Experimental report

18/09/2019

Proposal: **5-21-1115** **Council:** 4/2018

Title: Influence of dopant distribution on catalytic properties in Mn related hollandites

Research area: Materials

This proposal is a new proposal

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Samples: K0.12MnOáº
K0.12Mn0.95Fe0.05Oáº
K0.03Mn0.85Fe0.15Oáº
K0.11Mn0.92Ti0.08Oáº
K0.10Mn0.82Ti0.18Oáº
K0.09Mn0.88Fe0.12Oáº
K0.1Mn0.87V0.13Oáº

Instrument	Requested days	Allocated days	From	To
D2B	3	3	21/09/2018	24/09/2018
D1B	3	0		

Abstract:

hollandite related materials have been found as effective catalysts for CO oxidation. In this sense, we have undertaken the study of the influence of doping on the catalytic CO oxidation of hollandite related compunds. In this sense, different doped hollandites, with a general formula KnMn1-xDxOd; (D = Fe, Ti y V), have been synthesized and characterized.It is worth emphasizing that all of them are active at room temperature in CO oxidation.

A characterization by neutron diffraction is necessarily required to accurately determine the positions and occupations of oxygen atoms, hardly detectable by other techniques, as well as, the water molecules present in the tunnel.

Influence of dopant distribution on catalytic properties in Mn related hollandites

Octahedral molecular sieves (OMS) exhibit unique porous structures. Among them, manganese related oxides have received particular attention because of their outstanding properties in heterogeneous catalysis and rechargeable batteries [1,2] as a consequence of their one-dimensional framework and variable tunnel size, ion exchange ability and coexistence of different manganese oxidation states. For instance, hollandite type materials (OMS-2) consist of edge-sharing octahedral units (MnO_6) which interlink to form 2x2 tunnels of 0.46 nm (figure 1a). The corresponding manganese oxide framework is negatively charged due to Mn(III)/Mn(IV) mixed valence and, as a result, the tunnels can host diverse cations and water molecules. In the case of potassium hollandite, usually called cryptomelane (K_xMnO_2), the channels are occupied by K^+ keeping the structural charge neutrality [2].

These OMS-2 materials have been found as effective catalysts for different oxidation reactions, from simple catalytic model reactions, as CO oxidation, to more complex ones with particular industrial and environmental interest. On the other hand, the modification of cryptomelane by replacing Mn by transition metals has been reported to produce improvements on its catalytic activity. This enhancement should be due to the presence of dopants promoting the generation of defects and oxygen mobility [3]. This idea has been widely accepted and usually is related to the presence of anionic vacancies [4], although the amount of these vacancies has not been determined.

On the basis of these ideas, we have undertaken the study of the influence of doping on the catalytic CO oxidation of hollandite related compounds. In this sense, different doped hollandites, with a general formula $K_nMn_{1-x}D_xO_\delta$ (D = Fe, Ti y V), have been synthesized.

We collected diffraction data at high resolution powder diffractometer D2B at room temperature. In the Fe-doped materials, $K_nMn_{1-x}Fe_xO_\delta$ system, we collected diffraction data for $\mathbf{K_{0.12}Mn_{0.95}Fe_{0.05}O_\delta}$, $\mathbf{K_{0.09}Mn_{0.90}Fe_{0.10}O_\delta}$, $\mathbf{K_{0.03}Mn_{0.80}Fe_{0.20}O_\delta}$ **and** $\mathbf{K_{0.12}Mn_{0.75}Fe_{0.25}O_\delta}$ compositions.
On the other hand, in Ti-doped hollandites, two samples $\mathbf{K_{0.11}Mn_{0.90}Ti_{0.10}O_\delta}$ and the maximum $\mathbf{K_{0.10}Mn_{0.85}Ti_{0.15}O_\delta}$ were analyzed.

Finally, regarding to V-doped hollandites, three sample were studied $\mathbf{K_{0.1}Mn_{0.85}V_{0.15}O_\delta}$ $\mathbf{K_{0.1}Mn_{0.95}V_{0.05}O_\delta}$ and $\mathbf{K_{0.1}Mn_{0.90}V_{0.10}O_\delta}$.

The neutron diffraction study of this samples has permitted obtained the arrangement of the anionic vacancies and the cationic distribution of D (Fe, V) and Mn in the $K_xMn_{1-y}D_yO_\delta$ materials. For all hollandites the NPD data collected at room temperature were refined in the I4/m space group according to the single-crystal $K_{0.167}MnO_2$ [5]. The atomic coordinates, thermal parameters and occupancy factors of atoms were refined. The Rietveld refinement pattern and difference plot for $K_{0.11}MnO_\delta$, $K_{0.11}Mn_{0.95}Fe_{0.05}O_\delta$, $K_{0.09}Mn_{0.8}Fe_{0.2}O_\delta$, $K_{0.1}Mn_{0.85}Ti_{0.15}O_\delta$ are shown in Figure 1 a,b,c,d, respectively. This structure consists of octahedral units of edge-sharing manganese oxide octahedral (MnO6) which interlink to form tunnels of 2x2 dimensions. A schematic representation of this structure is depicted in Figure 2.

