



ORIGINAL ARTICLE

New way for iron introduction in LDH matrix used as catalysts for Friedel–Crafts reactions



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Abstract The alkylation of toluene, reaction employing benzyl chloride as the alkylating agent over basic hydrotalcite materials: Fe–Mg–Al-LDH prepared by different synthesis methods, including the method of co-precipitation, impregnation and a new method called the method of intercalation by anion exchange in the lamellar space of the host structure LDH. Our prepared solids were characterized by chemical analysis, XRD analysis, BET method and thermogravimetric analysis (TGA) and tested in the alkylation of toluene by benzyl chloride reaction. Fe–Mg–Al-LDH clay without or with calcination (at 773 K) has been investigated. The catalyst derived from the hydrotalcite by its calcination at 773 K shows high catalytic activity for the alkylation of toluene and other aromatic compounds. The catalytically active species present in the catalyst in its most active form are the oxides of iron on the catalyst surface.

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1. Introduction

Friedel–Crafts alkylations comprise a very important class of reactions, which are of common use in organic chemistry. The alkylation of toluene by benzyl chloride is interesting for the preparation of polyaromatic compounds, which are the basis of classical organic chemistry and enable the creation of C–C bonds. In the homogeneous phase, this reaction is

catalyzed at the industrial scale by AlCl_3 , FeCl_3 , BF_3 , ZnCl_2 and H_2SO_4 (Olah, 1973; Commandeur et al., 1991). The new environmental legislation pushes for the replacement of all liquid acids by solid acid catalysts which are environmentally more friendly catalysts and which lead to minimal pollution and waste (Clark et al., 1994; Cao et al., 1998). Fe-based acid solid catalysts are considered to be promising catalysts for the benzylation of benzene. Among these Fe-based solids we find: Fe-HZSM-5 (Choudhary et al., 1999), Fe-SBA-15 (Sun et al., 2006), Fe-MCM-41 (Arafat and Alhamed, 2009), Fe-modified ZSM-5 and H- β zeolites; Fe_2O_3 or FeCl_3 deposited on micro-, meso- and macroporous (Choudhary et al., 1999); Fe-containing mesoporous molecular sieve materials (Hentit et al., 2007; Benadji et al., 2010; Bachari et al., 2010; Merabti et al., 2010), and FeCl_3 supported on acidic alumina (Salavati-Niasari et al., 2004) for the alkylation reaction of toluene and other

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aromatic compounds. Nevertheless, it remains until now the discussion on the active sites for reaction. However, the reports on the use of basic catalysts for the alkylation reactions are scarce (Ono and Baba, 1997). Among these basic solids, the layered double hydroxides (LDHs), are the subject of considerable interest in recent years because of their electrochemical properties and anion exchange. Most applications of these materials are in the field of heterogeneous catalysis due to the production of different layers of cations and anions in interlayer by synthetic chemistry. Recently, Choudhary et al. found that Ga and In–Mg–hydrotalcite anionic clay, after its first use in the reaction or HCl gas pretreatment, shows very high activity in the benzylation of toluene even in the presence of moisture in the reaction mixture (Choudhary et al., 2001, 2002, 2005). Other side, Bachari et al. also found that Mg–Fe–LDH catalysts show remarkable activities for the benzylation of aromatics (Tahir et al., 2008).

Without knowing structure–reactivity relation, it is difficult to synthesize an efficient catalyst for the Friedel–Crafts alkylations and several efforts have been made to achieve this goal using different ways for the synthesis of Fe-containing solid catalysts. In the present work, we report the synthesis of Fe–Mg–Al–LDH using different ways for iron introduction in LDH structures such as coprecipitation, impregnation or a new way by intercalation method of guest anionic iron complexes into host Mg–Al LDH by anionic exchange (Chebout et al., 2010). Finally, our solids are tested in the alkylation of toluene with benzyl chloride reaction.

