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Extension of the modified Sanderson method to ternary mixed oxides derived from hydrotalcite-like compounds and its correlation to CO_2 (TPD-CO_2) desorption peak maxima

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

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A simple, intuitive and computationally non-intensive modified model, proposed first for the prediction of the catalyst basicity of binary mixed oxides, based simply on the chemical composition using the Sanderson Method was extended to ternary systems. The modification of the method allows the discrimination between the oxygen charge on different chemical environments (differences between local and global composition). TPD-CO_2 result was used to the validation between theoretical values and experimental results, letting us propose a correlation between the oxygen charge of the different clusters and the TPD-CO_2 peak maxima.

KEY WORDS: hydrotalcite, basicity, mixed oxides, electronegativity, TPD-CO_2

AMS subject classification: 92E10

1. Introduction

Hydrotalcite-like compounds (HTLCs) are layered-double hydroxides (LDHs) with similar structure to that of brucite ($Mg(OH)_2$) with general formula $(M^{2+}_{1-x}M^{3+}_x(OH)_2)^{x+}(A^{m-}_{x/m})\cdot nH_2O$ (where $M^{2+} = Mg^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}$; $M^{3+} = Al^{3+}, Fe^{3+}, Cr^{3+}$ and $A = OH^-, Cl^-, NO_3^-, CO_3^{2-}$), x taking values between 0.20 and 0.33 [1]. Positively charged layers are generated by the isomorphously replacement of M^{2+} cations by M^{3+} ones with similar radius. Its electrical neutrality is attained by compensating anions located in the interlayers along with water molecules [1,2].

The mixed oxides derived from HTLCs show basic properties, small particle size (nanoparticles), large specific surface area and a better resistance to sintering than the corresponding supported catalysts. Due to that characteristics, industrial interest are increasing, being used in aldol condensation of aldehydes and ketones [3–5], glycerolisis of fats for the manufacture of monoglycerides [6], methanol synthesis from syngas [7] and removal of SO*x* and NO*x* from FCC effluents [8,9].

In this work, the modified Sanderson method developed for binary mixed oxides [10] was extended to ternary systems. That method based on Sanderson's electronegativity model [11] provides us with an excellent tool for the classification of HTLCs which is based simply on the chemical composition (the most important parameter to the performing of fine tuning of the basic strength) and is intuitive and computationally non-intensive.

This model will also let us correlate the chemical compositions to the physico-chemical properties, by a single quantitative model.

As expected, the oxygen atoms of the solid are the basic sites, and this model let us calculate the average charge borne by oxygen, knowing the chemical composition. Although all oxygen atoms are potential basic sites, only the oxygen atoms which acquire the highest negative charge have a true basic character.

In this work, it was also employed thermal programmed desorption of CO_2 (TPD-CO_2) in an attempt to validate the results obtained by the modified Sanderson method, since TPD-CO_2 it is one of the most generalized methods for base characterization, providing useful information on the strength of basic sites on a catalyst.

2. Sanderson electronegativity model for ternary mixed oxides

In a molecule consisting of atoms with differing electronegativity (*S*), the electrons will be redistributed such that they are equally attracted to the nuclei in the bond. Sanderson therefore introduced the principle of electronegativity equalization, where two or more atoms initially different in electronegativity become adjusted to the same electronegativity within the compound. This intermediate electronegativity is very satisfactorily postulated to be the geometric mean of the electronegativities of the component atoms that make the compound formula.

Extending the method to ternary mixed oxides, we should have mixed oxides derived from hydrotalcite like compounds (HTLCs) with the formula $MA^{2+}_{1-x-y}MB^{2+}_{y}MC^{3+}_{x-z}\ MD^{3+}_{z}O_{1+x/2}$ (where MA^{2+} and MB^{2+} = Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}; MC^{3+} and MD^{3+} = Al^{3+}, Fe^{3+}, Cr^{3+}). So the modified intermediate electronegativity is given as

$$S_i = (S_A^{1-x-y} \times S_B^{y} \times S_C^{x-z} \times S_D^{z} \times S_O^{1+0.5x})^{\frac{1}{2+0.5x}}. \tag{1}$$

where S_A, S_B, S_C, S_D and S_O are the Sanderson's electronegativity value of atoms MA^{2+}, MB^{2+}, MC^{3+}, MD^{3+} and oxygen, respectively.

