

# Transition Metal Impregnated/Doped Aluminum Oxide/Fluoride Catalysts for Chlorofluorocarbon Reforming Reactions

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Beamline(s): X7B

**Introduction:** Chlorofluorocarbons (CFCs) are well known to have a considerable environmental impact with respect to depletion of the ozone layer and global warming. In 1987, the Montreal Protocol called for a 50 percent decrease in production and the eventual phase-out of CFCs. Unfortunately, the synthesis of HCFCs and HFCs involve complex strategies, as opposed to the single step processes for CFCs. As a result of the need to develop environmentally friendly CFC alternatives many new synthetic pathways have been discovered that involve halogen exchange, disproportionation, and halogenation reactions. Promising prospective catalysts for many CFC reforming reactions include transition metal impregnated/doped aluminum fluorides prepared through the fluorination of the appropriate oxides. Cobalt and zinc impregnated alumina catalysts, fluorinated with HF, are reported to be active catalysts for halogen exchange reactions,  $\beta$ -AlF<sub>3</sub> being reported as the active material present in these catalysts. [1] Using *in situ* methods developed at the x7b beamline we have been studying the activation and reactivity of transition metal impregnated and doped aluminum oxide catalysts. The goal of this work is to conclusively identify the active material present in these fluorinated catalysts and to understand the structure-directing nature of the transition metals with respect to fluoride formation. This information can then be used to target more efficient preparatory methods for making active catalysts.

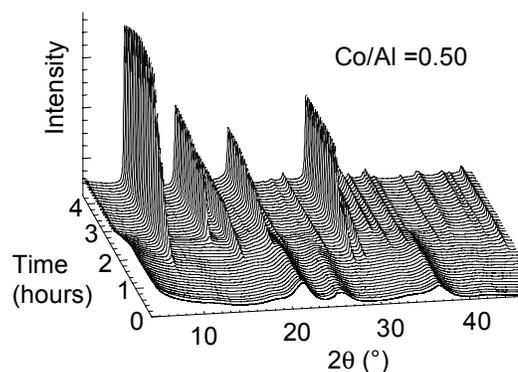
**Methods and Materials:** Impregnated alumina catalysts were prepared from the transition metal chloride salts and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. High surface area homogeneous mixed transition metal/aluminum oxides were prepared through the sol-gel method. Catalysts with various transition metal content were prepared. *In situ* diffraction methods were used to study the fluorination of the catalysts using HCFC-22 (chlorodifluoromethane) as both the fluorinating agent and to measure the reactivity. Time-resolved powder patterns were collected in the temperature range from 300 – 500 °C.

**Results:** Fluorination of the homogeneous mixed Co/Al and Zn/Al oxides resulted in the formation of multi-phase materials. In addition to a pattern that can be indexed based on the distorted ReO<sub>3</sub> structure of  $\alpha$ -AlF<sub>3</sub> at least one additional phase is present that cannot be indexed based on any known AlF<sub>3</sub>, transition metal fluoride, or mixed fluoride phases. The most intense reflections of the “new” phase in the Co/Al system seem to suggest that the structure may be a distorted form of either the pyrochlore or hexagonal bronze structure types, though new phase has not been definitely identified. The proportion of the new phase is drastically decreased in the impregnated versus the doped aluminum oxide, suggesting that the new material is indeed a new mixed fluoride.

**Conclusions:** *In situ* time resolved study of the fluorination of transition metal/aluminum oxide materials has led to the formation of “new” materials. Utilizing the time resolved data we will be able to identify appropriate transition metal/aluminum ratios for the formation of single-phase materials. Secondly, we have shown that fluorination of the sol-gel prepared homogeneous mixed oxides with a fluorocarbon is a more appropriate method for the formation of these “new” fluoride phases.

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**References:** [1]D.R. Corbin, V.N.M. Rao, U.S. Patent 5,300,710 (1994). D.R. Corbin, V.N.M. Rao, U.S. Patent 5, 300, 711 (1994).D.R. Corbin, V.N.M. Rao, U.S. Patent 6,040,486 (2000).



**Figure 1.** Time-resolved plot of the fluorination of a sol-gel prepared Co/Al oxide with HCFC-22 (Co/Al ratio of 0.50). The temperature program was as follows; one hour at 300 °C, two hours ramp to 500 °C, one hour at 500 °C. The wavelength was 0.90Å.