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Evolution of Brönsted and Lewis acidity of single and mixed pillared bentonite

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HIGHLIGHTS

- We study by IR spectroscopy the acidity of pillared clay.
- Aluminium pillared clay exhibited only Lewis acidity.
- Zirconium pillared clay exhibited both Lewis and Brönsted acidity.
- Adding aluminium in the zirconium solution leads to an enhancement of the acidity.
- Samples are used as catalyst in the reaction of 1,3-dioxolane synthesis.

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ABSTRACT

The surface acidity of different pillared clay, zirconium-, aluminium- and mixed zirconium–aluminium-pillared bentonite was determined by Fourier transform infrared spectroscopy technique using N-butylamine as probe molecule. The spectra obtained showed well resolved absorption bands for Lewis and Brönsted acid sites in the clay catalysts. In order to understand the role of acid sites present on clay catalysts, synthesis of 2,2-dimethyl-1,3-dioxolane by acetalyzation of acetone with ethylene glycol under autogenous pressure and without solvent has been studied. The Brönsted and Lewis acidity data obtained by FT-IR study for modified bentonite correlated well with the catalytic activity in the synthesis of 2,2-dimethyl-1,3-dioxolane reaction. Among the modified clay catalysts, Zr_{90}–Al_{10}-PILC bentonite catalysts showed good activity and aluminium rich PILC showed negligible activity in the acetalyzation reaction. This inactivity is attributed to the absence of Brönsted acidity.

1. Introduction

Acidity on catalyst surface plays an important role in bringing about various organic transformations. Pillared clays are widely used as solid acid catalyst in different selective organic transformations. This is an aspect of synthetic techniques under Green Chemistry. The pillaring process is known to generate Brönsted and Lewis acid centres in the inter-layer region of the clay. The nature and strength of the acid sites depend upon the starting clay and the pillaring agent [1]. There are several methods to determine the surface acidity of clay minerals such as Hammett indicator technique [2,3], n-butylamine back titration [4], microcalorimetry [5] and FT-IR spectroscopy of adsorbed basic probe molecules [6–12]. Another widely used method to study the surface acidity of a solid catalyst is through the product distribution analysis of some model catalyzed reactions. Isomerisation [13–15], catalytic dehydration [16], and dehydrogenation [17] are the most common typical model reactions used for investigating the acid-base properties of heterogeneous catalyst systems.

In this paper, we evaluate the nature and concentration of acid sites present in different pillared clays catalysts by FT-IR spectroscopic measurements using N-butylamine as a molecular probe. The acetalyzation reaction is selected to measure the activity of the pillared catalyst samples. The objective was to examine whether the acidity measured by the simplified method correlated with the activity of different PILCs in the acetalyzation of acetone with ethylene glycol to give 2,2-dimethyl-1,3-dioxolane.

2. Experimental

2.1. Starting materials

The starting mineral was a purified interstratified illite–smectite (denoted as Na–G) from Gafsa, southwest Tunisia, rich in smec-

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tite (78%) with the presence of small amount of the kaolinite. The smectite fraction had a cation exchange capacity (CEC) of 78 meq per 100 g of clay, a surface area of 107 m^2g^{-1} and a pore volume of 0.02 $cm^3\,g^{-1}$. Its structural formula is: $[Si_{7.43}Al_{0.57}]^{IV}[Al_{2.96}Fe_{0.73}Mg_{0.24}]^{VI}\,Na_{0.71}K_{0.21}Ca_{0.01}; O_{22}$.

2.2. Synthesis of PILCs with single and mixed oxide pillars

The Al-pillared clays were synthesized by intercalating sodium clays with hydroxy-aluminium cations. The pillaring solution was prepared by slow addition of a 0.2 mol/L NaOH solution to an $Al(NO_3)_3{\cdot}9H_2O$, under constant stirring until a OH/Al ratio equal to 2 (pH = 4.1) was reached. The stirring during the addition of NaOH was necessary to prevent local accumulation of hydroxide anions, which invariably produced precipitation of $Al(OH)_3$.

The oligomeric solution was aged for 24 h at home temperature. Then the pillaring solution was added dropwise to a suspension of 1 wt.% bentonite in deionized water. A pillaring stoichiometry of 10 mmol Al/g clay was used. The interchange process was carried out at room temperature for 24 h under constant stirring. The resulting product was separated by centrifugation and washed with distilled water (5 times). Finally it dried at 80 °C and was calcined for 2 h at 550 °C to convert cation-exchanged clay into aluminium-pillared clay. This sample is referred to Al–G.

The pillaring solution employed in the synthesis of Zr pillared clays was prepared by adding of a 0.2 mol/L NaOH to $ZrCl_4$. The pH value of the resulting solution was adjusted to 2.8 to form the pillars of the structure. Then the pillaring solution was added dropwise to a suspension of 1 wt.% bentonite in deionized water. The Zr/clay ratio was 10 mmol/g. The interchange process was carried out at room temperature for 24 h under constant stirring. Finally, the intercalated clay was separated by centrifugation and washed with distilled water (5 times) and then dried at 80 °C, and calcined at 550 °C. The resulting product is referred as Zr–G.

