



Esterification processes based on functionalized mesoporous solids



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ABSTRACT

The abilities of niobium and manganese to enhance oxidation of thiol groups in (3-mercaptopropyl)trimethoxysilane (MPTMS) used for functionalization of SBA-15 and MCF materials, by hydrogen peroxide in order to form catalysts with acidic properties were evaluated. Materials obtained were characterized by: N₂ adsorption, XRD, XRF, elemental and thermal analyses and titration of acid sites. The highest concentration of acidic sites was found for SBA-15 structure modified with niobium. The catalytic activities of materials obtained were examined in esterification of acetic acid with ethanol and 2-propanol. Both niobium containing samples (MP-NbSBA-15 and MP-NbMCF) showed high yields of ethyl and 2-propyl acetate. The amount of 2-propyl acetate formed was found to linearly depend on the number of acid sites on the catalyst surface. The reuse tests proved that the drop in the catalyst activity in consecutive catalytic cycles is not too high, which suggests possible application of the materials obtained after further optimization.

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1. Introduction

Esterification is a very important process in organic synthesis [1] as well as in fuel industry [2] mainly related to biodiesel production (formation of fatty acid esters). Despite the lower cost of fossil fuel in relation to biodiesel, the production of latter fuel is still increasing as this fuel is more environmentally friendly [3]. Esterification processes used in industry are mainly carried out in homogeneous phase in the presence of acidic catalysts like H₂SO₄, HCl, H₃PO₄ or *p*-toluene sulphonic acid. It implies some difficulties related to corrosion of the apparatus, separation of products and wastes. These problems can be overcome by the application of solid catalysts having acidic centres on the surface. Moreover, solid catalysts offer a possibility to conduct reactions in continuous, fixed bed reactors [4].

As mentioned above, esters of fatty acids are used in large quantities for biodiesel production. However, other esters of organic acids have a variety of applications. One of the acids commonly used for esterification is acetic acid. Transformation of this acid with ethanol leads to ethyl acetate, which is an important compound for many applications in chemical industry. For instance, ethyl acetate is used for the production of adhesives, coatings, perfumes or plasticizers [5]. 2-Propyl acetate is obtained in esterification of acetic acid with 2-propanol and mainly used as a solvent. Moreover, the heat

of combustion of ethyl acetate and 2-propyl acetate is ca. 50% and 35% lower, respectively, than for e.g. methyl oleate. This does not exclude the use of both esters as additives for biodiesel and what is more ethyl and 2-propyl acetates increase the cold resistance of biofuel.

Different heterogeneous catalysts were tested in the esterification of acetic acid with ethanol and 2-propanol, including carbon materials [6,7], zeolites [4,5,8], aluminophosphates [9], mesoporous solids [10], heteropolyacids [11–13] also including group five elements [12], montmorillonite [14] or resins [15–17]. However, because of the nature of esterification processes the very high yield of ester is limited by reaction equilibrium. It can be overcome by favouring of the product side by either the use of one reactant in excess over the other or the continuous removal of water formed [1].

In our previous works we developed a method for efficient formation of acid catalysts based on mesoporous materials functionalized with (3-mercaptopropyl)trimethoxysilane (MPTMS) [18,19]. The materials obtained were applied in acetic acid esterification with glycerol. It has been found that in the process mentioned, which proceeds via three steps (formation of monoacetylglycerols, diacetylglycerols and finally triacetylglycerol) not only the number but also the strength of acidic sites determine the formation of the target product, i.e. triacetylglycerol. In that case the catalytic results were not straightly dependent on acid site number. Therefore, in this paper we would like to check these properties in single step process. For that purpose the esterification of acetic acid with ethanol and 2-propanol

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(i.e. processes that are also relevant for industry) were chosen. Moreover, these processes were not much investigated using catalytic system applied in this study, especially in relation to MCF materials having high pore diameter. In this paper we obtained a series of catalysts differing in the number of acid sites, using the same methodology of preparation. For this purpose niobium and manganese were chosen as modifiers of mesoporous materials. Both metals play an important role in the oxidation of SH groups to sulphonic ones by H_2O_2 as evidenced in [20]. On the other hand manganese easily changes its oxidation state contrary to niobium species and it is more hardly introduced to mesoporous silica structure if used in the form of cationic species and under the conditions applied for SBA-15 and MCF syntheses. One can expect that such differences will be reflected in the anchoring of MPTMS and oxidation of SH groups to SO_3H and moreover, will allow checking if the effectiveness of oxidation of thiol groups by H_2O_2 depends or not on the incorporation of transition metal into the silica structure.

2. Experimental

2.1. Preparation of SBA-15 type catalysts

SBA-15 catalysts functionalized with MPTMS, (3-mercaptopropyl)trimethoxysilane and modified with Nb or Mn were prepared via hydrothermal synthesis. The synthesis was performed in polypropylene bottle (PP). The synthesis procedure was as follows. To the PP bottle the Pluronic P123 (Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Aldrich—8 g), HCl (Chempur 35%—17.52 g) and water (282.5 g) were added. When the surfactant was dissolved a TEOS (Aldrich—17.054 g) was dropwise inserted. After 45 min MPTMS (Aldrich—1.69 g) and hydrogen peroxide (Merck 35%—7.17 g) were added. For metal containing samples, ammonium niobate(V) oxalate (Aldrich) or manganese(II) nitrate tetrahydrate (Aldrich) were also added to the gel (10 min after TEOS addition) keeping Si/Nb or Si/Mn molar ratio 64. Final mixture was stirred at 313 K for 20 h and then heated at 373 K under static conditions for 24 h. The product was washed with water and dried at RT. The template was removed by constant extraction with ethanol in Soxhlet apparatus.

