



Alkaline-earth-doped mixed oxides obtained from LDH nanocomposites as highly basic catalysts

Iuliana Cota^a, Eliana Ramírez^a, Francisco Medina^a, Géraldine Layrac^b,
Redouane Chebout^{b,c}, Didier Tichit^{b,*}

^a Escola Tècnica Superior d'Enginyeria Química, Universitat Rovira i Virgili, Campus Sescelades, Avda. Països Catalans 26, 43007 Tarragona, Spain

^b Institut Charles Gerhardt, UMR 5253 CNRS/ENSCM/UM2/UM1, Matériaux Avancés pour la Catalyse et la Santé (MACS), Ecole Nationale Supérieure de Chimie, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France

^c Centre de Recherche Scientifique et Technique en Analyse Physico-Chimique (CRAPC), BP248, Alger RP, Alger 16004, Algeria

ARTICLE INFO

Article history:

Available online 2 September 2009

Keywords:

Layered double hydroxides

Basicity

Catalysts

Alkaline-earth cations

2,3-Dimethyl-1-butene

ABSTRACT

The anionic exchange of the nitrate compensating anions in host Mg/Al LDH by negatively charged $[M(\text{Edta})]^{2-}$ ($M = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$) guest entities has been performed. The increase from 0.83 nm to 1.5 nm of the d_{003} interlayer distance shows that intercalation has taken place leading to well ordered lamellar materials with 3–9 wt.% of alkaline-earth (AE) cations loading. The basic properties of the M/Mg(Al)O mixed oxides catalysts obtained by thermal decomposition of the $[M(\text{Edta})]\text{-Mg/Al}$ LDH precursors have been investigated by TPD of CO_2 , FTIR spectroscopy of adsorbed CDCl_3 and catalytic test reaction of 2-methyl-3-butyn-2-ol (MBOH). The AE-containing mixed oxides exhibit higher basicity than Mg(Al)O with, particularly, a large increase of the densities of sites of medium and high strength. Remarkably, the nature of the AE cations allows to finely tune the basicity. All the AE-containing mixed oxides are able to perform the isomerization reaction of 2,3-dimethyl-1-butene (DB-1) into 2,3-dimethyl-2-butene (DB-2), the Ca-containing sample being the most active according to its larger content of strong basic sites.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

In recent years layered double hydroxides (LDH) have attracted considerable attention as precursors of environmentally benign basic catalysts able to perform many reactions of interest in fine chemical synthesis [1–4]. A main advantage of the catalysts obtained from LDH is their high specific surface area and their versatile character which allows adjusting the nature and number of sites. Besides, their basic strength is generally found moderate. In other respects, AE metal oxides are known for their high basic strength and their low specific surface areas. An interesting route would be then to incorporate AE metal ions into LDH structures in order to enhance the basic properties and the catalytic activity of the mixed oxides obtained by thermal decomposition of the AE-containing LDH precursors. However, this cannot be achieved by direct incorporation of the AE cations in the brucite-like layers, due to their too large ionic size. Therefore, an alternative procedure must be found, which can be the intercalation of negatively charged complexes containing the required AE cations. This preparation route takes advantage of the anionic exchange

capacity (AEC) and the ability to expand the interlayer space of the LDH. With this aim, hybrid materials have been synthesized by anionic exchange of host Mg/Al LDH with guest entities previously formed by complexation of Ca^{2+} , Sr^{2+} or Ba^{2+} with Edta. The basic properties of the mixed oxides obtained by thermal activation of these intercalated LDH have been investigated by means of the disproportionation reaction of 2-methyl-3-butyn-2-ol (MBOH) [5] and by FTIR spectroscopy of adsorbed CDCl_3 as probe [6]. The catalytic activities of the samples in the isomerization reaction of 2,3-dimethyl-1-butene (DB-1) have been correlated to their basic properties.