An aluminium–zirconium polycation solution was prepared by slow addition of a 0.2 mol/L NaOH solution to Zr–Al 0.1mol/L solution under vigorous stirring, using a pH value equal 3.8. Three different molar ratios Zr/Al of 10/90, 50/50 and 90/10 were used. The Zr–Al solutions were added dropwise to a suspension of 1 wt.% bentonite in deionized water, using (Zr + Al)/ clay ratio of 10 mmol/g. The suspensions were kept in contact with the solution at room temperature for 24 h, then separated by centrifugation and washed with distilled water (5 times). The intercalated solids were finally dried at 80 °C and calcined at 550 °C. The resulting product was referred as Zr–Al–G. The subindex values indicate the metal percentage in the initial pillaring solution.

2.3. Methods of characterization

The X-ray diffraction (XRD) study was done in a 'Panalytical X'Pert HighScore Plus' device, which operates with Cu Kα radiation.

N_2 adsorption–desorption experiments were carried out at 77 K on Quantachrome, USA instrument. The N_2 isotherms were used to determine the specific surface areas (SA) using the BET equation. The micropore volume was determined using the *t*-plot method and the total pore volume of the samples, Vt, was calculated at $P/P_0 = 0.99$. Before each measurement the samples were outgassed for 2 h at 130 °C.

Surface acidity (Brönsted and Lewis acid centres) was determined by FT-IR spectroscopy method on the basis of adsorption of N-butylamine. With this method 1 mL of butylamine solution was added to 0.1 g of catalyst. The mixture was shaken at room temperature. After drying, each sample was calcined at different temperature ranging from 200 °C to 800 °C. The upper temperature was 800 °C because at this temperature neither characteristic band relative to Lewis nor to Brönsted acids was observed anymore in all samples. For comparison, FT-IR spectra of untreated raw and calcined sample (at 25 °C) are also included in all figures. FT-IR spectra were recorded in the region 1800–400 cm^{-1} on a Perkin–Elmer infrared Fourier transform spectrometer using the KBr pellet technique.

For ^{1}HNMR study, Different spectra were recorded at 300 MHz on Bruker AM 300 spectrometer using 5 mm outer diameter spinning samples tubes. Temperature was fixed at 25 °C using a Bruker VT 1000 variable temperature control unit, measured by calibrated Pt-100 resistance thermometer. The chemical shifts are given in ppm with respect to external TMS reference at 0 ppm.

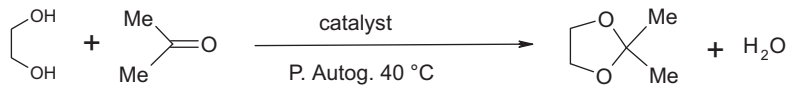
2.4. Catalytic study

For the present study, we have chosen the acetalyzation of acetone with ethylene glycol (Scheme 1). For this reaction 7.68 g (124 mmol) of ethylene glycol, 3.64 g (63 mmol) of acetone and 0.1 g (1 eq.) of PILCs were placed in an autoclave at 40 °C under autogenous pressure and without solvent. Reactions were complete in 96 h; there was no further increase in the yield on continuing the reaction up to 96 h. Then, the reaction mixture cooled, filtered to separate the clay catalyst. The residual ethylene glycol was eliminated by washing of the filtrate with water (20 mL). The mixture was finally concentrated under reduced pressure. The product was extracted with diethyl ether. The organic phase was collected and dried over manganese sulphate. The mixture was finally concentrated under reduced pressure and the 2,2-dimethyl-1,3-dioxolane was recuperated. After evaporation of solvent (ether and acetone), the product was identified by its IR, and ^{1}HNMR spectral analysis.

3. Results and discussion

The oriented powder X-ray diffractograms of pillared clays are shown in Fig. 1. Results indicates that the basal spacing values of Na–G is found to be modified after modifying the clay with simple oxide pillar (zirconium or aluminium) or mixed oxide pillar (zirconium–aluminium). In fact, the shifting of d_{001} basal spacing from 12 Å (starting clay) to 17.4–20.5 Å confirms the modification via pillaring. The incorporation of Al leads to an increase of the basal spacing. This enhancement of basal spacing depend in the amount of Al introduced. In fact d_{001} is 18.3, 19.23 and 20.5 Å for Zr_{10}–Al_{90}-PILC, Zr_{50}–Al_{50}-PILC and Zr_{90}–Al_{10}-PILC respectively. Thus, sample prepared with a small amount of Al (10%) seems to be the sample having the highest basal spacing.

The values of the specific surface area of different bentonite catalysts are summarized in Table 1. As can be seen, specific surface area also increased after pillaring. This increase of S_{BET} is essentially related to the creation of micropores by the pillaring process and confirms that pillar species used during preparation had entered between the clay layers, increasing the nitrogen accessibility.



Scheme 1. Schematic representation of acetalyzation of acetone with ethylene glycol.