As mentioned elsewhere [10], the oxygen partial charge (OC) is then given by

$$\mathrm{OC} = \frac{\mathrm{S_i} - \mathrm{S_O}}{2.08 \times \mathrm{S_O^{\frac{1}{2}}}}, \tag{2}$$

where $\mathrm{S_i}$ is the modified intermediate electronegativity and $\mathrm{S_o}$ is the oxygen electronegativity.

As stated for binary mixed oxides, this formalism does not differentiate between an element in two different chemical environments (it does not discriminate between local and bulk composition). That drawback was overcome by the use of a modification of the Sanderson formalism without altering the basic concept of electronegativity equalization, letting us use the model to ternary mixed oxides.

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

$$\mathrm{S_l} = \left((\mathrm{S_{MA}} \times \mathrm{S_O})^{0.5\times N} \times (\mathrm{S_{MC}^2} \times \mathrm{S_O^3})^{0.2\times M} \times (\mathrm{S_{MB}} \times \mathrm{S_O})^{0.5\times P} \times (\mathrm{S_{MD}^2} \times \mathrm{S_O^3})^{0.2\times Q}\right)^{\frac{1}{6}}, \tag{3}$$

where N, M, P and Q are integers, its sum is equal to 6 (octahedrally bonded) and they represent the atoms that surrender the oxygen atoms. As an example, an oxygen atom surrounded by six Mg cations will show N equal to 6 and M, P and Q equal to zero.

3. Experimental

The hydrotalcite-like compound used in this work was prepared by coprecipitation (higher homogeneity) at room temperature according to [12], with magnesium and aluminum nitrate at a 0.25 $\mathrm{M^{3+}/(M^{2+}+M^{3+})}$ ratio.

The mixed oxides were produced by the calcination of the HTLCs under dry air, using a heating rate of $10\,\mathrm{K\,min^{-1}}$, from room temperature to 1023 K and keeping at this temperature for 2 h.

The calcined sample was analyzed by temperature programmed $\mathrm{CO_2}$ desorption (TPD-$\mathrm{CO_2}$), carried out in a microflow reactor operating at atmospheric pressure. $\mathrm{CO_2}$ (10% in He) was adsorbed at room temperature and its desorption was carried under He atmosphere in the range 298–1073 K, using a heating rate of $5\,\mathrm{K\,min^{-1}}$ and keeping at 1073 K for 10 min. The outflowing gases were accompanied by on-line mass spectrometry using a Balzers quadrupole spectrometer (model PRISMA-QMS 200). The release of water ($m/z = 18$), carbon monoxide ($m/z = 12$ and 28) and carbon dioxide ($m/z = 12$, 28 and 44) was monitored.

4. Results and discussion

4.1. Ternary mixed oxides

Due to the higher complexity, the influence of the $M^{3+}/(M^{2+}+M^{3+})$ ratio could not be discussed in a simple way to a great number of cations, as done for the binary mixed oxides. To the evaluation of that influence, it will be used a FeAlMgHTC sample, since, as observed for binary systems, Mg containing samples were strongly influenced by the $M^{3+}/(M^{2+}+M^{3+})$ ratio [10] and also because iron is a very important element to a great number of catalysts for industrial processes.

As observed for binary samples, the increase of the $M^{3+}/(M^{+2}+M^{+3})$ ratio, for a ternary one (figure 1), increases the intermediate electronegativity and decreases basicity for all Fe/Al ratios. It can also be observed that the higher the Fe/Al ratio, the lower the basicity. Similar behavior was observed for oxygen charge (figure 2). In view of that results, the change on the $M^{3+}/(M^{2+}+M^{3+})$ ratio can also be a good technique to increase or decrease the basicity of ternary hydrotalcite-like compounds. As already mentioned for binary hydrotalcite, the use of $M^{3+}/(M^{2+}+M^{3+})$ ratios lower than 0.20 should originate segregated phases (such as MgO and Fe_3O_4) which will favor heterogeneity and a large difference between bulk and local electronegativities.

