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Effect of acid modification of kaolin and metakaolin on Brønsted acidity and catalytic properties in the synthesis of octahydro-2*H*-chromen-4-ol from vanillin and isopulegol

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ABSTRACT

Natural kaolin and the metakaolin obtained by calcination of kaolin at 650 °C were chemically activated using 0.25–3.0 mol/dm^3 HCl solutions. Structural and textural properties of samples were characterized by X-ray diffraction, elemental analysis and N_2-adsorption/desorption analyses. The amount of Brønsted acid sites (BAS) was determined by infrared spectroscopy using pyridine as probe molecule. The amount of BAS for kaolin rose with increasing HCl concentration up to 1.0 M, and decreased for higher concentrations, that is related with the leaching of Al from the solid. Effect of HCl concentration on amount of BAS was negligible for metakaolin. The catalytic performance of these materials was investigated in the Prins cyclization of (−)-isopulegol with vanillin to form octahydro-2*H*-chromen-4-ol, carried out in toluene at 50 °C. The reaction rate and the selectivity toward octahydro-2*H*-chromen-4-ol depended on the Bronsted acidity, structural and textural properties of the catalysts. The reaction rate in the presence of kaolin modified by HCl correlated with the amount of BAS. HCl-kaolin samples were more active compared with HCl-metakaolin, while selectivity reaction toward octahydro-2*H*-chromen-4-ol was larger in the presence of HCl-metakaolin.

1. Introduction

Clays are very versatile materials widely used in acid and oxidation catalysis, both as catalysts themselves and as supports of other active phases. Acid modification is one of the ways for improving the application of clays in acid catalysis. Modification of clays by acids proceeds via dissolution of soluble admixtures (such as calcite), replacement of interlamellar cations by protons and acid leaching of Mg^{2+}, Al^{3+} and Fe^{3+} from the octahedral layers, resulting in enhanced Brønsted acidity. Numerous studies have been reported on the acid treatment of clays, especially on montmorillonite and kaolin [1–4]. Several reaction parameters may be tailored in the process, as the nature of the acid and of the clay, acid concentration, temperature, time, and acid/clay ratio, allowing to control the level of clay modification. The use of various types of acids, such as H_2SO_4, HCl, HNO_3, CH_3COOH, etc., for acid treatment has been reported, HCl and H_2SO_4 are the most widely used due to their large effect on the process parameters (specific surface area, porosity, acidity etc.).

The catalytic application of acid-activated clays has been reported for several reactions, such as isomerization [1,5], alkylation [6,7], acylation [8] and various transformations of terpenoids

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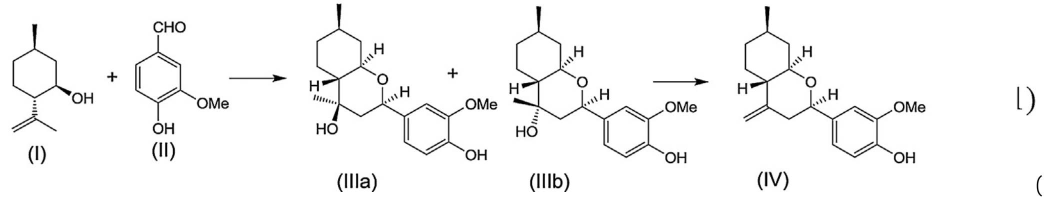
[9,10]. Recently, acid-activated clays were suggested as catalysts for the reaction of homoallylic alcohols with aldehydes (variant of the Prins cyclization reaction) which is one of the routes for the synthesis of a wide range of tetrahydropyran derivatives [11–14]. Montmorillonite clays have been generally the most popular catalysts for this type of reactions. Thus, the reaction of (−)-isopulegol with various types of aldehydes led to various octahydro-*2H*-chromen-4-ols with good yields in the presence of acid-activated montmorillonite [12,13]. It is remarkable that these compounds possess biological activity.

In a previous work [15], we have also demonstrated the applicability of montmorillonite modified by 0.125–3.0 mol/dm^3 HCl (HCl-MM) for the synthesis of octahydro-*2H*-chromen-4-ol from (−)-isopulegol (I) and vanillin (II) (Reaction (1)). The effect of the acid-activation on the surface acidity and the porous structure of montmorillonite, and, therefore, on the catalytic efficiency of HCl-montmorillonite, was evaluated. It was found that the amount of Brønsted acid sites (BAS), which rose with increasing HCl concentration, was a key factor for the adjustment of the reaction rate and the selectivity of the reaction. The increase of the amount of BAS led to the increase in the reaction rate and the decrease in the selectivity toward (IIIa + IIIb) due to dehydration of (III) to (IV).