2.2. Preparation of MCF type catalysts

MCF catalysts functionalized with MPTMS, (3-mercaptopropyl)trimethoxysilane and modified with Nb or Mn were prepared via hydrothermal synthesis similar like for SBA-15. 1,3,5-trimethylbenzene (Aldrich—12 g) and NH_4F (Aldrich—0.0934 g) were added under vigorous stirring after dissolving of Pluronic P123. TEOS was added one hour after 1,3,5-trimethylbenzene and NH_4F addition. Next steps were the same as for SBA-15.

2.3. Characterization techniques

The materials prepared were characterized using different analytical techniques: N_2 adsorption/desorption, XRD, XRF, elemental analysis and amperometric titration.

XRD patterns were recorded at room temperature on a Bruker AXS D8 Advance apparatus using $Cu K\alpha$ radiation ($\alpha = 0.154$ nm), with a step of 0.02° and 0.05° in the small-angle and wide-angle, respectively.

N_2 adsorption/desorption isotherms were obtained on a Micrometrics ASAP 2010. First, samples (200 mg) were outgassed under vacuum at 423 K to remove water or solvent, like ethanol from pores. The surface area was calculated using the BET method. Pore volume, cells and windows diameter of MCF materials were estimated according to Broekhoff-de Boer method with Frenkel–Halsey–Hills approximation [21].

X-ray fluorescence (XRF) using MiniPal-Philips instrument was applied to determine the real molar ratio of Si/Nb or Ta in materials prepared. The calculations were performed using calibration curve based on reference mixtures of silica (Degussa) and metal oxide Nb_2O_5 (Alfa Aesar). The calibration curves consisted of 10 points related to different Si/Nb molar ratio in the range from 3 to 300. The metal concentration in a sample was established by the amount of emitted X-ray radiation related to the values in the calibration curves.

Elemental analyses of materials obtained were performed using Elementar Analyser Vario EL III.

Titration of acidic sites was performed using 100 mg of anhydrous material (dried at 423 K for 12 h). Catalyst was immersed in a 2 M NaCl solution (60 cm^3) and stirred at RT for 18 h. After this time the solution was titrated with 0.005 M NaOH solution.

2.4. Esterification processes

Esterification of acetic acid with ethanol or 2-propanol was performed in a liquid phase in batch reactor without usage of any solvents. The reactor was equipped with a condenser and a process was conducted at autogenously pressure. The reaction was carried out for 4 h at 363 K and 373 K for ethanol and 2-propanol, respectively. Before reaction catalyst was activated in oven at 423 K for 12 h. 12 g of acetic acid was used for all reaction keeping molar ratio of acetic acid to alcohol 2:1. The volume of solution after the reaction was checked each time to indicate that there is no leak in the system. For selected catalysts the reuse test was performed. Prior this process the catalyst after the first run of reaction was separated from reactant mixture by centrifugation and dried in oven overnight at 423 K. Then the catalysts were applied for the next use. The composition of products were analysed by a gas chromatograph (Thermo Scientific—Focus) equipped with 60 m DB-1 capillary column, worked at the temperature range of 313–523 K (temperature ramp 10 K min^{-1}), and MS detector. The quantitative analysis were performed by acetic acid titration with sodium hydroxide solution.

3. Results and discussion

3.1. Texture/structure parameters

Two different types of mesoporous materials, i.e. SBA-15 and MCF, were functionalized with MPTMS using one-pot synthesis procedure in the presence of hydrogen peroxide. H_2O_2 was applied to oxidize thiol species. Moreover, the materials were also modified with Mn or Nb mainly to enhance the efficiency of sulphonic species formation [22]. The choice of different structured materials (SBA-15 with hexagonally ordered mesopores and mesoporous cellular foams (MCF) containing big cells and windows) was dictated by the expected differences in the location of the active sites and in their availability to reagents. SBA-15 based samples show typical XRD patterns characteristic of this solid material (Fig. 1). An intensive peak assigned to (1 0 0) plane is observed at 2 theta below 1° . The structure of SBA-15 samples is also ordered in long distance, which is testified by the presence of two additional peaks at 2 theta between 1 and 2° . These peaks are assigned to (1 1 0) and (2 0 0) planes, respectively. XRD patterns of MCF materials do not show peaks in this region (data not shown here). This is typical of samples with relatively high mesoporous diameter. It is known, that the increase in pore diameter shifts the position of (1 0 0) plane to a lower value of 2 theta.

The structure of MCF materials can be confirmed by their sorption properties. Fig. 2 presents the N_2 adsorption/desorption isotherms and the parameters calculated from it are shown in Table 1. The shape of isotherms presented in Fig. 2 is

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