As mentioned, the difference between local and bulk composition also affects the basicity of the oxygen atoms. For the sample MgAlFeHTC (with a $M^{3+}/(M^{+2}+M^{+3})$ ratio of 0.25), statistic calculations shows more than 20

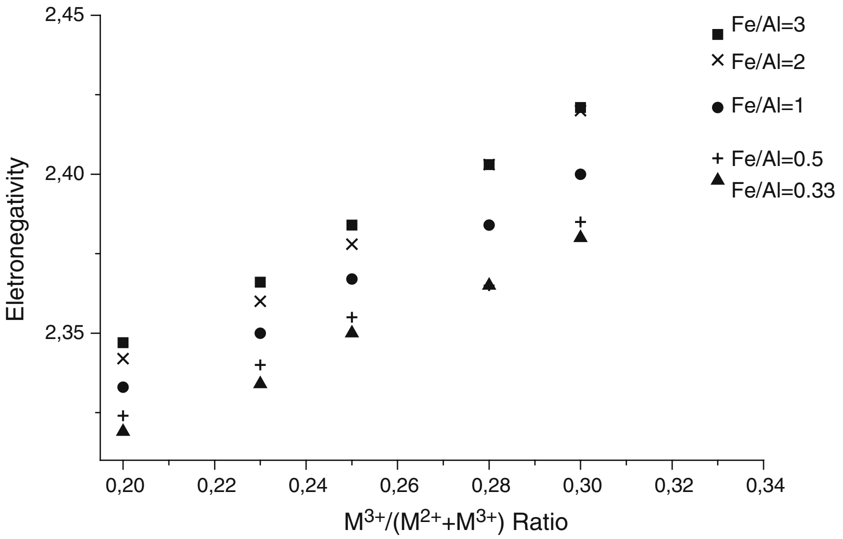

Figure 1. Influence of $M^{3+}/(M^{2+}+M^{3+})$ ratio on local electronegativity for different Fe/Al ratio.

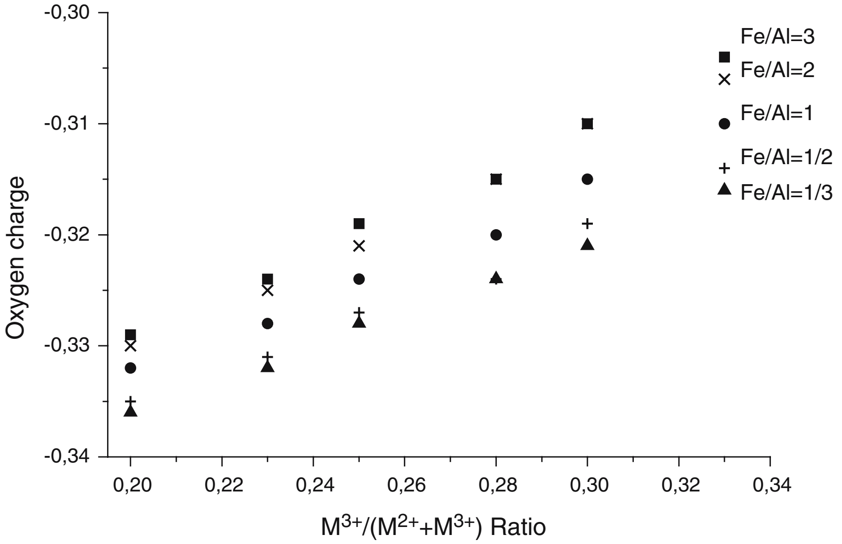

Figure 2. Influence of $M^{3+}/(M^{2+}+M^{3+})$ ratio on oxygen charge for different Fe/Al ratio.

possible local oxygen charge. The most basic clusters are show in figure 3. The local electronegativity for that sample will be given by equation 4 (obtained from equation 3).

$$S_l = ((S_{Mg} \times S_O)^{0.5\times N} \times (S_{Al}^2 \times S_O^3)^{0.2\times M} \times (S_{Fe}^2 \times S_O^3)^{0.2\times Q})^{\frac{1}{6}}. \tag{4}$$

For random incorporation, the probability of an oxygen atom be surrounded by nMg atoms, mAl atoms and $(6 - n - m)$ Fe atoms is given by:

$$P(n,m) = \frac{6!}{(6-n-m)!n!m!} \times p^n \times q^{\mathrm{m}}(1-p-q)^{6-n-m}, \tag{5}$$

where p is the probability to find Mg atoms (molar ratio between magnesium and the sum of metallic cations) and q is the probability to find Al atoms (molar ratio between aluminum and the sum of metallic cations).

To illustrate the proposed model, taking into account the iron containing sample with $M^{2+}/(M^{2+}+M^{3+})$ ratio of 0.25 and Fe^{3+}/Al^{3+} ratio of 1, p is 3/4 and q is 1/8.