2. Experimental

2.1. Materials

The host Mg/Al LDH ($\text{Mg}^{2+}/\text{Al}^{3+} = 2$) was synthesized by co-precipitation of a first aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.2 M) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.6 M) delivered by a chromatography-type pump (2 mL min^{-1}) into a beaker containing 100 mL of water and a second solution of NaOH (2 M) added using a pH-Stat apparatus (718 Stat Titrino, Metrohm) in order to keep the pH at a constant value of 10 ± 0.2 . The suspension was aged overnight at 333 K under vigorous stirring. Finally, the precipitate was filtered and washed

* Corresponding author. Tel.: +33 467 163477; fax: +33 467 163470.
E-mail address: didier.tichit@enscm.fr (D. Tichit).

with distilled water. The $\text{NO}_3\text{-Mg/Al}$ LDH host thus obtained was dried overnight in an oven at 373 K.

The guest $[\text{M}(\text{Edta})]^{2-}$ ($\text{M} = \text{Ca}^{2+}$, Sr^{2+} , Ba^{2+}) entities were obtained by complexation of the M cations with Edta in aqueous solution. For this purpose, SrCO_3 or BaCO_3 was added to the Edta disodium salt solution (0.08 M) at a molar ratio $[\text{M}]/[\text{Edta}] = 1$ and heated at 363 K. In the case of Ca^{2+} , the commercially available product, Edta calcium disodium salt (Aldrich, 98%), dissolved in water was likely used.

The intercalated materials were synthesized by dispersion of the host Mg/Al-NO_3 LDH (1 g) into the amount of the freshly prepared aqueous suspension of the guest entity corresponding to 2 times the theoretical AEC of the LDH ($\sim 3.8 \text{ mequiv. g}^{-1}$). The suspension was then hydrothermally treated in a batch reactor at 393 K under 5 MPa nitrogen pressure for 4 h. The solid was then recovered by centrifugation, washed with deionized water and dried overnight at 353 K. The samples thus obtained were hereafter labelled as $\text{M}(\text{Edta})\text{-Mg/Al}$ ($\text{M} = \text{Ca}^{2+}$, Sr^{2+} , Ba^{2+}).

The $\text{M/Mg}(\text{Al})\text{O}$ ($\text{M} = \text{Ca}^{2+}$, Sr^{2+} , Ba^{2+}) catalysts were obtained by thermal decomposition of the $\text{M}(\text{Edta})\text{-Mg/Al}$ LDHs in air flow at 923 K for 8 h.

2.2. Characterization

Powder X-ray diffraction patterns (XRD) of the samples were collected in a Siemens D5000 diffractometer using (40 kV, 20 mA) using monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) and a scan rate of 1 K min^{-1} . N_2 adsorption and desorption isotherms at 77 K were measured using a Micromeritics ASAP 2000 surface analyzer on samples previously calcined at 923 K under argon for 5 h and degassed in vacuum at 523 K (10^{-4} Pa). Specific surface areas were calculated using the BET method. Chemical composition of the samples was determined by ICP-OES at the Central Analysis Service of the CNRS (Solaize, France). The basic properties of the solids were characterized by means of DRIFT spectroscopy with adsorbed CDCl_3 as probe molecule. DRIFT spectra were recorded using a Bruker-Equinox-55 FTIR spectrometer in the region of $400\text{--}4000 \text{ cm}^{-1}$ at the resolution of 4 cm^{-1} ; the number of scans was equal to 64. The sample, previously calcined at 923 K, was pressed into the DRIFT cell and pretreated in a helium stream ($10 \text{ cm}^3 \text{ STP min}^{-1}$) at 873 K for 1 h. The sample cooled at 303 K was then treated in a helium stream saturated with CDCl_3 for 20 min. Spectra were measured each 5 min until achieving sample saturation. The basic sites densities of the samples calcined at 923 K were determined by TPD of CO_2 in a Thermo Finnigan TPD/R/O 1100 equipped with a programmable temperature furnace and a TCD detector. Typically, $\sim 200 \text{ mg}$ of the solid were placed between quartz wool in a quartz reactor. After adsorption of CO_2 (3 vol.% CO_2 in He ; $20 \text{ cm}^3 \text{ STP min}^{-1}$) for 10 min, the catalyst was treated in He ($20 \text{ cm}^3 \text{ STP min}^{-1}$) at 373 K to remove the physically adsorbed CO_2 . The CO_2 uptake was measured by treating the sample from room temperature up to 1223 K at a heating rate of 10 K min^{-1} . The basic sites number was calculated from the CO_2 peaks deconvolution using the software of the equipment, assuming that one molecule of CO_2 adsorbs on each basic site.

