.J. Pluth and J.V. Smith, J. Am. Chem. Soc. **105**, 51 (1983); J.J. Pluth and J.V. Smith, J. Am. Chem. Soc. **105**, 1192 (1983); J.B. Parise, D.R. Corbin and L. Abrams Acta. Cryst. **C40**, 1493 (1984).
- (7) D.R. Corbin, R.D. Farlee and G.D. Stucky, Inorg. Chem. **23**, 2920 (1984).