ACID–BASE PROPERTIES OF MgCuAl MIXED OXIDES

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Abstract

MgCuAl layered double hydroxides (LDHs) with a hydrotalcite like structure containing different proportions of Mg^{2+} and Cu^{2+} cations have been prepared. Thermogravimetry and X-ray diffraction data indicated that the transformation of LDH into mixed oxides is effective after calcination at 723 K, irrespective of the composition. The acid–base properties of these mixed oxides have been investigated using adsorption microcalorimetry and X-ray photoelectron spectroscopy with NH_3 (for acidity) and SO_2 (for basicity) as probe molecules. Their catalytic behaviour for the conversion of cyclohexanol has been tested. The acid–base properties and the selectivity of catalysts has been related to their composition.

Keywords: acidity, basicity, cyclohexanol conversion, layered double hydroxides, MgCuAl mixed oxides, microcalorimetry, XPS

Introduction

LDHs (layered double hydroxides) belong to the large class of natural and synthetic anionic clays. These materials crystallise in a layer-type lattice and are characterised by the following formula: $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$ with $M(II)=Mg^{2+}$, Cu^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}…, $M(III)=Al^{3+}$, Cr^{3+}, Fe^{3+}… and $A^{n-}=CO_3^{2-}$, NO_3^{2-} ….[1]. The thermal decomposition of these materials gives rise to mixed oxides of industrial interest in heterogeneous catalysis [1, 2] because of their acid–base and/or redox properties, their homogeneous composition, their resistance to sintering…This paper deals with LDHs containing Mg^{2+} and/or Cu^{2+} as divalent and Al^{3+} as trivalent cations.

In a previous work [3], we investigated the influence of the presence of Ni cations, besides Mg^{2+}, in LDH stuctures on the properties of precursors and the calcined materials. This study revealed an increase of the concentration and strength of acid sites with the nickel content and evidenced the synergetic effect of the magnesium and nickel cations on the basic properties. So, in this work we replaced nickel cations by copper ones in order to establish a correlation between the composition, the struc-

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tural characteristics and the activity of these catalysts. The activity of these catalysts related to their acid–base and/or redox (when they contain a reducible metal) properties, depends on their composition and the treatment conditions.

Experimental

These materials were synthesised by coprecipitation under low supersaturation (the precipitants –NaOH, Na_2CO_3– and metal nitrates were added slowly at a constant pH of 9). The samples are labelled according to their atomic ratios in magnesium, copper and aluminium LDH structure. The M(II)/M(III) ratio is closed to 2, while the relative proportion of Mg and Cu are variable in order to study the influence of the neighbourhood of M(II) cations on the properties of the materials.

After calcination at 723 K (2 h), the adsorption of NH_3 and SO_2 over mixed oxides was performed at 353 K under helium flow. The samples were then analysed by XPS (SSI spectrometer coupled to a glove box) at ambient temperature. The heats of adsorption were measured with a Tian Calvet (C80 from Setaram) microcalorimeter linked to a volumetric line allowing the introduction of small doses of reactive gaseous probes (NH_3, SO_2) at 353 K, until a final equilibrium pressure of 67 Pa. The irreversibly chemisorbed amount (Virr) is the difference between the primary and the secondary isotherms obtained after desorption under 10^{-4} Pa at 353 K and readsorption of the gas under an equilibrium pressure of 27 Pa.

The TPR (Temperature Programmed Reduction) experiments were carried out in a flow system (GIRA, X-Sorb model) equipped with a TCD (Thermal Conductivity Detector). The experimental profiles were obtained by sending a H_2 (5%)/Ar (95%) mixture onto about 100 mg of sample with a heating rate of 10 K min^{-1}

The catalytic reactions were run in a pulse type microreactor (stainless steel, inner diameter 3.5 mm, and length 80 mm) containing 20 mg of catalyst with particle size of 0.25–0.43 mm. 0.1 µL of cyclohexanol was injected under nitrogen flow (20 mL min^{-1}, 250 kPa) at a constant temperature (648 K). The reaction products were analysed by an on-line GC equipped with FID or TCD and computing integrator, using various columns.