2.3. Catalyst test reactions

Decomposition of 2-methyl-3-butyn-2-ol (MBOH) and isomerization of 2,3-dimethyl-1-butene (DB-1) were chosen as model reactions. MBOH conversion was performed under atmospheric pressure in a microflow fixed-bed reactor using 120 mg of catalyst previously calcined at 923 K for 18 h. MBOH was fed by bubbling N_2 (0.05 L min^{-1}) through a saturator at 298 K ($P_{\text{MBOH}} = 2.5 \text{ kPa}$). The MBOH vapor stream was then introduced in the reactor containing the catalyst at 388 K in order to have moderate conversions and the

effluent stream was sampled every 5 min for analyzing on line with a gas chromatograph (Hewlett Packard Model 5890) equipped with a Megabore capillary column ($30 \text{ m} \times 0.546 \text{ mm}$) and FID detection. All connecting lines were heated.

The DB-1 isomerization reaction was carried out into a quartz glass fixed-bed reactor where the catalyst (200 mg) was previously calcined at 923 K for 18 h in order to avoid its exposure to air after activation. The DB-1, without further purification, was fed by bubbling He (0.005 L min^{-1}) through a saturator at 175 K ($P_{\text{DB-1}} = 0.002 \text{ kPa}$). This stream was then introduced in the reactor heated at 343 K and the reaction products were analyzed on line by gas chromatography using a 30 m HP-5 column.

3. Results and discussion

3.1. Composition and structure

The XRD patterns of $\text{NO}_3\text{-Mg/Al}$ and of the $\text{M}(\text{Edta})\text{-Mg/Al}$ samples are depicted in Fig. 1. That of $\text{NO}_3\text{-Mg/Al}$ is typical of a LDH phase. Sharp and symmetric reflections ascribed to the basal (003), (006) and (009) planes, and broad and asymmetric reflections ascribed to the non-basal (012), (015) and (110) planes in the space group R-3m are clearly distinguished. The interlayer spacing $d_{003} = 0.83 \text{ nm}$ is consistent with the presence of NO_3^- as charge compensating anions. Comparatively to $\text{NO}_3\text{-Mg/Al}$, the d_{003} interlayer distance increases to 1.50 nm in the $\text{M}(\text{Edta})\text{-Mg/Al}$ samples. This value is close to that previously reported for a $[\text{Eu}(\text{edta})]\text{-Mg/Al}$ LDH [7] and shows that the intercalation of the $[\text{M}(\text{Edta})]^{2-}$ complexes has taken place. The presence in the intercalated LDHs of several intense basal (00*l*) reflections account for well ordered layered structures probably resulting from the hydrothermal conditions of the anionic exchange. Comparatively to $\text{NO}_3\text{-Mg/Al}$, an inversion of intensity between the two first (00*l*) peaks is observed. This can account for the high electron density induced by the presence of the metal complexes in the interlayer space as previously reported [7,8].

The same value of the cell *a* parameter ($a = 0.303 \text{ nm}$), calculated from the position of the (110) diffraction peak ($a = 2 \times d_{110}$), is

