

Influence of the composition on the electronegativity and on the oxygen charge distribution in a binary hydrotalcite-like by modified Sanderson method

Alexandre Carlos Camacho Rodrigues

*NUCAT/PEQ/COPPE/UFRJ, Universidade Federal do Rio de Janeiro, Ilha do Fundão,
P.O. Box 68502, 21945-970, Rio de Janeiro, Brazil*

E-mail: camacho@peq.coppe.ufrj.br

Received 28 June 2004; revised 5 July 2004

An intuitive and computationally non-intensive model for the classification of Hydrotalcite-like compounds (HTLCs) based simply on the chemical composition using the Sanderson Method led to good prediction of basicity and different basic sites (oxygen atoms with different charge). That model was evaluated at different $M^{3+}/(M^{2+}+M^{3+})$ ratio and with different divalent and trivalent metallic cations.

KEY WORDS: hydrotalcite, basicity, copper, cobalt, iron

AMS subject classification: 92E10

1. Introduction

Hydrotalcite-like compounds (HTLCs) are layered-double hydroxides (LDHs) with lamellar structure and general formula $(M_{1-x}^{2+}M_x^{3+}(\text{OH})_2)^{x+}(A_{x/m}^{m-})\cdot n\text{H}_2\text{O}$ (where $M^{2+} = \text{Mg}^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}$; $M^{3+} = \text{Al}^{3+}, \text{Fe}^{3+}, \text{Cr}^{3+}$ and $A = \text{OH}^-, \text{Cl}^-, \text{NO}_3^-, \text{CO}_3^{2-}$), x taking values between 0.20 and 0.33 [1]. These materials consist of infinite sheets in octahedral symmetry [1–4], held together by weak interactions through hydrogen bonds [1–3]. The isomorphous replacement of M^{2+} cations by M^{3+} ones with similar radius generates positively charged layers, which can be compensated by anions located in the interlayers along with water molecules [1,2].

The mixed oxides derived from HTLCs have many industrial applications, such as aldol condensation of aldehydes and ketones [5], methanol synthesis from syngas [6] and removal of SO_x and NO_x from FCC effluents [7]. These mixed oxides show basic properties, small particle size (nanoparticles), large specific surface area [3,4,8,9] and a better resistance to sintering than the corresponding supported catalysts. Since a comparison between the properties of different samples is not straightforward, a single quantitative model,

related to the physico-chemical properties, is therefore required. It will follow that Sanderson's electronegativity model [10] provides us with an excellent tool for a classification of HTLCs which is based simply on the chemical composition and is intuitive and computationally non-intensive. The average electronegativity of the compound can be easily related to its various physical and chemical properties, and includes, simultaneously, the effects of $M^{3+}/(M^{2+} + M^{3+})$ ratio and cations. This model also allows us to compute the average charge borne by oxygen, since they are expected to be the basic sites of the mixed oxides.

In this work, a great variety of divalent and trivalent cations, such as Mg^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Al^{3+} , Fe^{3+} , and Cr^{3+} were employed trying to cover a great amount of promising catalysts and the application of the modified method was carried out only on binary mixed oxides.

2. Sanderson electronegativity model

Since the electronegativity (S) is defined as the power of an atom in a molecule to attract electrons to itself, a redistribution of electrons is expected when a molecule consists of atoms with differing electronegativities. Sanderson therefore introduced the principle of electronegativity equalization which is stated as: "When two or more atoms initially different in electronegativity combine, they become adjusted to the same electronegativity within the compound". This intermediate electronegativity is very satisfactorily postulated to be the geometric mean of the component atoms that make the compound formula.

For the mixed oxides derived from hydrotalcite like compounds (HTLCs) with the formula mentioned above, we can expect a formula $M_{1-x}^{2+}M_x^{3+}O_{1+x/2}$ (where $M^{2+} = Mg^{2+}$, Zn^{2+} , Ni^{2+} , Co^{2+} ; $M^{3+} = Al^{3+}$, Fe^{3+} , Cr^{3+}). So the modified intermediate electronegativity is given as

$$S_i = (S_A^{1-x} \times S_B^x \times S_O^{1+0.5x})^{\frac{1}{2+0.5x}}, \quad (1)$$

where S_A , S_B and S_O are the Sanderson's electronegativity value of atoms M^{2+} , M^{3+} and oxygen, respectively [11,12].

