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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.

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 $(NO_3)_2.6H_2O$ (0.2 M) (Aldrich–Chemie), Al $(NO_3)_3.6H_2O$ (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 $Mg(NO_3)_2.6H_2O$ (0.2 M), $Al(NO_3)_3.6H_2O$ (0.06 M) and $Fe(NO_3)_3.9H_2O$ (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 $(NO_3)_3.9H_2O$ (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 (citrates)–Mg–Al-LDH by the intercalation method «LDH hybrid» (organic and inorganic)

Pre-chelation of Fe^{3+} cation with $C_6O_7H_3^{-3}$((citrates)$^{-3}$) complexing agent was previously performed. For this purpose, aqueous solutions of Fe $(NO_3)_3.9H_2O$ (0.1 M) and Na_3 (citrates) (0.12 M) were mixed according to the stoichiometry ((citrates)$^{3-}$)/Fe^{3+} = 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 (citrates) 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 NO_3^- by the anionic Fe^{3+} 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 Kα1 radiation (λ_α = 1.54184 Å, 40 kV and 50 mA). Data were collected between 2° and 70° 2θ, 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. N_2 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 cm^3) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture-free nitrogen N_2 (flow rate = 30 cm^3 min^{-1}) through the liquid reaction mixture, at the following reaction conditions: reaction mixture = 15 ml of moisture-free liquid aromatic compound

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