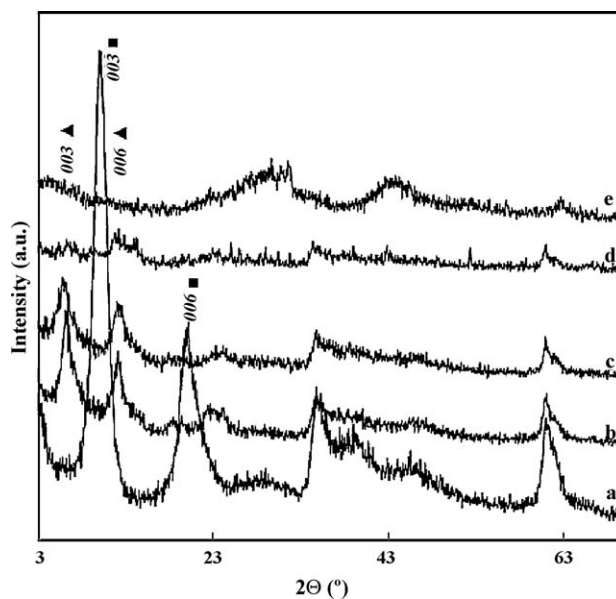


Fig. 1. XRD patterns of (a) $\text{NO}_3\text{-Mg/Al}$, (b) $\text{Ca}(\text{Edta})\text{-Mg/Al}$, (c) $\text{Sr}(\text{Edta})\text{-Mg/Al}$, (d) $\text{Ba}(\text{Edta})\text{-Mg/Al}$ and (e) $\text{M/Mg}(\text{Al})\text{O}$ calcined at 923 K samples; (■) corresponds to the basal reflections of $\text{NO}_3\text{-Mg/Al}$ and (▲) corresponds to the basal reflections of $\text{M}(\text{Edta})\text{-Mg/Al}$.

Table 1

Elemental analysis, proposed formula and BET specific surface area of the nanocomposites.

Sample	Chemical composition (wt.%)					Suggested formula	S _{BET} ^a (m ² g ^{−1})
	Mg	Al	M ²⁺	C	N		
NO ₃ –Mg/Al	16.7	9.06		0.30	5.04	[Mg _{0.66} Al _{0.34} (OH) ₂][(NO ₃) _{0.35} (CO ₃) _{0.02}].0.72H ₂ O	137
Ca(Edta)–Mg/Al	13.14	7.49	3.37	11.86	3.22	[Mg _{0.66} Al _{0.34} (OH) ₂][(Ca(Edta)) _{0.1} (Edta) _{0.02} (NO ₃) _{0.039}].1.14H ₂ O	100
Sr(Edta)–Mg/Al	13.71	8.12	6.46	10.32	2.32	[Mg _{0.66} Al _{0.34} (OH) ₂][(Sr(Edta)) _{0.08} (Edta) _{0.015}].1.06H ₂ O	153
Ba(Edta)–Mg/Al	14.02	7.37	8.44	11.03	2.42	[Mg _{0.68} Al _{0.32} (OH) ₂][(Ba(Edta)) _{0.072} (Edta) _{0.035}].0.94H ₂ O	111

^a BET surface area determined on samples calcined at 923 K and outgassed at 523 K.**Table 2** ν_{CD} frequencies of CDCl₃ adsorbed on the M/Mg(Al)O catalysts and the number of the surface basic sites.

Sample	Total Nb ^a (μmol m ^{−2})	Basic sites					
		W		M		S	
		ν_{CD} (cm ^{−1})	Nb ^b (μmol m ^{−2})	ν_{CD} (cm ^{−1})	Nb ^b (μmol m ^{−2})	ν_{CD} (cm ^{−1})	Nb ^b (μmol m ^{−2})
Mg(Al)O	0.75	2254	0.70	2230	0.07	2181	0.04
Ca/Mg(Al)O	1.06	2243	0.74	2213	0.07	2191	0.24
Sr/Mg(Al)O	0.67	2251	0.29	2228	0.26	2187	0.12
Ba/Mg(Al)O	0.77	2248	0.10	2225	0.60	2183	0.07

^a Determined by TPD of CO₂ of samples calcined at 923 K.^b Estimated by deconvolution of CDCl₃ DRIFT spectra of samples calcined at 923 K.

found in NO₃–Mg/Al LDH and in the M(Edta)–Mg/Al samples showing the stability of the host structure during the anionic exchange. This value corresponds to an Mg/Al molar ratio close to 2 in the brucite-like layers.

The elemental analysis of the samples allows proposing the structural formula reported in Table 1. The Mg/Al molar ratio in the nanocomposites is close to that of the host NO₃–Mg/Al LDH. Excepted for Ca(Edta)–Mg/Al, the initial NO₃[−] anions of the host NO₃–Mg/Al LDH are totally displaced by both [M(Edta)]^{2−} complexes and free [Edta]^{4−} during the exchange. Molecular dynamic studies of the AE cations complexes of Edta in aqueous solution have already shown that in the *endo* complex type, the AE cation is coordinated by four monodentate carboxylate groups and two nitrogen atoms of Edta. An *exo* complex is also obtained in the case of Ca²⁺ coordinated by two bidentate carboxylate groups. Moreover, the relative stabilities of the complexes with [Edta]^{4−} ranges from Ca²⁺ to Sr²⁺ and Ba²⁺ [9]. This order of stability is in agreement with the exchange rate of the host LDH by the [M(Edta)]^{2−} complexes and then with the AE cations content of the M(Edta)–Mg/Al samples.

