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Basic properties of MgLaO mixed oxides as determined by microcalorimetry and kinetics

A. Desmartin-Chomel, B. Hamad, J. Palomeque [1], N. Essayem, G. Bergeret, F. Figueras *

Institut de recherche sur la catalyse et l'environnement de Lyon, UMR5256 CNRS-UCB, 2 av. A. Einstein, 69626 Villeurbanne, France

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ABSTRACT

The surface properties of magnesias and of La oxides supported on MgO and MgAl hydrotalcites were compared, using the adsorption of carbon dioxide followed by microcalorimetry. The differential heat of adsorption of CO_2 as a function of coverage is the same for MgO of different surface areas, ranging from 30 to 590 m^2/g, showing that the average coordination of Mg does not change, in agreement with the results reported for the structure of these materials. In the case of La catalysts, an effect of the support is noticed on the distribution of basic strengths, with a higher basicity for MgLa mixed oxides. MgAlLaO mixed oxide is also a strong solid base in spite of much lower La content. These catalysts are active for the transesterification of soybean oil with methanol at 338 K, using a ratio methanol/oil = 6, and give a rate comparable to that reported for anchored guanidines, considered as superbases.

1. Introduction

In the general definition of acid–base properties, acid centres are positive charges and basic sites are negatively charged species. At a surface of oxides, or fluorides, both sites coexist with the presence of cations and anions (OH, lattice oxygen, fluoride). The basic strength is related to the density of charge, which can be calculated from Sanderson's theory of electronegativity [1], or determined by XPS [2]. This model applies to zeolites exchanged by alkaline cations [3,4], oxides [5], and hydrotalcites of different compositions [6]. This simple model predicts that strong bases are to be found among large cations of low electronegativity, for instance Cs or La compounds, and could account for the higher basicity of hydrotalcites exchanged for butyrate or fluoride anions [7]. For simple oxides such as MgO and CaO, the basic sites have been identified to lattice defects on the basis of both experimental results [8,9] and quantum chemical calculations [10]. These sites are more numerous on small crystals, therefore a well dispersed La oxide supported by MgO could also be a strong base, since a high dispersion is then expected. Indeed, pure La oxides show low surface area, typically 10–15 m^2/g, when prepared from hydroxides by thermal treatment at 673 K in vacum [11]. Hydrotalcite containing rare earths have been recently reported [12]: a solid of average composition $Mg_{0.75}Al_{0.23}La_{0.02}$ was prepared which showed practically the same number of basic sites as the parent MgAl hydrotalcite, with however a lower number of strong basic sites. In spite of a low La content, this solid was biphasic, due to the size of La^{3+} cation, bigger than Al^{3+}.

By contrast, samples obtained by coprecipitation of Mg and La, calcined at 923 K, exhibited the same catalytic properties for Michael reactions, as a $P(CH_3NCH_2CH_2)_3N$ proazaphosphatrane superbase [13]. The surface area of this mixed oxide was about 38 m^2/g, and a better dispersion of La_2O_3 was expected using a ternary MgAlLa oxide, since the surface area of hydrotalcites is about 230 m^2/g.

We report here the preparation of Mg–La–O and Mg–Al–La–O catalysts by coprecipitation from nitrate solutions. The basic properties were measured by microcalorimetry using CO_2 as probe molecule, and La catalysts were compared to a MgO aerogel of high surface area [14], the basic properties of which have been extensively investigated [15–19]. The La oxides are precipitated using KOH, and extensively washed, but still contain residual K, and we have investigated the effect of the K content on the basic properties. The basic properties are best demonstrated by the catalytic properties, using organic reactions of known mechanism, for instance Michael additions or transesterification. The choice of substrates of high pK_a permits to probe the reactivity of the sites of higher basicity.

2. Experimental

La promoted Mg and Mg–Al catalysts were prepared by coprecipitation at constant pH, at room temperature by mixing a 1 M nitrate solution of $Mg(NO_3)_2 \cdot 6H_2O$, $La(NO_3)_3 \cdot 6H_2O$ and

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* Corresponding author. Tel.: +33 4 7244 5399; fax: +33 4 7244 5399.
E-mail address: francois.figueras@ircelyon.univ-lyon1.fr (F. Figueras).