Results and discussion

The chemical composition (ICP-AES) of the LDH precursors is reported in Table 1.

As reported in the literature [2, 4–6], the TG and XRD analyses (not included in this paper for a non-exhaustive presentation, but we have to mention that all the samples were pure and fully crystalline hydrotalcite-like materials, except sample MgCuAl 0/2/1 which showed traces of malachite) indicate that the conversion of layered double hydroxides into poorly crystallised oxide materials (MgO and CuO) is considered as effective at 723 K whatever the sample composition. Therefore, the properties of the synthesised materials have then been studied after calcination at this temperature.

Table 1 Elemental composition (ICP-AES) of the studied LDHs

Usual name	Formula
0/2/1	$[Cu_{0.68}Al_{0.32}(OH)_2](CO_3^{2-})_{0.25}\cdot0.98H_2O$
1/1/1	$[Mg_{0.40}Cu_{0.30}Al_{0.30}(OH)_2](CO_3^{2-})_{0.20}\cdot6.69H_2O$
1.67/0.33/1	$[Mg_{0.54}Cu_{0.13}Al_{0.34}(OH)_2](CO_3^{2-})_{0.21}\cdot1.54H_2O$
0.33/1.67/1	$[Mg_{0.12}Cu_{0.56}Al_{0.32}(OH)_2](CO_3^{2-})_{0.21}\cdot3.59H_2O$

The acidic and basic properties of catalysts has been characterised with the help of two physico-chemical techniques, microcalorimetry and X-ray photoelectron spectroscopy (XPS) already used for the study of the acidity and the basicity of oxides [7–12], as well as with the help of a test-reaction, namely the catalytic conversion of cyclohexanol. The acidic character of solids has been followed by ammonia adsorption. In our case, the materials contain residual carbonates (discussed at the end of this paper) after calcination, so the basic properties have been analysed using SO_2 as acidic probe rather than the more commonly used CO_2. Sulphur dioxide is a stronger acid than carbon dioxide, so it displaces the last one partly and the presence of strong basic sites is better detected by SO_2 than by CO_2 [2]. The data of this study are compared with the results obtained about the cyclohexanol conversion. With acid assistance [13], this reaction leads to cyclohexene (dehydration), while, with a concerted mechanism (acidic and basic centres) [14], the cyclohexanol is converted in cyclohexanone (dehydrogenation):
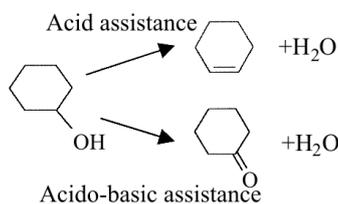
Scheme 1

Acid properties

The differential heats of NH_3 adsorption as a function of the ammonia uptake for the MgCuAl mixed oxides are reported in Fig. 1. The curves decrease relatively fast from an initial value included between 110 and 155 kJ mol^{-1} down to 70 kJ mol^{-1} (value usually considered as the chemisorption–physisorption limit) with the exception of MgCuAl 0/2/1 which shows only few acid sites. The amount of adsorbed ammonia associated to differential heats higher than 70 kJ mol^{-1} follows the same order as the amount of acid sites measured by the irreversibly adsorbed amount (V_{irr}) of ammonia (Table 2).

It is maximal for MgCuAl 1/1/1 (104 µmol g^{-1}) and decreases for MgCuAl 1.67/0.33/1 (74 µmol g^{-1}) and MgCuAl 0/2/1 (44 µmol g^{-1}). This study shows that the most important concentration of acid sites is achieved for the composition
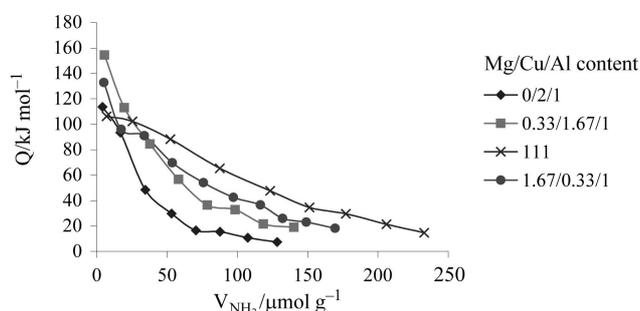
Fig. 1 Variation of the differential heat of NH_3 adsorption *vs.* adsorbed NH_3 amount

MgCuAl 1/1/1, although the other samples seem to have some stronger acid sites corresponding to the initial adsorption heats.