Taking into account the probability of appearance of each cluster (table 1), the adsorption can take place in six different types of oxygen atoms (six different basic sites: Mg_6, Mg_5Al, Mg_5Fe, Mg_4Al_2, Mg_4AlFe and Mg_4Fe_2), with more than 5%.

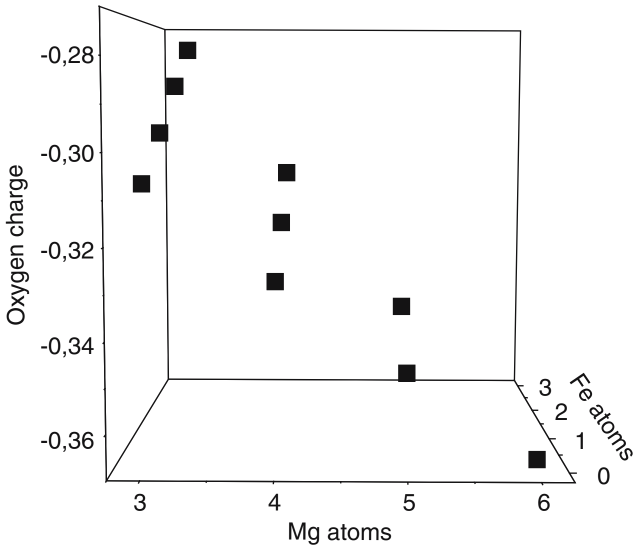

Figure 3. Influence of surrounding Mg and Fe atoms on oxygen charge.

Table 1

Cluster occurrence (theoretical probability) on ternary FeMgAlHTC with $M^{3+}/(M^{2+}+M^{3+})$ ratio equal to 0.25.

Cluster	Theoretical (%)
Mg_6	18
Mg_5Al	18
Mg_5Fe	18
Mg_4Al_2	7
Mg_4Fe_2	7
Mg_4AlFe	15
Mg_3Al_3	2
Mg_3Fe_3	2
Mg_3Al_2Fe	5
Mg_3AlFe_2	5
Remaining	3

4.2. TPD-CO_2

For the simplest compound (binary mixed oxides with Mg and Al), 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 or four main types of oxygen atoms (and of course three or four different basic sites).

For random incorporation, the probability to oxygen atom be surrounded by n Mg atoms and $(6-n)$ Al atoms is given by:

$$P(n) = \frac{6!}{(6-n)!n!} \times p^n \times (1-p)^{6-n}, \tag{6}$$

where p is the probability to find Mg atoms instead of Al atoms (molar ratio between magnesium and the sum of metallic cations).

For our intent, to validate the proposed model, a TPD-CO_2 was carried on that binary mixed oxides with $M^{3+}/(M^{2+}+M^{3+})$ ratio of 0.25, where p will be 3/4.

The results can be seen in table 2. It is clear that no more than four peaks related to different basic sites should be observed, independent of the probe used, since the clusters Mg_2Al_4, $MgAl_5$ and Al_6 (being Mg_2Al_4 an oxygen atom surrounded by two magnesium atoms and four aluminum atoms) are present at extremely low percent. It must also be pointed that besides the low percent, these clusters show higher oxygen charges (lower basicity), which must lead to a weaker adsorption.

Figure 4 shows typical TPD-CO_2 profile of the MgAlHTC sample. The desorption profile can be deconvoluted into five peaks. The first peak, at 330 K (close to the temperature used for the CO_2 adsorption) can be attributed to weak physisorption and will not be considered in our discussion. The percent results (without the first peak) are also shown at table 2 and fit well to the theoretical values.

The basic sites were classified according to their different strengths as type I ($T_D = 371$ K), II ($T_D = 450$ K), III ($T_D = 514$ K) and IV ($T_D = 589$ K).

Since the basic strength was evaluated from the TPD-CO_2 peak temperatures, its correlation to the oxygen charge was proposed (figure 5). From that result, based on the oxygen charge, one can find the temperature of the peak maxima for any basic site.

Table 2
Cluster occurrence (theoretical probability and experimental results) on binary MgAlHTC with $M^{3+}/(M^{2+}+M^{3+})$ ratio equal to 0.25.

Cluster	Theoretical (%)	Experimental (%)
Mg_6	18	10
Mg_5Al	36	33
Mg_4Al_2	30	34
Mg_3Al_3	13	22
Mg_2Al_4	3	NO
$MgAl_5$	–	NO
Al_6	–	NO

NO – not observed.