The M/Mg(Al)O mixed oxides catalysts obtained after thermal decomposition of the M(Edta)–Mg/Al LDHs at 923 K exhibit XRD patterns characteristics of the periclase-like structure. These XRD patterns are also similar to that of the Mg(Al)O mixed oxide obtained by calcination of NO₃–Mg/Al at 923 K and depicted in Fig. 1e. The specific surface areas of the mesoporous M/Mg(Al)O mixed oxides ranges from 100 to 153 m² g^{−1}. They are similar to that of Mg(Al)O at 137 m² g^{−1}. These results show that the introduction of the AE cations into the Mg(Al)O mixed oxides does not significantly modifies its structural and textural properties.

3.2. Basic properties

TPD of CO₂ allows to determine the total density of surface basic sites of the different mixed oxides which varies as follows: Sr/Mg(Al)O < Mg(Al)O ~ Ba/Mg(Al)O < Ca/Mg(Al)O (Table 2). There is a clear tendency towards an increase of the basic sites density when alkaline-earth cations are introduced. The lower sites density observed for Sr/Mg(Al)O than for Mg(Al)O accounts for the high specific surface area of the former mixed oxide almost 50% higher than the other M/Mg(Al)O mixed oxides.

The adsorption of the acidic CDCl₃ probe molecule has been also successfully used to characterize the number and strength of the different basic sites of LDHs and of binary oxides [4,10]. The ν_{CD} frequency value of the H-bonded complexes of CDCl₃ adsorbed on the different basic sites decreases as their strength increases. The DRIFT spectra in the ν_{CD} region (2300–2120 cm^{−1}) of CDCl₃ adsorbed at 303 K on the M/Mg(Al)O catalysts and, for the sake of comparison, on Mg(Al)O are reported in Fig. 2. In all cases broad

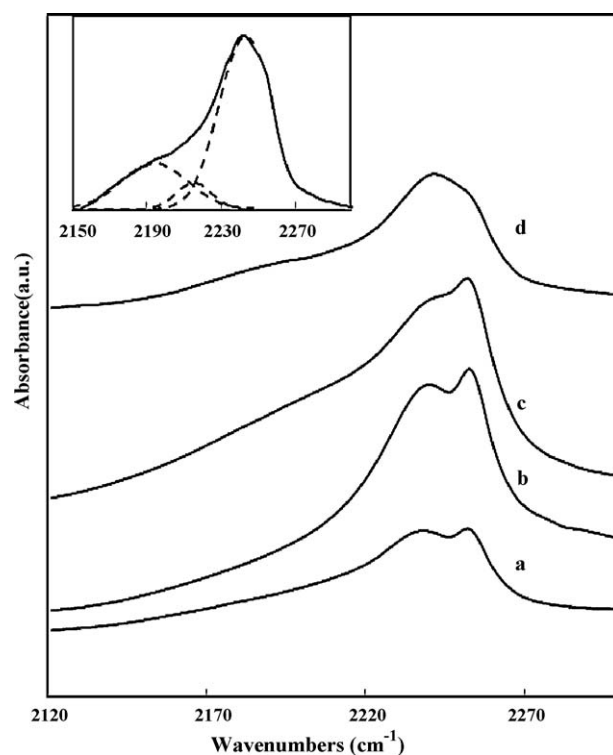


Fig. 2. DRIFT spectra (ν_{CD} region) of CDCl₃ adsorbed at 303 K on (a) Ba/Mg(Al)O, (b) Mg(Al)O, (c) Sr/Mg(Al)O and (d) Ca/Mg(Al)O. For sake of clarity the spectra have been shifted vertically. Insert shows the deconvolution of the 2190–2300 cm^{−1} region of Ca/Mg(Al)O.