XPS analyses allow to identify the nature of acid sites on the solid surface. According whether an ammonia molecule reacts with a Brönsted or Lewis site, the neighbourhood of its nitrogen atom is modified differently. The former leads to the formation of an ammonium ion characterised by a N1s binding energy higher than 402 eV [7, 8]. The Lewis acid is defined as an acceptor of electronic doublet and the N1s binding energy for chemisorbed ammonia on this site is lower than 401 eV. In our case, the adsorption of ammonia reveals only the presence of Lewis sites, as the N1s binding energy is about 400 eV.

Table 2 Irreversibly chemisorbed NH_3 and SO_2 amount (V_{irr}) at 353 K

MgCuAl content	V_{irr} (NH_3)/µmol g^{-1}	V_{irr} (SO_2)/µmol g^{-1}
0/2/1	44	56
0.33/1.67/1	55	137
1/1/1	104	262
1.67/0.33/l	74	228

As regards the test reaction, we could note that the calorimetric data are in agreement with the catalytic results (Fig. 2) indicating (except for MgCuAl 0/2/1) the same order for the selectivity towards cyclohexene. Thus, this selectivity seems to follow the amount of weak and medium acid sites and to be a good catalytic test for the study of acidity of solids. Note that concerning MgCuAl 0/2/1 which does not follow this order, our XRD analysis, in agreement with the literature [1], indicates two phases (LDH and malachite) before calcination due to Jahn Teller effect and two types of copper oxide after calcination. These two kinds of copper oxide are evidenced by TPR curves (discussed below in the text – Fig. 5a) where the peak at low temperature (reduction of Cu^{II}) may be decomposed into two components.
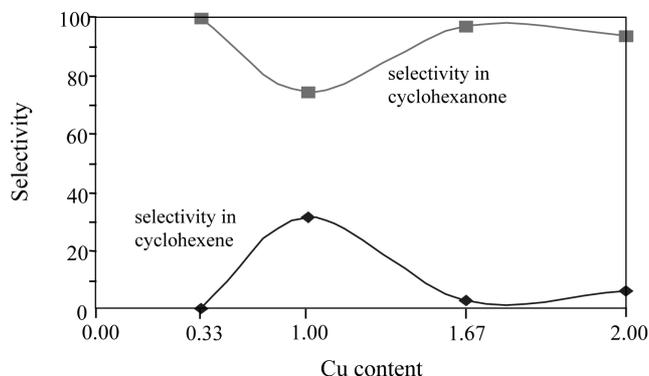
Fig. 2 Conversion of cyclohexanol: evolution of the selectivity towards cyclohexene
and cyclohexanone with the catalyst composition

Basic properties

Figure 3 shows the differential heats of SO_2 adsorption *vs.* coverage. The evolution of the adsorption over basic sites is evidently a function of the magnesium content. The initial heats are in the range of 190–200 kJ mol^{-1} except for MgCuAl 1/1/1 (170 kJ mol^{-1}). These curves show a quasi plateau in the range 150–170 kJ mol^{-1}, corresponding to the homogenous medium basic sites, with a concentration and a strength increasing with magnesium content. At 70 kJ mol^{-1}, the amount of SO_2 adsorbed follows the same order as the concentration of basic sites. It is the most important for MgCuAl 1/1/1 oxide, as well as for the Mg-rich catalyst, as confirmed by V_{irr} values. Indeed, V_{irr} decreases from 262 and 228 μmol g^{-1} for respectively MgCuAl 1/1/1 and MgCuAl 1.67/0.33/1 materials to 137 and 56 μmol g^{-1} for MgCuAl 0.33/1.67/1 and MgCuAl 0/2/1.
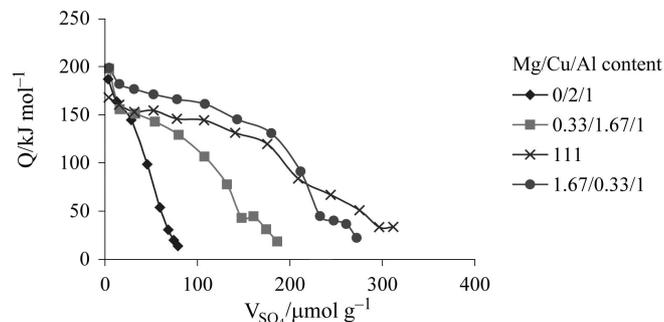
Fig. 3 Variation of the differential heat of SO_2 adsorption *vs.* adsorbed SO_2 amount