2. Experimental

2.1. Catalysts preparation

2.1.1. Preparation of Mg–Al–LDH and Fe–Mg–Al–LDH by the co precipitation method

The Mg–Al LDH (Mg/Al = 2) was prepared by coprecipitation at a constant pH (=10) of suitable amounts of Mg (NO_3)₂·6H₂O (0.2 M) (Aldrich–Chemie), Al (NO_3)₃·6H₂O (0.1 M) (Aldrich–Chemie) with a 2 M NaOH solution. In order to maintain the pH constant, the addition of the alkaline solution was controlled by a pH-STAT Titrino (Metrohm) apparatus. The suspension was aged at 353 K for 17 h. The precipitate formed was separated by centrifugation, thoroughly washed with distilled water (Na < 100 ppm), and dried overnight at 80 °C. Same steps are followed for Mg–Al–Fe LDH (Mg/(Al + Fe) = 2) preparation with suitable amounts of Mg(NO_3)₂·6H₂O (0.2 M), Al(NO_3)₃·6H₂O (0.06 M) and Fe(NO_3)₃·9H₂O (0.04 M) (Aldrich–Chemie).

2.1.2. Preparation of Fe/Mg–Al–LDH by the impregnation method

The solid Fe/Mg–Al LDH was prepared by the impregnation method at constant pH, which is permeated iron by adding a metal salt Fe (NO_3)₃·9H₂O (0.04 M) (Aldrich–Chemie) to the solution containing the Mg–Al LDH defined by a molar ratio of Mg/Al = 2 and Mg/Fe = 5. These two solutions are mixed for 5 min at room temperature and maintained at a constant pH value alkaline (pH 10). The precipitate is filtered and the solid obtained is washed several times with double distilled water until complete elimination of excess ions in the solid

(NO_3^- , Na^+ , etc.). The impregnated support is then dried in an oven at 353 K overnight.

2.1.3. Preparation of Fe (citrate)³⁻–Mg–Al–LDH by the intercalation method «LDH hybrid» (organic and inorganic)

Pre-chelation of Fe³⁺ cation with C₆O₇H₃³⁻((citrate)³⁻) complexing agent was previously performed. For this purpose, aqueous solutions of Fe (NO_3)₃·9H₂O (0.1 M) and Na₃ (citrate) (0.12 M) were mixed according to the stoichiometry ((citrate)³⁻)/Fe³⁺ = 1.5/1. Then the pH of the solutions was increased to ca. 10.5 by adding the required amount of a 0.5 M NaOH solution to obtain [Fe (citrate) OH]⁻ complex. That led to stable and clear suspensions which have been used as freshly prepared for intercalation. The solid was prepared from the host Mg–Al LDH by anionic exchange of the nitrate ions NO₃⁻ by the anionic Fe³⁺ cation-containing complexes. The Mg–Al LDH (3 g) was dispersed in the required amount (100–150 ml) of a suspension corresponding to 2.5 times the theoretical anionic exchange capacity (AEC) of the sample (~3.8 mequi. g⁻¹). The exchange process was performed by stirring the mixture at room temperature for 18 h. The solid was then recovered and washed by dispersion and centrifugation in deionized water, and finally dried at 353 K for 12 h.

2.2. Activation of the samples

The mixed oxides were obtained by calcination of the samples at 773 K in a dry synthetic air flow (100 ml min⁻¹). The temperature was raised at the rate of 1 °C min⁻¹ up to 773 K, and then maintained for 4 h.

2.3. Characterization techniques

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Cu K α 1 radiation ($\lambda_\alpha = 1.54184 \text{ \AA}$, 40 kV and 50 mA). Data were collected between 2° and 70° 2 θ , with a step size of 0.02° and a counting time of 1 s/step.

Chemical analyses of both as-prepared samples and calcined materials were carried out by inductively coupled plasma atomic emission spectroscopy (ICP–AES).

Coupled thermogravimetric (TGA) and differential thermal analysis (DTA) were performed in a Setaram apparatus at a heating rate of 5 °C min⁻¹, in air, using 40 mg of each sample.

The surfaces of samples were measured using the BET adsorption. N₂ sorption experiments at –77 K were performed on samples previously calcined at 773 K for 5 h and degassed at 523 K (10⁻⁴ Pa) with a Micromeritics ASAP 2000 instrument. As micropores were always present, the surfaces were calculated from the *t*-plot method.