The partial charge can be derived as the ratio of the change in electronegativity undergone by an atom in joining the compound to the change (electronegativity equivalence method). For the oxygen atom, the partial charge (OC) is then given by

$$OC = \frac{S_i - S_o}{2.08 \times S_o^{\frac{1}{2}}}, \quad (2)$$

where S_i is the modified intermediate electronegativity and S_o is the oxygen electronegativity.

While this formalism predicts good trends in electronegativity and on oxygen partial charge, it has one disadvantage, since it does not differentiate

between an element in two different chemical environments (it does not discriminate between local and bulk composition). To overcome this drawback, Carver et al. [13] proposed a modification of the Sanderson formalism without altering the basic concept of electronegativity equalization, which will be adapted to our case, since it was used on finite compounds and HTLCs consists of infinite sheets.

To that intent we can define the local electronegativity (S_l) as below, taking into account that

$$S_l = ((S_{M(II)} \times S_O)^{0.5 \times P} \times (S_{M(III)}^2 \times S_O^3)^{0.2 \times Q})^{\frac{1}{6}}, \quad (3)$$

where P and Q are integers and its sum is equal to 6 (octahedrally bonded).

3. Results and discussion

Figure 1 shows that increasing $M^{3+}/(M^{2+}+M^{3+})$ ratio increases the intermediate electronegativity and decreases basicity, exception for the samples containing Cu(II), Co(II) and Ni(II) (higher atomic electronegativity) in which no difference was observed. In view of that results, except for the samples with Cu, Co or Ni, the change on the $M^{3+}/(M^{2+} + M^{3+})$ ratio is a good technique to increase or decrease the basicity of hydrotalcite-like compounds. One could expect that ratios lower than 0.20 should be used to increase basicity, but these ratios should originate segregated phases (such as MgO and CuO) which will favor heterogeneity and a great difference between bulk and local electronegativities.

By means of figure 2, it could be observed that oxygen partial charge showed similar trend to the one observed for intermediate electronegativity. Basic

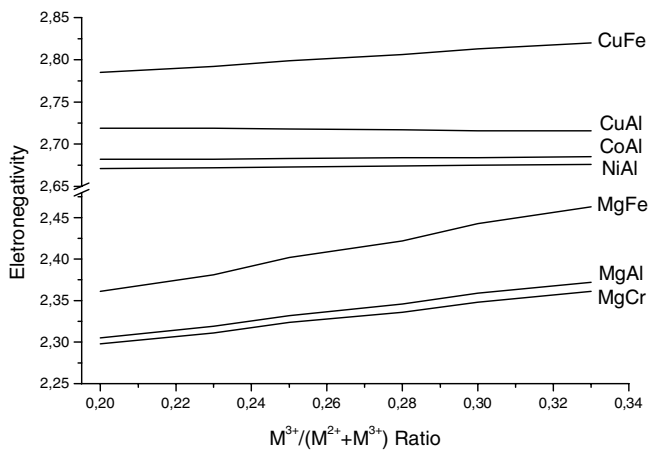


Figure 1. Influence of $M^{3+}/(M^{2+} + M^{3+})$ ratio and cations on electronegativity.

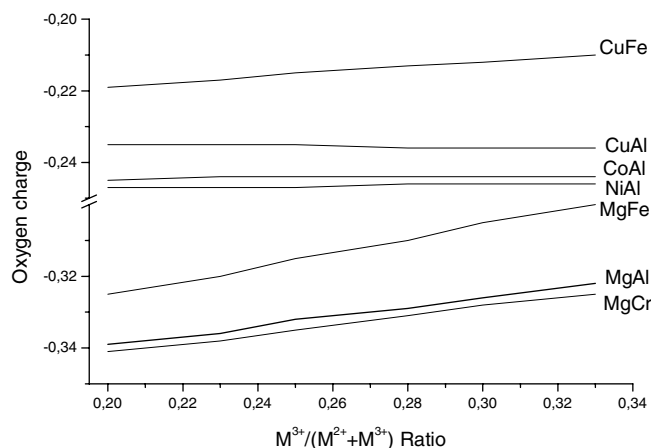


Figure 2. Influence of $M^{3+}/(M^{2+} + M^{3+})$ ratio and cations on oxygen charge.

character decreased in the order $MgCr > MgAl > MgFe > NiAl > CoAl > CuAl > CuFe$. As observed, magnesium containing oxides showed higher basicity (lower intermediate electronegativity) than the other ones, presenting higher negative oxygen charge.