[1] Present address: Instituto Mexicano del Petroleo, Eje Central 152, CP 07730, Mexico DF, Mexico.

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Table 1
Chemical analysis of lanthanum catalysts.

Catalyst	Mg (%)	La (%)	Al (%)	C (%)	Theoretical ratio M^{II}/M^{III*}	Real ratio M^{II}/M^{III*}	La anal in M^{III} (mol%)	Crystal size La carbonate (nm)
Mg–La-2	12.8	39.4	–	4.5	2	1.86	–	40
Mg–La-3	6.4	52.6	–	3.9	3	0.69	–	80
Mg–La-4	7.6	49.5	–	4.0	4	0.88	–	65
Mg–La-10	5.5	52.1	–	4.7	10	0.61	–	45
Mg–La-20	9.9	45.2	–	4.4	20	1.25	–	80
Mg–Al–La-5	18.3	2.2	11.9	2.6	2	1.65	3.5	–
Mg–Al–La-10	18.1	4.5	11.4	2.7	2	1.64	7.1	50
Mg–Al–La-20	17.7	8.8	9.6	3.0	2	1.73	15.1	50
Mg–Al–La-50	14.6	21.5	5.9	3.6	2	1.63	42.1	50

* M^{III} = La or Al + La.

$Al(NO_3)_3$, with a solution of KOH 0.5 M and K_2CO_3 0.5 M. The solution of nitrates was added at controlled velocity of 2 ml/min, and the basic solution added in order to maintain the pH of the resulting solution at 9. After precipitation, the temperature was raised to 353 K, maintained for 18 h. The solids were filtered, washed with warm deionized water and dried at 393 K for 12 h. The samples (about 0.15 g) were activated at 923 K in an air flow, using a temperature ramp of 10 K/min. Just before use, they were reactivated at 773 K in air and not rehydrated.

The magnesium oxides used were a commercial MgO (Aldrich) denominated CM-MgO (30 m^2/g), a NA-MgO sample (SSA: 250 m^2/g) prepared by decomposition of $Mg(OH)_2$, and an aerogel denominated NAPMgO (SSA: 590 m^2/g), obtained as reported by Klabunde et al. [14], who reported a careful characterization of the structure.

The solids were analysed by ICP after dissolution by acid attack. The surface areas were determined from the isotherms of adsorption of N_2 at 77 K using the BET equation. X-ray powder diffraction patterns were recorded on a Phillips instrument using Cu Kα_1 radiation. The isotherm for N_2 adsorption at 77 K was determined on solids activated at 723 K in N_2 or air, then desorbed in situ in vacuum. Basicities were characterized by microcalorimetry using CO_2 adsorption at 303 K with a Tian–Calvet calorimeter on samples activated in vacuum at 723 K [20]. In a few cases the basic properties were estimated by analysing the amount of CO_2 contained in the effluents during the thermal analysis of a solid, using a TGDT A92 from SETARAM coupled with a mass spectrometer.

The transesterification of soybean oil was investigated in a 50 ml glass flask, heated by an oil bath, at the boiling point of the alcohol. 0.3 g of catalyst freshly activated were added to 9.42 g of alcohol and 10 g of oil, and the slurry was stirred for several hours. At the end of the reaction, the catalyst was filtered out and the whole reaction mass was dissolved in THF. An aliquot was taken, octadecane was added as external standard and the mixture analysed by GPC. The mass balance was usually better than 90%.