2.4. Catalytic testing

The alkylation reactions over our catalysts were carried out in a magnetically stirred glass reactor (25 cm³) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture-free nitrogen N₂ (flow rate = 30 cm³ min⁻¹) through the liquid reaction mixture, at the following reaction conditions: reaction mixture = 15 ml of moisture-free liquid aromatic compound

(or 2.5 ml of moisture-free aromatic compound mixed with 12.5 ml of moisture-free solvent) + 1.0 ml of benzyl chloride, amount of catalyst = 0.1 g, and reaction temperature = 353 K. The reaction was started by heating the reaction mixture containing toluene, benzyl chloride, and *n*-pentadecane to the reaction temperature then injecting the catalyst in the reactor. Measuring quantitatively, the HCl evolved in the reaction by acid–base titration (by absorbing the HCl carried by N₂ in a 0.1 M NaOH solution containing phenolphthalein indicator) followed the course of the reaction. The polybenzyl chloride (which is formed by the condensation of benzyl chloride) was isolated from the reaction mixture by the procedure given by Choudhary et al. (2000). In all the cases, the major product formed was mainly Benzyl toluene compound along with Poly-benzyl toluene as side product depending upon the condition used. Samples were analyzed periodically on a gas chromatograph (HP-6890) equipped with a FID detector and a capillary column RTX-1 (30 m × 0.32 mm i.d.). The products were also identified by GC-MS (HP-5973) analysis.

3. Results and discussion

3.1. Structure and composition

The XRD patterns of the as-prepared samples are shown in Fig. 1. The patterns of Mg–Al-LDH, Mg–Fe–Al-LDH and Fe/Mg–Al-LDH are characteristic of LDH structure (Chebout et al., 2010). The diffraction peaks can be indexed in a hexagonal unit cell with R-3m rhombohedral symmetry. The sharp and symmetric diffraction peaks at 2θ , 9.92° and 19.90° are ascribed to (003) and (006) planes. The corresponding interlayer spacing d_{003} is near to 0.8 nm for the our three samples, is consistent with Mg/Al molar ratio close to two in the brucite-like layers and the presence of NO₃⁻ as charge compensating anions. The absence of the iron characteristic peaks in the Fe/Mg–Al-LDH is can be to the good dispersion of the last on the LDH surface. The values of *a* parameter, which represents the average distance between the cations within the layers, obtained from the position of the (110) diffraction line ($a = 2 * d_{110}$), are comparable, we notice the difference in the value of *a* parameter between coprecipitated samples (0.3 nm (Mg–Al-LDH); 0.2 nm (Mg–Fe–Al-LDH)); this confirms the change in the composition of LDH layers with Fe³⁺ presence. The XRD pattern of Fe (citrates)–Mg–Al-LDH shows broader and less intense reflection peaks which reveal an important decrease of crystallinity. The position of the (003) reflection corresponding to a d_{003} value of 1.92 nm shows that, compared to the host LDH, the interlayer distance increases due to the intercalation of the citrate-containing