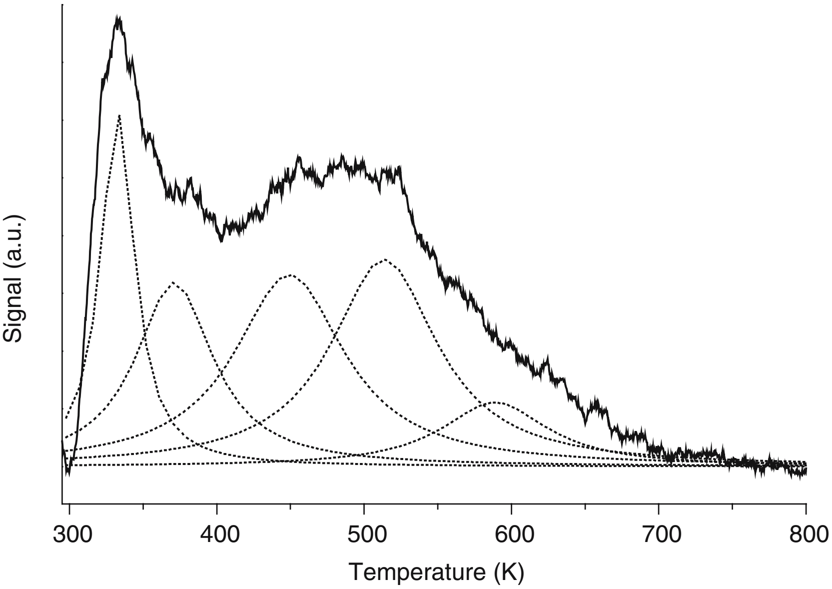

Figure 4. TPD-CO_2 of sample MgAlHTC (dot – deconvoluted peaks).

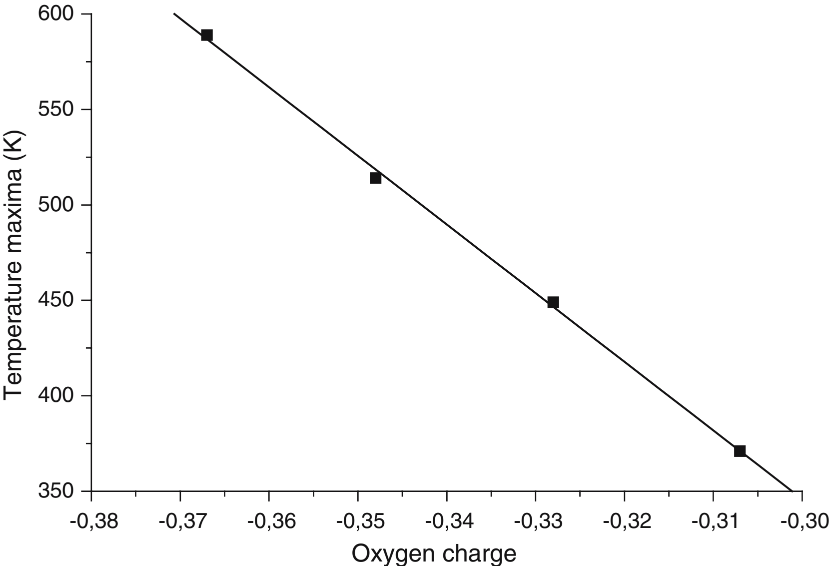

Figure 5. Correlation between TPD-CO_2 peak maxima and oxygen charge.

Taking into account the results shown in figure 5, it can also be expected that oxygen atoms with charge higher than −0.30 will not exhibit adequate basic strength to promote CO_2 adsorption.

5. Conclusion

The results made evident that the increase on $M^{3+}/(M^{2+}+M^{3+})$ ratio increased the intermediate electronegativity and decreased basicity. Oxygen partial charge showed similar trend to the one observed for intermediate electronegativity.

TPD-CO_2 profile of the MgAlHTC sample agreed with theoretical values predicted by the modified model. For a $M^{3+}/(M^{+2}+M^{+3})$ ratio of 0.25, four basic sites were observed and were classified according to their different strengths as type I ($T_D = 371\,K$), II ($T_D = 450\,K$), III ($T_D = 514\,K$) and IV ($T_D = 589\,K$). A correlation between oxygen charge and TPD-CO_2 peak maxima was also proposed, confirming that CO_2 is an adequate probe for some basic materials. By TPD-CO_2, only oxygen atoms with charge lower than -0.30 can be considered. For oxygen atoms with charge higher than -0.30, other probes should be used.

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