3. Results and discussion

The chemical compositions of MgLaO and MgAlLaO samples are reported in Table 1. The DRX patterns reported in Fig. 1 show that Mg–LaO is composed of a mixture of small amounts of brucite (hexagonal $Mg(OH)_2$) with orthorombic La hydroxy-carbonate (ancylite ($La(CO_3)_2(OH){\cdot}H_2O$). The size of the crystals of La carbonate is about 40 nm on MgLa-2 and tends to increase with the La content, reaching about 80 nm on MgLa-20. The DRX patterns of Mg–Al–LaO solids, reported in Fig. 2, contain not brucite, but hydrotalcite mixed with ($La(CO_3)_2(OH){\cdot}H_2O$, the content of which increases with the La content. Hydrotalcite structure HT-13 prepared and characterized elsewere [21] has been added for comparison in this figure. In that case, the size of the crystals of La carbonate is about 50 nm, independent of the La content. From this XRD analysis, both MgLaO and MgAlLaO appear then as composites containing a carbonated La hydroxide. After calcination, the La phase consists mainly in hexagonal La_2O_3, of crystal size of about 20 nm.

The textural analysis of La catalysts is reported in Table 2. Mg–La-2 shows the highest pore volume (0.27 cm^3/g) in in this series. The surface area decreases with the La content, and Mg–La-3 shows the lowest superficial area, 13.1 m^2/g. The same tendency is appreciated for pore volume with a higher value of 0.74 cm^3/g for Mg–Al–La-5 and attributed to the highest aluminium content. It has to be emphasized that the surface area of the solid decreases significantly when the % La increases. This suggests that some solid

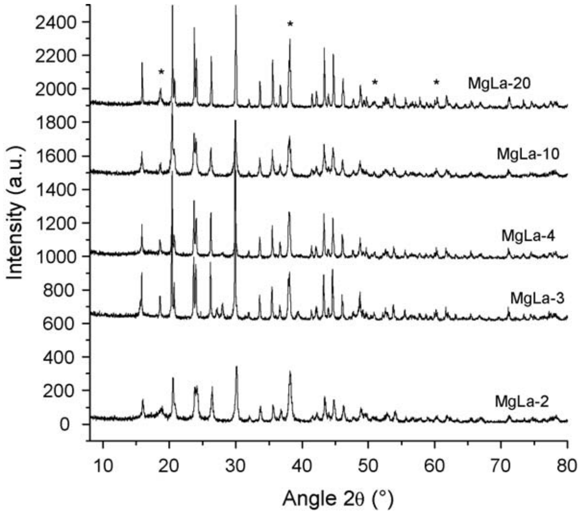

Fig. 1. DRX in Mg–La series; the lines relative to magnesia are marked by an asterisk.

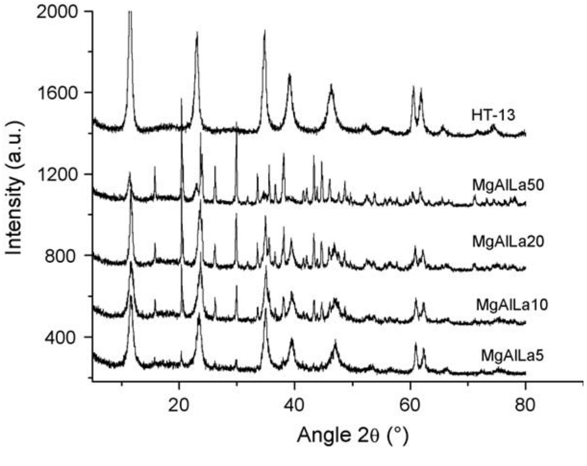

Fig. 2. DRX patterns of MgAlLa samples.

Table 2
Textural analysis of the La catalysts.

Catalyst	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Mg–La-2	57.5	0.3	3–5
Mg–La-3	13.1	0.0	3–5
Mg–La-4	21.6	0.1	5–9
Mg–La-10	53.6	0.1	2–5
Mg–La-20	54.8	0.1	2–5
Mg–Al–La-5	184.0	0.8	5–10
Mg–Al–La-10	181.8	0.8	5–10
Mg–Al–La-20	71.5	0.4	4–19
Mg–Al–La-50	63.0	0.3	3–14