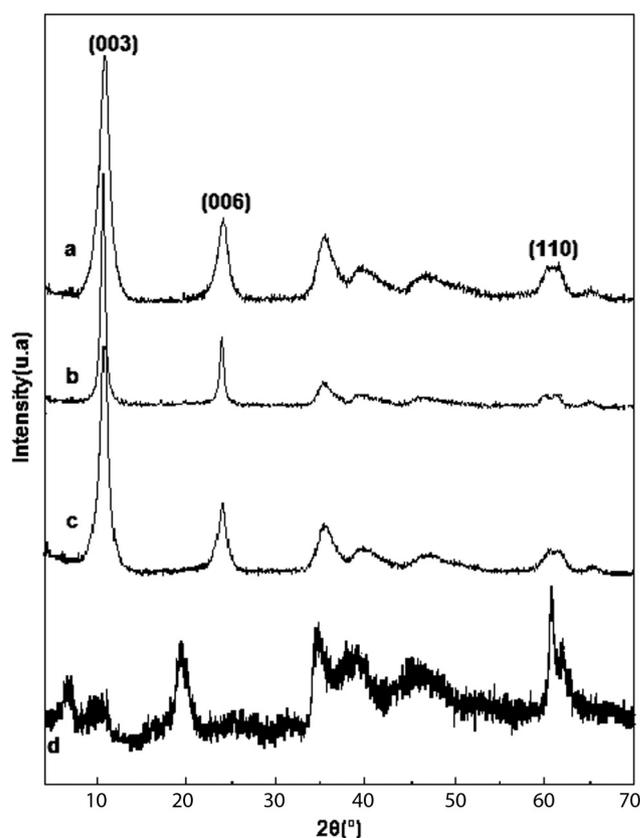


Figure 1 XRD pattern of Mg–Al LDH(a); Mg–Al–Fe LDH(b); Mg–Fe–Al-LDH(c); Fe (citrates)–Mg–Al LDH (d) samples (*: NO₃–LDH, +: Fe (citrates)-LDH).

complexes. The value of the d_{003} distance is in agreement with those reported in the literature for Ni(citrates)–Mg–Al-LDH ($d_{003} \approx 1.20$ nm) Cavani et al., 1991; Gerardin et al., 2005, 2008. The values of the parameter are comparable with the host Mg–Fe–Al-LDH and the Fe (citrates)–Mg–Al-LDH ($a = 0.3$ nm). This suggests that the Mg/Al molar ratios are similar. The elemental analyses of the samples are reported in Table 1. The results show that the molar ratios of M²⁺/M³⁺ hydrotalcites are in good agreement with those calculated taking into account the initial concentrations of salts (theoretical ratio M²⁺/M³⁺ = 2). The Mg/Al molar ratio increases slightly for the intercalated Fe (citrates)–Mg–Al-LDH. This can be considered as a consequence of the possible chelation of Al³⁺ by citrate. Actually it is easier to complex Al than Mg (Choudhary et al., 2002).

Table 1 Theoretical molar ratios and experimental molar ratios of M²⁺/M³⁺.

Samples	Mg/Al theoretical molar ratios	Mg/Al experimental molar ratios	Mg/Fe theoretical molar ratios	Mg/Fe experimental molar ratios
Mg–Al-LDH	2	1.96 ≈ 2	–	–
Mg–Fe–AL-LDH	3.33	3.5	5	5.4
Fe/Mg–Al-LDH	2	1.98 ≈ 2	5	–
Fe (citrates)–Mg–Al-LDH	2	2.2	5	4.6