bands are observed which account for the formation of several H-bonded complexes. A shoulder towards lower frequencies, absent in Mg(Al)O, is noted in the M/Mg(Al)O mixed oxides, particularly in the Ca- and Sr-containing ones. Deconvolution of the bands using the scientific graphing and data analysis software package Origin fits well considering three components at 2251–2243, 2228–2213 and 2191–2183 cm^{-1} characteristic of the H-complexes of CDCl_3 with weak (W), medium (M) and strong (S) basic sites, respectively. The ν_{CD} frequencies and the contents of the W, M and S sites on the different catalysts are reported in Table 2. Mg(Al)O is found as weakly basic. W basic sites indeed represent about 95% of the total number with the highest value of the ν_{CD} frequency. Relatively to Mg(Al)O, the introduction of AE cations modifies significantly the basic properties as shown by: (i) the shift of the ν_{CD} frequencies by 2–17 cm^{-1} to lower values for W and M sites, and in contrast by 2–10 cm^{-1} to higher ν_{CD} frequencies for S sites; (ii) an increase of M and S sites densities at the expense of the W sites density.

These evolutions account for a general increase of the average basic strength after introduction of the AE cations in the Mg(Al)O mixed oxides. Moreover, the nature of the AE cations influences the relative densities of M and S sites which behave in opposite way, the former being in larger amount for Ba and the latter for Ca. It is noteworthy, regarding on one hand the density and on the other hand the strength of S sites evaluated by the ν_{CD} frequency shift of the CDCl_3 peak, that they vary in opposite way. So, Ba/Mg(Al)O actually contains a small number of basic sites, but of very high strength.

The conversion of MBOH is increasingly used to characterize the acido-basicity of oxides, likely those with basic character, as recently reviewed [11]. Indeed, dehydration of MBOH into 3-methylbut-3-en-1-yne occurs on acid sites, while disproportionation into acetone and acetylene occurs on basic sites, allowing clear identification of the predominant acidic or basic nature of the catalytic sites of the materials. However, this test reaction is not able to infer on the Brønsted or Lewis nature of the different sites. All the mixed oxides of the study, i.e. Mg(Al)O and M/Mg(Al)O, behave as basic catalysts yielding only acetylene and acetone in stoichiometric amounts as reaction products. It is worthy to note that: (i) the M/Mg(Al)O mixed oxides whose MBOH conversion ranges from 17.3 to 24.8% after 1 h reaction time are more active than Mg(Al)O (conversion = 2.8%) and that among the AE-containing mixed oxides the order of reactivity is: Ba/Mg(Al)O > Sr/Mg(Al)O > Ca/Mg(Al)O. This behavior, when it is compared to the previous results obtained by FTIR of CDCl_3 , shows that the conversion of MBOH follows the increase in the sum of M and S sites density in the catalysts (Fig. 3).

In summary, characterization of the basicity of the M/Mg(Al)O catalysts by means of TPD of CO_2 , FTIR spectroscopy of CDCl_3 and catalytic test reaction of MBOH reveals that the introduction of AE cations into Mg(Al)O allows to increase the density of basic sites, particularly those of medium and high strength. Moreover, the content of M and S sites behave in opposite way in function of the nature of the AE cations.

3.3. Catalytic activity

The double bond migration of DB-1 to the more thermodynamically stable DB-2 is known to proceed only on strong basic catalysts [12]. Accordingly M/Mg(Al)O catalysts give rise to conversions ranging from 19 to 67% which follow the same trend, i.e. Ba/Mg(Al)O < Sr/Mg(Al)O < Ca/Mg(Al)O (Fig. 3), as their relative content in both W and S sites determined by FTIR spectroscopy of CDCl_3 (Table 2). As Mg(Al)O, which possesses the higher number of W sites, has been reported almost inactive for