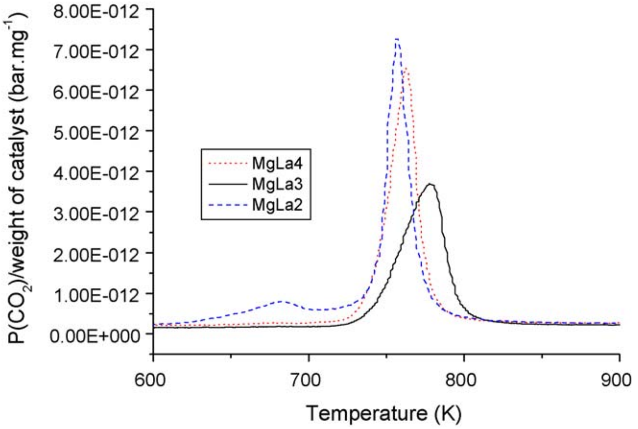

Fig. 3. Temperature programmed desorption of CO_2 followed by mass spectrometry for MgLa samples.

phase reaction occurs between the La oxide and hydrotalcite. These characterizations suggest that both systems consist of a layer of La oxide supported by MgO or hydrotalcites.

The basic properties have been determined by TPD of CO_2 using mass spectrometry (Fig. 3), and microcalorimetry using CO_2 adsorption. The TPD of CO_2 shows small differences between the MgLa samples, with a higher strength for MgLa-3. Due to this result, MgLa-3 only was further investigated. The calorimetric results are reported in Fig. 4 for MgO of different surface areas, and Figs. 4 and 5 for La catalysts. The values of the enthalpies of adsorption on the pure oxides are those reported by Auroux and Gervasini [5] for La oxide and for a MgO sample of surface area 200 m^2/g. Concerning the amount of CO_2 adsorbed, a linear increase with the surface area is observed for MgO samples, while La catalysts adsorb much less, whatever their surface area, and therefore show a lower number of sites, close to that of MgO of low surface area.

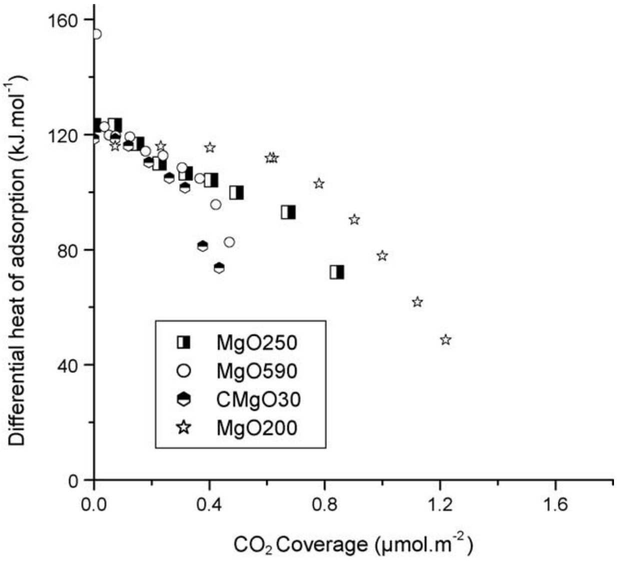

Fig. 4. Differential heats of adsorption for MgO samples of different surface area.

All MgO samples show a rather homogeneous surface, with a small variation of the heat of adsorption with the coverage. The differential heat is the same for the different MgO, leading to the conclusion that the type of site is also the same: changing the surface area of magnesia (with the type of preparation used) does change the number of sites but not their strength. MgO of high surface is a base of medium strength, comparable to fluorinated hydrotalcite. This result does not contradict the proposal that the base strength changes with the coordination of Mg, since the examination of these high surface area MgO shows an octahedral shape, with well-defined surface planes [14]. In that case the more basic sites are the corner and edge sites, which are not different from those found on larger particles.

The differential heat of adsorption of La catalysts shows higher variations, i.e. the surface is much less homogeneous. As shown in Fig. 5, evacuation at 923 K, increases the number of strong sites but not the differential heat. Therefore this temperature is not high enough to create defects which could have been strongly basic sites. It can be pointed out that the differential heat reaches however about 160 kJ mol^{-1}, a value reported by Bordawekar and Davis [22] for NaN_3 loaded on NaY zeolites.