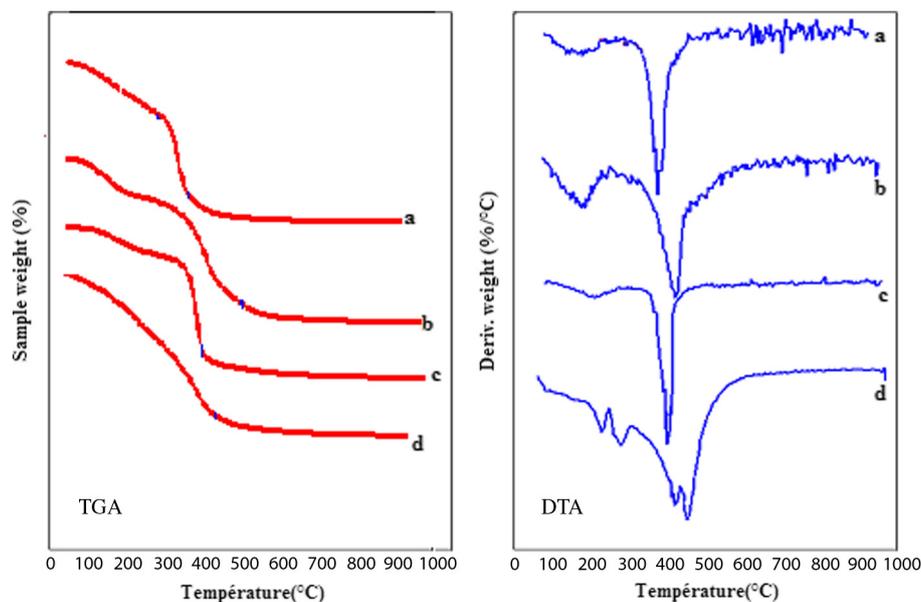


Figure 2 Thermal behavior of materials is followed by TGA/DTA: (a) Mg–Al-LDH; (b) Mg–Fe–Al-LDH; (c) Fe/Mg–Al-LDH; (d) Fe (citrates)–Mg–Al-LDH.

Thermal behavior of materials is followed by TGA/DTA presented in Fig. 2. All the synthesized LDH exhibited two-step decomposition upon heating under air. The first step occurred at temperatures up to 220–250 °C and accounted for an 8–12.0% weight loss due to the desorption of physisorbed water and to the release of structural water. The second step took place at 350–500 °C, which was due to LDH dehydroxylation (forming water as product) and decomposition of incorporated anions. The observed loss in sample weight was about 25–33% for conventionally synthesized Mg–Al-LDH, Mg–Fe–Al-LDH and Fe/Mg–Al-LDH, for materials prepared via pre-chelation of Fe with citrate the lost weight is 31%. An interesting feature can be seen upon comparison of differential thermogravimetry (Fig. 2 DTA/d) is the presence of two endothermic peaks in the second loss for the Fe (citrates) intercalated LDH, according to the given literature (Wang et al., 2007), these two peaks are respectively attributed to the liberation of both water and carbon dioxide, then to the liberation of CO₂ only.

The BET results for Mg–Al-LDH, Mg–Fe–Al-LDH and Fe (citrates)–Mg–Al-LDH are shown in Table 2. All solids show diameter pores between 25 and 500 Å. Moreover, the distribution of pore radius is between: 50 Å < *d* < 500 Å, this confirms that these solids are mesoporous materials. Fe (citrates)–Mg–Al-LDH shows a higher surface area compared to Mg–Al-LDH, Mg–Fe–Al-LDH and Fe/Mg–Al-LDH. The

Table 2 Textural analysis results.

Samples	Surface spécifiques (m ² /g)	Rayon de pore (Å)
Mg–Al-LDH	185	120
Fe–Mg–Al-LDH	188	50
Fe/Mg–Al-LDH	176	85
Fe (citrates)–Mg–Al-LDH	203	180

reason is that when complex molecules are incorporated into the LDH layers, the expansion took place (i.e. increase in basal spacing from 0.8 nm to 1.92 nm). As a consequence of which the surface area of Fe (citrates)–Mg–Al-LDH increases from to 202 m²/g.

The mixed oxides obtained after thermal decomposition of the nanocomposite at 773 K exhibit XRD pattern characteristics of the periclase-like structure.

3.2. Catalytic results

3.2.1. Effect of the addition of iron by different synthesis methods to the catalytic performance of the solid Mg–Al-LDH

We studied the effect of the iron addition by three synthesis methods, namely: co precipitation, impregnation and intercalation. Table 3 reports the results of this study. The results show that the iron catalysts are more active than the catalyst Mg–Al-LDH uncalcined (nc). Furthermore, the catalyst Fe (citrates)–Mg–Al-LDH_{nc} prepared by the method of intercalation, has a constant apparent highest speed compared to the other two solids prepared by other synthesis methods. In addition, we also find that these catalysts control the selectivity ortho/para of this reaction. Indeed, a similar distribution of isomers was found for the catalyst FeCl₃ tested in the same reaction (Choudhary et al., 2005). The order of decreasing activity for the four solids is: Fe (citrates)–Mg–Al-LDH_{nc} > Fe–Mg–Al-LDH_{nc} > Fe/Mg–Al-LDH_{nc} > Mg–Al-LDH_{nc}.

