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A Combined Powder Diffraction and Solid State NMR Study of the Structure of Fluorinated Aluminas: Implications for Catalysis

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Beamline(s): X7B

Introduction: In recent years, fluorinated aluminas have found widespread application in the production of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs).[1,2] There have been many reports in the literature on the preparation of catalytically active fluorinated aluminas, including gas phase fluorination with fluorine gas, hydrofluoric acid, HFCs, or HCFCs, and aqueous impregnation with ammonium fluoride. The numerous reports found in the literature have disclosed diverse findings regarding the bulk structures formed following fluorination, which include amorphous phases, aluminum hydroxyfluorides, and different aluminum fluoride phases. Fluorinated aluminas, as a class of catalytic materials, are inherently heterogeneous, and are often disordered, partially amorphous, or mixtures of multiple phases. Our approach has been to use combined methods to study these systems.

Methods and Materials: Fluorinated alumina catalysts were prepared from zinc impregnated gamma-Al_2O_3. The fluorinated catalysts were prepared through gas phase fluorination of the gamma-Al_2O_3 starting material in a flowing feed stream of HF and N_2. Various concentrations of HF were used to obtain materials with differing fluorination levels. X-ray synchrotron powder diffraction data were collected at the X7B beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). A MAR-345 image plate (IP) detector mounted normal to the beam path was used to collect full-circle powder patterns. An external LaB_6 standard was used to determine the tilt angle, sample to detector distance, wavelength, and tilting angle of the IP. Integration of the full-circle powder patterns was performed with Fit-2d.[3]

Results: We have investigated the structures of a series of pristine and Zn-impregnated aluminas following fluorination with HF, which are highly active in fluorocarbon catalysis, using both solid state NMR and X-ray powder diffraction methods. In the absence of any cation impregnation, alpha-AlF_3 and small amounts of beta-AlF_3 are formed at a temperature of 400 °C with a HF/N_2 ratio of 1:1. Even higher fractions of beta-AlF_3 are formed from the impregnated phases for HF levels of 30 percent in N_2 and higher, along with a significant concentration of alpha-AlF_3. In contrast, fluorination of Zn-impregnated gamma-Al_2O_3 in dilute HF feeds resulted in the almost complete conversion to the aluminum (hydroxy)fluoride pyrochlore phase, AlF_2OH. Thus, even very low levels of transition metals (< 2% by weight) appear to play an important role in controlling the phase formed during the fluorination reaction.

Conclusions: The work reported here demonstrates that the structures of fluorinated aluminas can be altered by varying the fluorination conditions and by impregnation of the surface with transition metal cations.

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