On MgAlLaO oxides the heat of adsorption increases with the La content of the solid. As reported above, the modification of the surface area of hydrotalcite upon the addition of La suggests a reaction of La with the surface, can account for a partial inhibition of the basic properties at low La content. Differential energies of about 150 kJ mol^{-1} are obtained for La contents of 21.5 wt%, on MgAlLaO mixed oxides, as well as on MgLaO containing 52 wt% La (Fig. 6). Due to a higher surface area of the supported sample, the number of sites is however increased. This is interesting from the practical point of view since a reduced amount of La still yields a strong base. It was indeed expected that a higher surface area would correspond to a better dispersion of La oxide, but the basic strength of these catalysts is comparable to that of pure La oxide, and it can be concluded that the dispersion reached is not enough to decrease significantly the average coordination of La cations. This is in agreement with the relatively large size of the crystals estimated from XRD measurements.

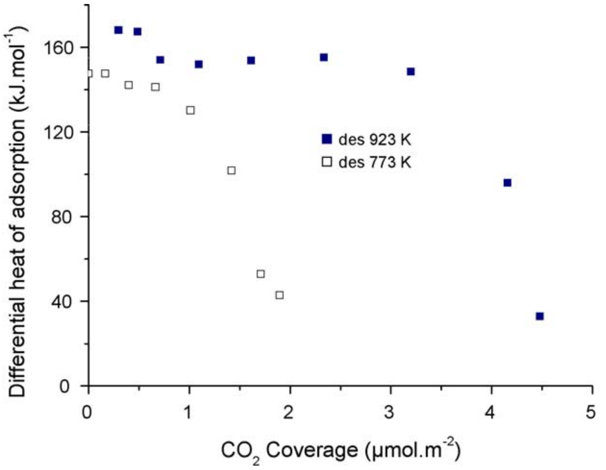

Fig. 5. Effect of the evacuation temperature on the basic strengths of MgLaO-3 mixed oxide.

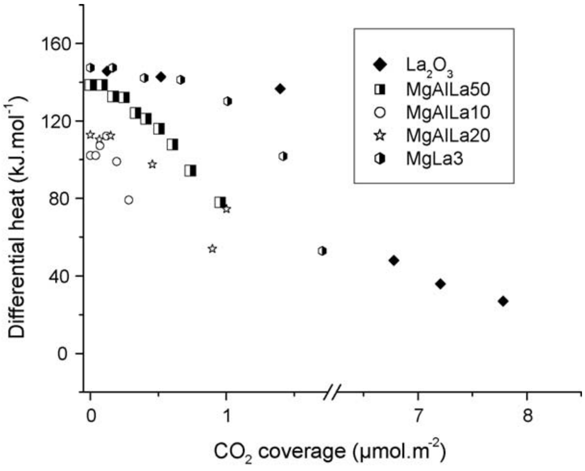

Fig. 6. Distribution of basic strengths for La catalysts.

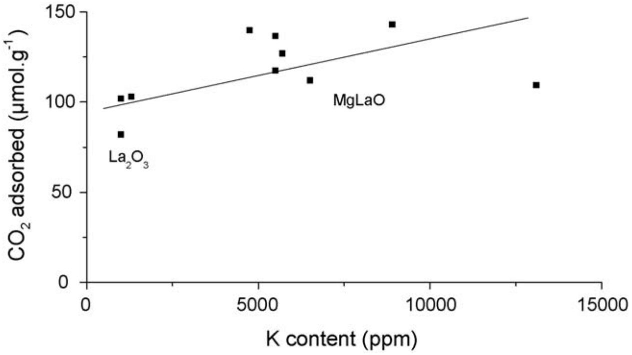

Fig. 7. Effect of K content on the number of basic sites of La and MgLaO oxides.