3.2.2. Reaction kinetics

The kinetic data for the toluene alkylation reaction in excess of toluene (stoichiometric ratio Tol/BzCl = 15) over the Fe (citrates)–Mg–Al-LDH calcined at 773 K (Fe–Mg–Al-LDH-773) catalyst could be fitted well to a pseudo-first-order rate law: $\log[1/1-x] = (k_a/2.303)(t-t_0)$, where *k_a* is the apparent first-order rate constant, *x* the fractional conversion of benzyl

Table 3 Catalytic activities of Fe–Mg–Al-LDH catalysts prepared by different synthesis methods.

Catalysts	Time ^a (min)	Selectivity (%) benzyl toluene (BTol) (%)		Apparent rate constant K_a ($\times 10^3 \text{ min}^{-1}$)	Isomer distribution		
		Benzyl toluene	Poly-benzyl toluene		o-BTol	m-BTol	p-BTol
Mg–Al-LDH nc	220	83.4	16.6	10.9	38.0	2.2	43.2
Fe/Mg–Al-LDH nc	160	88.7	11.3	22.3	40.7	2.3	45.7
Fe–Mg–Al-LDH nc	110	99.6	0.4	32.6	46.1	2.5	51.0
Fe (citrates)–Mg–Al-LDH	90	99.8	0.2	36.8	46.2	2.5	51.1

^a Time required for total conversion of benzyl chloride.

Table 4 Catalytic activities of Fe (citrates)–Mg–Al-LDH-873 catalyst at different temperatures: 333, 343 and 353 K.

Temperature (K)	Time ^a (min)	Selectivity benzyl toluene (%) (BTol) (%)		Apparent rate constant K_a ($\times 10^3 \text{ min}^{-1}$)	Isomer distribution		
		Benzyl toluene	Poly-benzyl toluene		o-BTol	m-BTol	p-BTol
333	20.2	100	–	144.3	46.3	2.5	51.2
343	16.3	100	–	189.9	45.3	2.5	52.2
353	12.5	99.6	0.4	249.0	44.2	2.4	53.0

^a Time required for total conversion of benzyl chloride.

Table 5 Influence of the stoichiometric ratio between toluene and benzyl chloride for the benzylation of benzene at 353 K over Fe (citrates)–Mg–Al-LDH-873 catalyst.

Toluene/benzyl chloride ratio	Time ^a (min)	Selectivity benzyl toluene (BTol) (%)		Apparent rate constant K_a ($\times 10^3 \text{ min}^{-1}$)	Isomer distribution		
		Benzyl toluene	Poly-benzyl toluene		o-BTol	m-BTol	p-BTol
5	19.9	84.7	15.3	143.9	38.7	2.0	44.0
15	12.5	99.6	0.4	249.0	44.2	2.4	53.0

^a Time required for total conversion of benzyl chloride.

chloride, t the reaction time and t_0 the induction period corresponding to the time required for reaching equilibrium temperature. A plot of $\log[1/(1-x)]$ as a function of the time gives a linear plot over a large range of benzyl chloride conversions.

The effect of temperature reaction on the rate was studied by conducting the reaction at 333, 343, and 353 K under the standard reaction conditions (stoichiometric ratio Tol/BzCl = 15 and 0.1 g catalyst). The results showed that the catalytic performances of our catalyst increased strongly with the reaction temperature (Table 4). By contrast, the selectivity to benzyl toluene remains approximately constant while conducting the reaction at 343, 348, and 353 K under the standard reaction conditions (stoichiometric ratio Tol/BzCl = 15 and 0.1 g catalyst). The estimated activation energy thus obtained was 20.7 kJ mol⁻¹. In fact, this value can probably suggest that no interference of diffusional limitations exists. Two Tol/BzCl ratios have been investigated. The results obtained are reported in Table 5. It appears that the stoichiometric ratio between toluene and benzyl chloride has a strong influence on the selectivity to benzyl toluene. With a low ratio, the secondary reaction to poly-benzyl toluene was favored. Results showing the influence of different substituent groups attached to the aromatic benzene nucleus on the conversion of benzyl chloride in the alkylation of corresponding substituted benzenes at 353 K over the Fe (citrates)–Mg–Al-LDH-773 catalyst are presented in Table 6. According to the classical mechanism of the Friedel–Crafts type acid catalyzed alkylation reaction, the

Table 6 Reaction rates for substituted benzenes.