As already mentioned before, the difference between local and bulk composition also affects the basicity of the oxygen atoms. Figure 3 shows for the simplest compound, the MgAl, that increasing Mg surrounding atoms increases basicity. One could expect a great number of different oxygen atoms, although, for the possible $M^{3+}/(M^{2+} + M^{3+})$ ratios, a simple statistic calculation shows that these materials usually have three main types of oxygen atoms (and of course three different basic sites) at a 0.20 ratio (Mg_6 , Mg_5Al and Mg_4Al_2 clusters)

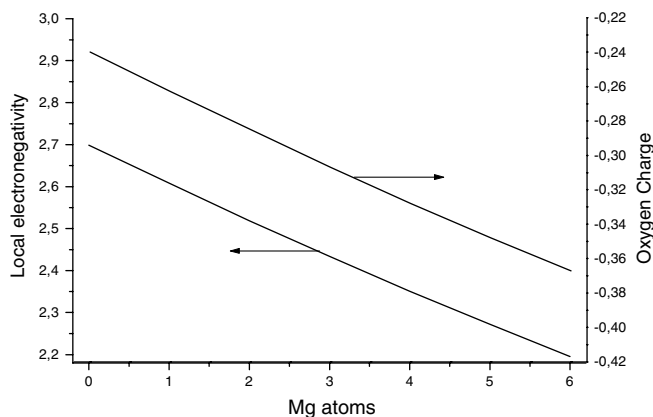


Figure 3. Influence of surrounding Mg atoms on electronegativity and on oxygen charge.

and three different oxygen atoms for samples with a 0.33 ratio (Mg_5Al , Mg_4Al_2 and Mg_3Al_3 clusters), being Mg_6 an oxygen atom surrounded by 6 magnesium atoms.

References

- [1] F. Cavani, F. Trifiro and A. Vaccari, *Catal. Today* 11 (1991) 173.
- [2] W.T. Reichle, *Chemtech.* 16 (1986) 58.
- [3] A.L. McKenzie, C.T. Fishel and R.J. Davis, *J. Catal.* 138 (1992) 547.
- [4] D. Tichit, M.H. Lhouty, A. Guida, B.H. Chiche, F. Figueras, A. Auroux, B. Bartalini and E. Garrone, *J. Catal.* 151 (1995) 50.
- [5] M.J. Martínez-Ortiz, D. Tichit, P. Gonzalez and B. Coq, *J. Mol. Catal. A: Chem.* 201 (2003) 199.
- [6] J. Li, W. Zhang, L. Gao, P. Gu, K. Sha and H. Wan, *Appl. Catal. A: Gen.* 165 (1997) 411.
- [7] A.E. Palomares, J.M. López-Nieto, F.J. Lázaro, A. López and A. Corma, *Appl. Catal. B: Environ.* 20 (1999) 257.
- [8] A.C.C. Rodrigues, C.A. Henriques and J.L.F. Monteiro, *Mat. Res.* 6 (2003) 563.
- [9] F. Rey, V. Fornés and J.M. Rojo, *J. Chem. Soc. Faraday Trans.* 88 (1992) 2233.
- [10] R.T. Sanderson, *Chemical Bonds and Bond Energy* (Academic Press, New York, 1976).
- [11] R.T. Sanderson, *J. Am. Chem. Soc.* 105 (1983) 2259.
- [12] R.T. Sanderson, *Inorg. Chem.* 25 (1986) 3518.
- [13] J.C. Carver, R.C. Gray and D.M. Hercules, *J. Am. Chem. Soc.* 96 (1974) 6851.