The strong correlation between the temperature factor and the site occupation factors for potassium cation does not allow quantifying the potassium composition so the value obtained by EDS has been fixed in the refinement of the all hollandites. Besides, the occupancy factors of the oxygen atoms reveal the anionic sublattice is not complete. Actually, the refinement of the oxygen occupancy shows the presence of anionic vacancies in O2.

The results of this work will provide an exhaustive structural characterization of these nano-hollandites.

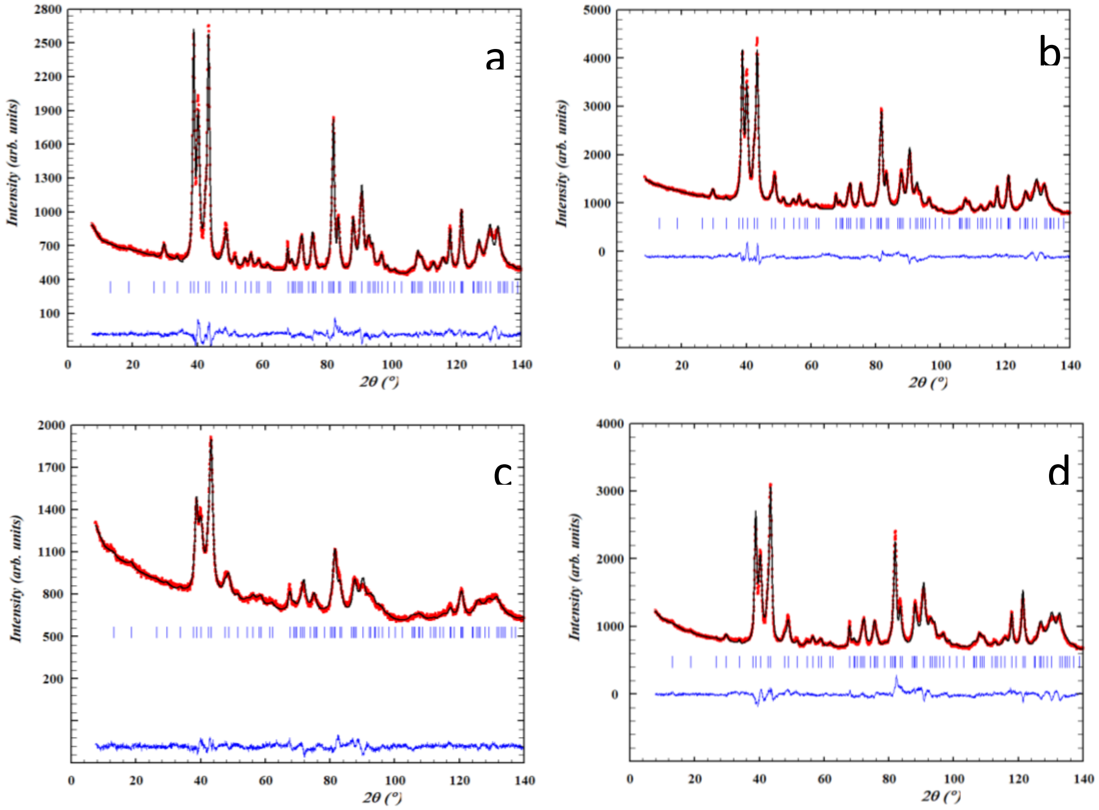

Figure1. Observed, calculated, and difference profile of neutron diffraction patterns for a) $K_{0.11}MnO_{1.958(12)}$, b) $K_{0.11}Mn_{0.946(2)}Fe_{0.054(2)}O_{1.899(14)}$, c) $K_{0.09}Mn_{0.844(2)}Fe_{0.156(2)}O_{1.904(17)}$ and d) $K_{0.1}Mn_{0.82}Ti_{0.18}O_{1.964(8)}$ samples.

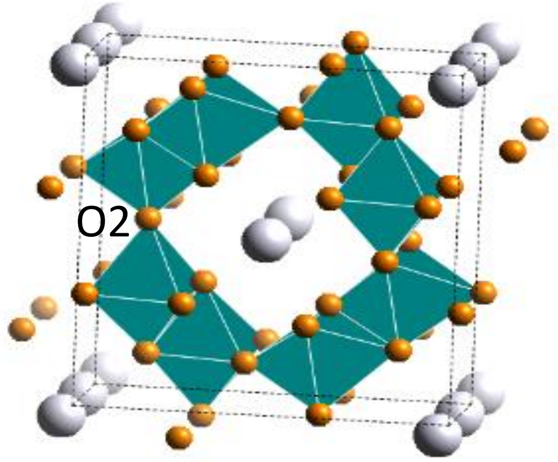

Figure 2. Structural model for $K_nMn_{1-x}D_xO_\delta$ (D = Fe, Ti y V) hollandites.

[1] S.L. Suib et al., *J. Mater. Chem.*, **2008,** 18, 1623-1631.
[2] D. Portehault et al., *Chem. Mater.*, **2007**, 19, 5410-5417.
[3] J. Cai et al., *Chem Mater.*, **2001**, 13, 2013-2422.
[4] Hernández, W. Y., et al., Catal. Today **2010,** 157(1): 160-165.
[5] J. Vicat et al., Acta Crystallogr. Sect. B 42, **1986,** 162-167.