Substrates	R	Apparent rate constant K_a ($\times 10^3 \text{ min}^{-1}$)
Benzene	H	260.0
Toluene	CH ₃	249.0
P-xylene	2 CH ₃	240.2
Anisole	OCH ₃	191.0

alkylation of an aromatic compound is easier if one or more electron donating groups are present in the aromatic ring (Olah, 1973). Hence, the order for the rate of alkylation for the aromatic compound is expected as follows: anisole > p-xylene > toluene > benzene. But, what is observed in the present case is totally opposite to that expected according to the classical mechanism. The first-order rate constant for the alkylation of toluene and substituted benzenes is in the following order: benzene > toluene > p-xylene > anisole. This indicates that, for this catalyst, the reaction mechanism is different from that of the classical acid catalyzed alkylation reactions. In fact, the probable redox mechanism for the activation of both benzyl chloride and toluene by these catalysts leading to the alkylation of toluene reaction is proposed:

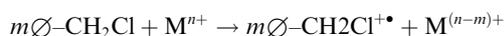
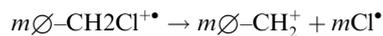


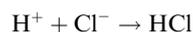
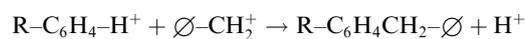
Table 7 Effect of recycling of the Fe (citrates)–Mg–Al-LDH-873 catalyst in the alkylation of toluene with benzyl chloride at 353 K.

	Time ^a (min)	Selectivity benzyl toluene(BTol) (%)		Apparent rate constant K _a (×10 ³ min ⁻¹)	Isomer distribution		
		Benzyl toluene	Poly-benzyl toluene		o-BTol	m-BTol	p-BTol
Fresh	12.5	99.6	0.4	249.0	44.2	2.4	53.0
First reuse	13.1	99.2	0.8	241.3	44.0	2.2	53.0
Second reuse	13.6	97.9	2.1	240.9	43.2	1.3	53.4

^a Time required for total conversion of benzyl chloride.



where M = Fe; $n = 3$ and $m = 1$



The redox mechanism is similar to that proposed earlier for the toluene alkylation reactions (Brio et al., 2001; Choudhary et al., 2002). Moreover, in order to rule out the influence of steric effect on the rate of reaction, we have applied the Taft relation (March, 1985) According to this relation, when a steric effect influences the reaction, there is a linear relation between the rate and the parameter E_s values considered to be representative of the size of the substituting group of the studied aromatic compounds. Using the E_s parameter tabulated by Charton (Charton, 1975) we have shown that such a relation did not exist.

3.2.3. Recycling of the catalysts

The stability of the catalysts has been studied by running the reaction successively with the same catalysts Fe (citrates)–Mg–Al-LDH-773 under the same conditions without any regeneration between two runs. The reaction was first run under the standard conditions (toluene-to-benzyl chloride ratio of 15, 353 K) to the complete conversion of benzyl chloride. Then, after a period of 10 min, another quantity of benzyl chloride was introduced in the reaction mixture leading to the same toluene-to-benzyl chloride ratio. After the achievement of the second run, the same protocol was repeated a second time. The results, presented in Table 7, showed that the catalyst could be used several times in the toluene alkylation process without a significant change of its catalytic activity.

4. Conclusion

In conclusion, Fe (citrates)–Mg–Al-LDH catalysts show amazing activities for the alkylation of aromatics. The mechanism involves a redox step at the reaction initiation. This gives a greater independence to the effect of substituents, and these catalysts can, therefore, be used with substrates of low reactivity. Indeed, the catalytic activity increases with increase in the calcination temperature, this is probably due to the formation of the metal oxide Fe_2O_3 phase. A comparison between the behaviors of the different mixed oxides allows to conclude that the cations dispersion into the mixed oxides govern the basicity of the samples. Therefore, the LDH hybrid route appears very

efficient to obtain highly basic mixed oxides by improving cations dispersion.

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