This phenomenon is confirmed by XPS analyses (after SO_2 adsorption). Note that the curves fit for core peaks were obtained using fixed amplitude ratio ($2p^{3/2}/2p^{1/2}$=2), fixed spin-orbit split (1.2 eV) and fixed FWHM (full width at half maximum: 1.9 eV) deduced from the analysis of reference compounds. A minimum number of doublets has al-
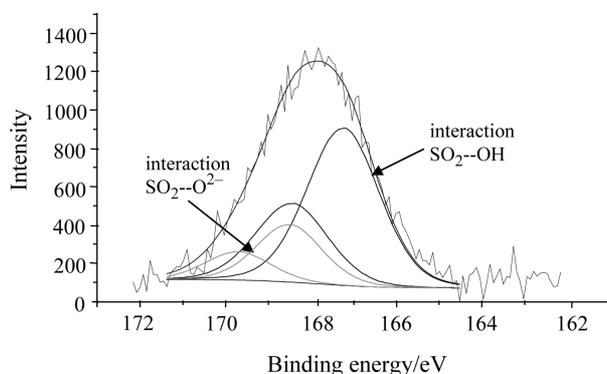
Fig. 4 Example of S2p peak of sulphur atom after SO$_2$ adsorption

ways been used in order to fit the experimental curves. An example of S2p peak is reported in Fig. 4. This peak is decomposed into two doublets (2p$_{3/2}$–2p$_{1/2}$) irrespective of the sample composition. The first one appeared between 166 and 167.5 eV and the second one between 168 and 169 eV. The first doublet can be assigned to the interaction of SO$_2$ molecules with hydroxyl (OH$^-$) surface groups. Indeed, after adsorption of SO$_2$ over LDH before calcination (SO$_2$ on hydroxyl groups), S2p$^{3/2}$ peak is located between 166.9 and 167.2 eV depending on the LDHs composition. The second doublet corresponds to SO$_2$ in interaction with O^{2-} anions (168–169 eV) [11]. The relative proportion of these components (respectively 75 and 25 %) shows that the main part of the basicity is due to the surface OH groups. Furthermore, the XPS calculated ratio S/Al follows this order:

$$MgCuAl\ 1/1/1 > 1.67/0.33/1 > 0.33/1.67/1 > 0/2/1$$

$$0.15 > 0.13 > 0.09 > 0.06$$

This evolution is in agreement with the calorimetric data and underlines that the concentration of surface basic sites is the most important for the Mg-rich catalysts.

Table 3 XPS S/Al ratios of MgCuAl catalysts after adsorption of SO$_2$ at 353 K

	MgCuAl catalyst			
	0/2/1	0.33/1.67/1	1/1/1	1.67/0.33/1
S/Al	0.06	0.09	0.15	0.13

The selectivity towards cyclohexanone (Fig. 2) is much more important than that towards cyclohexene (twice in the case of the Mg/Cu/Al 1/1/1 compound) which agrees with the microcalorimetric analyses (the concentration of basic sites is higher than of acid centres). Moreover, this reaction reveals that the lowest selectivity to cyclohexanone is obtained with the MgCuAl 1/1/1 catalyst. This reaction needs an acid–base mechanism and thus we can not directly correlate the basicity to the catalyst results. Then, the difference between physico-chemical and chemical results could be explained by the important

acid character of this material and/or by the lack of strong basic sites as indicated by microcalorimetry (for the Mg/Cu/Al 1/1/1 compound, the initial heat of adsorption is around 170 kJ mol^{-1} instead of 190–200 kJ mol^{-1} for other compositions). The presence of residual carbonates at the chosen calcination temperature could also justify this low selectivity.