(1)

In a further investigation, it was found that kaolinitic clays, namely the kaolin from Kampanovsk (Krasnoyarsk, Russia), and the metakaolin obtained by its calcination at 650 °C, can also be successfully used as catalysts for this reaction [16]. The activities and selectivities of montmorillonite, kaolin and metakaolin modified by 0.5 mol/dm^3 HCl were compared, finding that the reaction proceeded at 35 °C in the presence of montmorillonite, while it was necessary to increase the temperature to 50 °C in the presence of kaolin and metakaolin. The main products of the reaction were the isomers (IIIa,b). In the presence of acid activated metakaolin, the selectivity toward (III) was higher (89.8%) than when using acid activated montmorillonite and kaolin, while the conversion of (II) was lower (25.5%).

In our previous research [16], the effect of acid-activation intensity on the catalytic efficiency of kaolin and metakaolin was not investigated. Thus, the catalytic performance in Prins cyclization (Reaction 1) of two series of solids prepared by the acid activation of the kaolin from Kampanovsk (Krasnoyarsk, Russia) and the metakaolin obtained by its calcination at 650 °C is now reported. The main objectives of this study is to reveal the effect of the HCl concentration used for the acid-activation on the surface acidity and the porous structure of kaolin and metakaolin, and the subsequent influence on the catalytic performance of the resulting solids in the Prins cyclization reaction of (−)-isopulegol with vanillin to octahydro-2*H*-chromen-4-ol.

2. Experimental

2.1. Materials

(−)-Isopulegol and vanillin were purchased from Acros Organic. Tridecane and toluene were purchased from Aldrich. Kaolin was obtained from a deposit located in Kampanovsk (Krasnoyarsk, Russia). Metakaolin was prepared by the calcination of kaolin in air at 650 °C for 4 h. Chemical composition and textural properties of kaolin and metakaolin are shown in Tables 1 and 2.

2.2. Modification of clays by HCl

The acid activation of the clays was carried out by the following method: 5.0 g of kaolin or metakaolin were suspended in 150 cm^3 of aqueous solutions of 0.25; 0.50; 1.0 or 3.0 mol/dm^3 of HCl, and the mixture was stirred at room temperature for 7 days. Then, the solid was separated, washed with water and dried at room temperature. The notation and the chemical compositions of the acid activated samples are presented in Table 1.

2.3. Instrumental measurements

The chemical analyses of the solids were carried out by means of inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The X-ray diffraction patterns from random samples were collected on a X-ray diffractometer (Ultima-IV, Rigaku), acquired as part of the Moscow State University Development Program, with Cu-Kα radiation ($\lambda = 1.54056$ Å), rapid detector D/Tex-Ultra, scan range 3.6–65° 2θ, scan speed 5°/min, step 0.02° 2θ, and maximum intensity ~25,000 counts. Mineral composition was estimated using Rietveld method [17] with PROFEX GUI for BGMN, the calculation accuracy was 5%.

The porous structure of the materials was studied from nitrogen (Air Liquide, 99.999%) adsorption at −196 °C using a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyser). All samples (0.2 g) were degassed for 24 h at 200 °C at a pressure lower than 0.133 Pa. The specific surface area (S_{BET}) was calculated from the adsorption data over the relative pressure range between 0.05 and 0.20. The total pore volume (V_{Σ}) was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.99. The micropore volume ($V\mu$) and the external specific surface area (S_{ext}) were calculated using the *t*-plot method, and the pore diameter applying the BJH method [18].

2.4. Infrared spectroscopy measurements

For studies of Brønsted surface acidity, the samples were pressed into self-supporting wafers (10–25 mg/cm^2) and pre-treated within the IR cell by heating at 500 °C under vacuum for 1 h and then in air before the adsorption experiments. Then, the samples were exposed to saturated pyridine vapors at room temperature for 10 min and under vacuum for 15 min at 150 °C. Then pyridine was desorbed until a pressure of 10^{-6} mbar, when there is no more physisorbed pyridine on the wafers. The strength of Brønsted acid sites (BAS) was characterized by the proton affinity values (PA) calculated using Eq. (1) [19]:

$$PA = \frac{\log(3400 - \nu_{NH})}{0.0023} - 51 \qquad (1)$$

where PA (kJ/mol) is the energy of the proton elimination from the acid residue, 3400 cm^{-1} is the wavenumber of the band of the undisturbed N—H bond in the pyridinium ion, and ν_{NH} (cm^{-1}) is the wavenumber of the centre of gravity of the stretching vibration band of the pyridinium ion, which depends on the basicity of the acid residue and is determined from the contour of the ν_{NH} band.