The solids retain small amounts of K after washing, and the effect of these residual cations on basicity was investigated measuring the CO_2 adsorption on samples containing different levels of K. The results are reported in Fig. 7, in which the amount of CO_2 adsorbed is plotted against the K content of a series of La (the three points at low K content) and MgLa oxides (all other points). The K content was varied by the number of washings. There is indeed a small contribution of the K content to the number of basic sites, but the main contribution is due to La oxide. The heat of adsorption reported in Fig. 8, shows that the K content is not directly correlated to the heat of adsorption. K cations are then probably trapped into the lattice and not accessible.

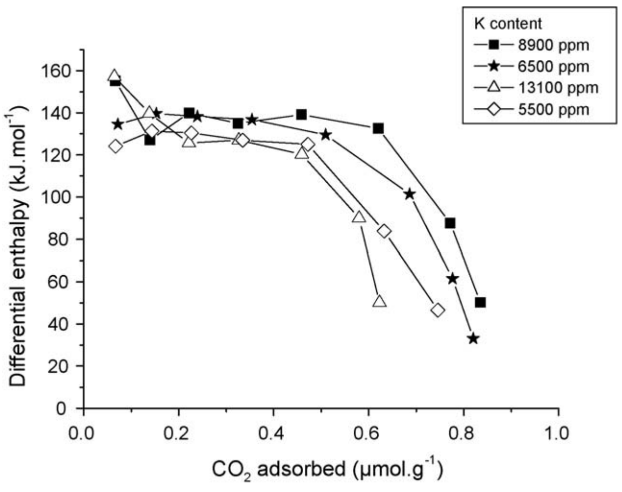

Fig. 8. Effect of the K content on the differential heat of adsorption of CO_2 on MgLa oxides.

The high basicity of MgLaO mixed oxides is confirmed by their catalytic properties. Earlier work had shown that these solids catalyse the reaction of chalcone with nitromethane ($pK_a = 17.2$), in a ratio of substrates 1:1, at room temperature, at a rate similar to that reported for phosphatrazanes super bases [13]. At room temperature, they give good yields for the aldol-type condensation of aldehydes and imines with ethyl diazoacetate (EDA) in water as solvent, giving β-hydroxy-α-diazo carbonyl compounds and β-amino-α-diazo carbonyl compounds. The catalyst could be recovered and reused for several cycles with consistent activity [23].

The catalytic properties for the transesterification of soybean oil by methanol and ethanol have now been investigated on MgLaO mixed oxides. The reactions were run at 338 K with methanol (ratio methanol/oil = 6), and 352 K with ethanol (ratio ethanol/oil = 58), using 0.5 g of catalyst activated at 773 K. The yield in monoester after 5 h reaches 58% with ethanol ($pK_a = 29.8$), and 60% with methanol ($pK_a = 29$). These results can be compared with those reported by Schuchardt et al. [24] for the same reaction with methanol, performed in the same conditions of temperature and ratio of reactants, using as catalyst anchored guanidines containing a density of 0.8 mequiv. g^{-1} of active sites: the yield reached 90% after 3 h. If we take into account that MgLaO mixed oxides show only 0.01 mequiv. g^{-1} of sites (Fig. 5), the activities per active site are rather similar. Guanidines, and probably anchored guanidines, are considered to be superbases. The high catalytic properties of MgLa mixed oxides suggest that they are also superbases. Moreover, the mixed oxides are not lixiviated in the reaction medium, and are real heterogeneous catalyst that can be regenerated by calcinations if required.

4. Conclusions

A strong solid base can be obtained using hydrotalcites or magnesia as support of lanthanum oxide. Both calorimetry and catalytic tests confirm the high basic strength of these solids. For the solids using hydrotalcites as support, it can be concluded that a reaction of La with the support occurs leading to the partial loss of basic sites. These solids appear however as more basic than those described earlier [12] probably due to the higher La content. In spite of thorough washings, traces of K are trapped by La catalysts, but cannot account for their basic properties. The strong basic properties can be inferred from the high heat of adsorption of CO_2, which reaches 160 kJ mol^{-1} after outgassing at 923 K, and from the high activity for the transesterification of soybean oil with methanol. This reaction performed at 338 K with a ratio methanol/oil = 6, gives a rate comparable to that reported on superbases.

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