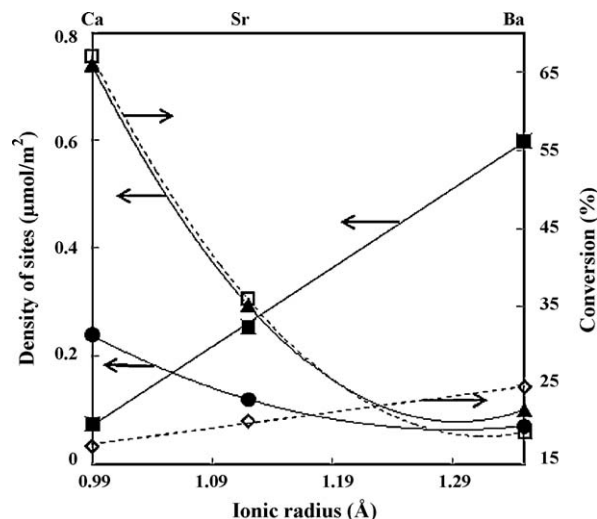


Fig. 3. Density of (▲) weak, (■) medium and (●) strong basic sites and catalytic activity in the (◇) MBOH conversion and (□) DB-1 isomerization in function of the ionic size of the alkaline-earth cations.

this reaction [13], the previous results confirm that the strong basic sites created by introduction of the AE cations into the M/Mg(Al)O catalysts are responsible for their catalytic activity in the isomerization of DB-1. Remarkably, the catalytic activity of Ca/Mg(Al)O (67%) is in the range of that reached using a Ca(Al)O mixed oxide (89%) obtained from the decomposition of a Ca/Al-LDH precursor [13].

4. Conclusions

New basic mixed oxides catalysts were obtained when AE cations complexed with Edta and intercalated into Mg/Al LDH were used as precursors. The introduction of the AE cations does not significantly modifies the structural and textural properties of the Mg(Al)O mixed oxide but increases its content in basic sites of medium and high strength. An important feature is that the nature of the AE cations allows to finely control the basicity in order to perform reactions requiring different basic strength. Ba-containing mixed oxides with the largest content of sites of medium and high strength are consequently the most active for MBOH conversion. Due to their larger content of strong basic sites, the AE-containing mixed oxides are able to perform the highly demanding isomerization reaction of DB-1. The most active catalyst is in this case Ca/Mg(Al)O which possesses the largest number of strong basic sites.

References

- [1] M.J. Climent, A. Corma, S. Iborra, A. Velty, J. Catal. 221 (2004) 474.
- [2] S. Abelló, F. Medina, D. Tichit, J. Pérez-Ramírez, Y. Cesteros, P. Salagre, J.E. Sueiras, Chem. Commun. 11 (2005) 1453.
- [3] A. Guida, L.M. Hassane, D. Tichit, F. Figueras, P. Geneste, Appl. Catal. A 164 (1997) 251.
- [4] F. Winter, X. Xia, B.P.C. Hereijgers, J.H. Bitter, A.J. van Dillen, M. Muhler, K.P. de Jong, J. Phys. Chem. B 110 (2006) 9211.
- [5] H. Lauron-Pernot, F. Luck, J.M. Pota, Appl. Catal. 78 (1991) 231.
- [6] E.A. Paukshtis, P.I. Soltanov, E.N. Yurchenko, K. Jiratova, Collect. Czech. Chem. Commun. 47 (1982) 2044.
- [7] C. Li, G. Wang, D.G. Evans, X. Duan, J. Solid State Chem. 177 (2004) 4569.
- [8] E.M. Sabbar, M.E. de Roy, F. Leroux, J. Micropor. Mesopor. Mater. 103 (2007) 134.
- [9] S. Durand, J.P. Dognon, P. Guilbaud, C. Rabbe, G.J. Wipff, Chem. Soc. Perkin Trans. 2 (2000) 705.
- [10] A.S. Ivanova, B.L. Moroz, E.M. Moroz, Y.V. Larichev, E.A. Paukshtis, V.I. Bukhtiyarov, J. Solid State Chem. 178 (2005) 3265.
- [11] H. Lauron-Pernot, Catal. Rev. 48 (2006) 315.
- [12] T. Seki, S. Ikeda, M. Onaka, J. Micropor. Mesopor. Mater. 96 (2006) 121.
- [13] H. Handa, Y. Fu, B. Toshihide, Y. Ono, Catal. Lett. 59 (1999) 195.