In order to verify this hypothesis, we have examined the amount of residual carbonates by temperature programmed reduction (TPR). The curves show two reduction peaks (Fig. 5). The first one at low temperature (190–200°C) is attributed to the reduction of Cu^{2+} in agreement with the literature [15], while the other one appearing for Mg-rich samples at about 600°C, corresponding to the reduction of residual carbonates. This study highlights an important proportion of these anions in MgCuAl 1/1/1 compared to Cu-rich materials. Carbonate anions could partly cover the strongest basic sites, preventing them from being active for cyclohexanol conversion.
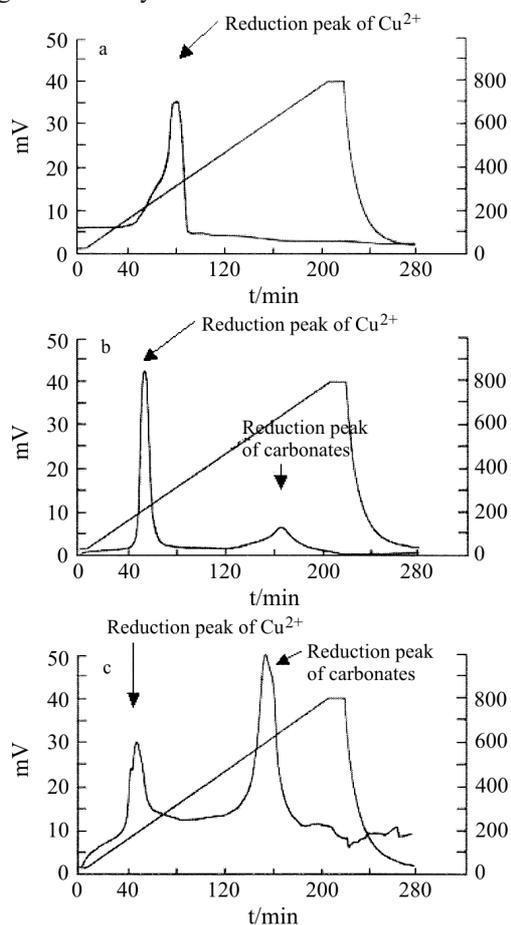
Fig. 5 TPR curves of MgCuAl mixed oxides; a – MgCuAl 0/2/1; b – MgCuAl 1/1/1; c – MgCuAl 1.67/0.33/1

Conclusions

In this work, the acid–base properties of several MgCuAl mixed oxides resulting from LDH decomposition at 723 K have been investigated.

The adsorption data indicate an optimum of the concentration and strength of acid sites for MgCuAl 1/1/1 material. The irreversibly adsorbed volume of NH_3 follows the same evolution and this oxydic material presents a maximal acidity compared to others. XPS analyses reveal the nature of acid sites (Lewis). These results obtained by the means of the physico-chemical methods agree with the results obtained from the catalytic conversion of cyclohexanol to cyclohexene: the MgCuAl 1/1/1 catalyst presents the highest selectivity to cyclohexene. XPS and microcalorimetry data indicate that the basicity (number and strength) is the most important for Mg-rich samples. The decomposition of XPS band S2p suggests that the main part of the basicity is due to the remaining OH groups on the surface. The concentration of basic sites is much more important than that of acidic sites, in agreement with the catalytic results. The MgCuAl 1/1/1 catalyst only has a low selectivity to cyclohexanone. Referring to the basic properties, the apparent discrepancy between the physico-chemical and catalytic results comes from the higher selectivity to cyclohexene and could be due partly to the presence of residual carbonates evidenced by the temperature programmed reduction experiments.

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