

# Microstructure of the Proton-Exchanged Transition Metal Oxides Obtained by Acid Treatment and Their Catalytic Activities

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The intercalation and ion-exchange chemistry provides new routes for material design. These soft chemistry reactions play an important role in the electrochemical reduction and oxidation by lithium of many solid electrodes, particularly in the light of secondary lithium batteries.

The  $\text{LiMn}_2\text{O}_4$  spinel and the layered  $\text{ABO}_2$  compound such as  $\text{LiCoO}_2$  and  $\text{NaCrO}_2$  exhibit that the lithium or sodium ions exchange with protons in aqueous acid solutions preserving the structural framework of their original crystal structures. For the proton-exchanged  $\text{LiMn}_2\text{O}_4$  the  $\text{Mn}_2\text{O}_4$  framework remains stable even by the removal of proton as hydrogen and the valence state of surface manganese ions can vary in accordance with the hydrogen removal. The same phenomenon takes place for the proton-exchanged  $\text{LiCoO}_2$  and  $\text{NaCrO}_2$ . We therefore investigated both catalytic activities of these proton-exchanged metal oxides for the oxidation of hydrogen and hydrocarbons in relation to their microstructures and physico-chemical properties.

The Lithium-ion extraction for  $\text{LiMn}_2\text{O}_4$  spinel powders were made by stirring in a  $\text{HNO}_3$  solution with different concentrations each at room temperature. The amount of extracted lithium ions was determined from lithium concentration in the  $\text{HNO}_3$  solution, which was measured by atomic absorption spectrometry. The acid-treated sample was filtered, washed with distilled water, and dried at 353 K. The proton-exchange treatment for  $\text{LiCoO}_2$  and  $\text{NaCrO}_2$  powders were made in 0.5M  $\text{HCl}$  and 1M  $\text{HNO}_3$  solutions, respectively. The contents of extracted alkaline ions were determined using atomic absorption spectroscopy. The products were washed with distilled water and subsequently dried at 353 K.

The proton-exchanged  $\text{LiMn}_2\text{O}_4$  showed the highest catalytic activity for the oxidation of methane and n-butane compared with  $\text{MnO}_2$  and  $\text{LiMn}_2\text{O}_4$ . The activity sharply decreases with the decomposition of the spinel framework into the  $\text{MnO}_2$  framework. X-ray photoelectron spectroscopic analysis of the sample surface and X-ray diffraction analysis of the sample powder both kept at different temperatures showed that the average valence state of manganese ions contributes to the activation of surface reaction of adsorbed hydrocarbon molecules and adsorbed oxygen.

The acid treatment of  $\text{LiCoO}_2$  and  $\text{NaCrO}_2$  samples yielded a significant amount of  $\text{HCoO}_2$  and  $\text{HCrO}_2$  formations, respectively. X-ray diffraction patterns of these proton-exchanged products indicate that the crystal structure is highly oriented in parallel with the basal plane of the hexagonal system. Line broadening in the X-ray reflection peaks was observed with the progress of the ion-exchange. The broadening is more significant in the  $\text{HCrO}_2$  phase than in the  $\text{HCoO}_2$  phase. Microstructure of  $\text{HCrO}_2$  by transmission microscopy revealed a fine layered structure (Fig. 1). The microstructure of these proton-exchanged oxide is affected by the morphology and crystalline state of the starting oxide, which has a possibility of controlling the catalytic activity for combustion reaction. The transformation of the starting phase to the proton-exchanged phase accompanies a decrease in crystallite size and/or an introduction of strains. The structural

collapse during the ion-exchange reaction easily occurs in the layered oxides having a relatively wide interlayer spacing. This could account for the broadening in the X-ray reflection peaks of the  $\text{HCrO}_2$  phase transformed from the starting  $\text{NaCrO}_2$  phase.

High-resolution electron micrographs of proton-exchanged  $\text{LiCoO}_2$  oxide powders revealed a formation of micro domains after the proton-exchange treatment. This characteristic domain structure is most likely to produce the active sites for the oxidation reaction with the specific surface valence states of cobalt ions.

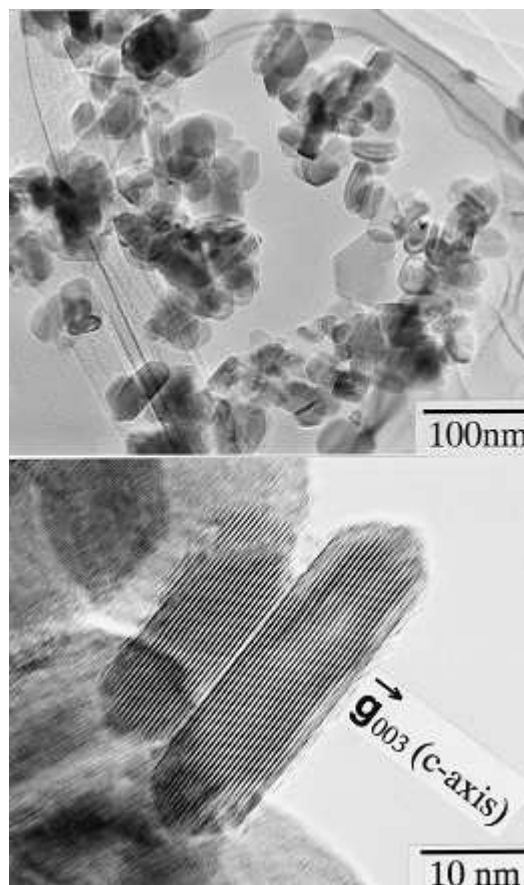


Fig. 1 Bright-field image of  $\text{HCrO}_2$  particles.

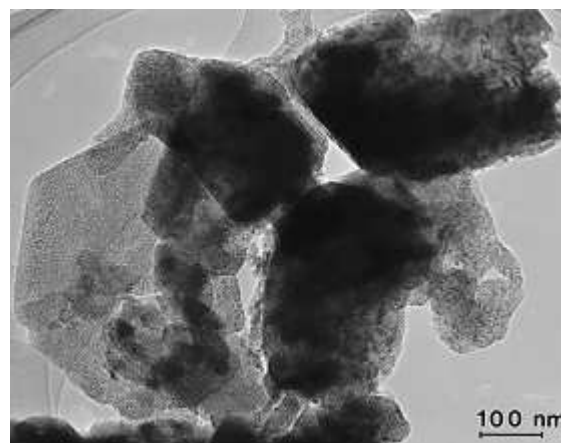


Fig. 2 Bright-field image of acid-treated  $\text{LiCoO}_2$  particles ( $\text{HCoO}_2$  coexists with  $\text{LiCoO}_2$ ).