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Isomerization of α-pinene oxide catalyzed by iron-modified mesoporous silicates

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ABSTRACT

Iron-modified mesoporous silicates (Fe-MCM) were prepared through a direct hydrothermal method and characterized by N_2 adsorption–desorption, XRD, Mössbauer spectroscopy and SEM-EDS techniques. The nature of the iron precursor (Fe^{2+} or Fe^{3+}) strongly affected the textural and morphological properties of the materials. Fe^{2+}-MCM presented the morphology similar to sheets with nanometer dimensions, while Fe^{3+}-MCM was more similar to the non-modified MCM. Characterizations suggest that most of the introduced iron species present on the material surface rather than in the silicate framework. Besides the framework included Fe^{3+} ions (0.2–0.3 wt.%), both materials contain only the trivalent iron (as hematite). Hematite nanoparticles are highly dispersed on the Fe^{3+}-MCM surface, whereas in Fe^{2+}-MCM, hematite forms particles of both low and high dispersion. The materials were shown to be efficient heterogeneous catalysts for the transformation of α-pinene oxide in various value-added fragrance compounds, with the product distribution being remarkably dependent on the solvent nature.

1. Introduction

Ordered mesoporous molecular sieves, such as MCM-41, discovered by Mobil Company in 1992, have received considerable attention in catalysis research over the last decades [1–3]. These solids are synthesized in the presence of surfactants that act as structure templates directing the formation of solids from silicate gels. The MCM-41 materials possess a high surface area (above 700 $m^2 g^{-1}$) and hexagonal array of uniform mesopores (2–10 nm) with narrow pore size distribution. Such large pore solids are especially important as catalysts to transform bulky substrate molecules in the fine chemicals industry. The catalytic processes based on MCM-41 are usually not complicated by diffusion problems [4].

The main problems in using MCM-41 for catalysis are its poor acidity and low thermal stability. However, silicon substitution by metal, e.g., iron, could result in a catalytically active solid with tunable properties [5]. Doping mesoporous silicates with iron renders to the material the Lewis-type acidity and the possibility of reversible valency changes. This opens a perspective to use iron-containing silicates, such as Fe-MCM-41, as heterogeneous catalysts in both oxidative and acid catalysis [6].

Although iron catalysts are widely used in oxidation reactions (e.g., in Fenton processes [7–10]), the potential of heterogeneous iron-containing materials as Lewis acid catalysts has been much poorly explored. In particular, Fe-MCM-41 catalysts were employed in a wide variety of oxidative transformations, such as dehydrogenation [11,12], oxidation of aromatics [13–15] and desulfurization (ODS) [16]. However, the applications of Fe-MCM-41 in acid catalyzed reactions are scarce, being mainly restricted to Friedel–Crafts alkylation of benzene [17,18] and aminolysis of epoxides [19].

It is well established that the method applied for the incorporation of transition metals into mesoporous molecular sieves strongly affects the properties of the resulted solid. The doping metal can be introduced either by post-synthesis impregnation or by direct in situ inclusion during the synthesis of the silicate. Most of the included Fe-MCM-41 materials reported in the literature were prepared using ferric salts (usually $Fe(NO_3)_3$) as a starting material. In the present work, we decided to verify, for the first time to our knowledge, the effect of iron precursor (ferrous, Fe^{2+}, or ferric, Fe^{3+}) on the morphology of the modified mesoporous molecular sieves and their catalytic properties. The isomerization of α-pinene oxide, which is one of the most important processes in the fragrance industry, has been chosen as a test reaction.

Terpenic compounds, in general, are an important renewable feedstock for the fragrance industry. In particular, α-pinene oxide can be converted by acid-catalyzed transformations in various expensive compounds, such as campholenic aldehyde, *trans*-carveol and *trans*-sobrerol [20–27]. Due to the high reactivity of this substrate in the presence of acid, the development of

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the process, which is selective for one or two particular products is a difficult task. In this direction, heterogeneous catalysts based on the iron-modified mesoporous silicates, which combine a high surface area, large pores and specific active sites, can be an attractive option. As far as we know, no attempt to use iron-containing silicates for the isomerization of α-pinene oxide has been made so far.

2. Experimental

2.1. Synthesis and characterization

The Fe-containing mesoporous silicates were prepared by the direct incorporation of either Fe^{2+} or Fe^{3+} into silicate structure. In the synthesis of Fe-MCM, cetyltrimethylammonium bromide (1.63 g, 4.47 mmol, Vetec) was dissolved in a mixture of aqueous sodium hydroxide (10.0 mL, 1 M, Aldrich), water (30.0 mL) and $FeSO_4{\cdot}7H_2O$ (0.16 g, 18.4 mmol, Vetec) to obtain the Fe^{2+}-MCM material or $Fe(NO_3)_3{\cdot}9H_2O$ (0.23 g, 18.4 mmol, Aldrich) to obtain the Fe^{3+}-MCM material. Next, tetraethyl orthosilicate (TEOS) (3.7 mL, 17.0 mmol, Aldrich) was added dropwise. The mixtures were stirred at 25 °C for 2 h with pH being maintained at 11 through the addition of sodium hydroxide. The solids obtained were filtered, washed with water, dried and calcined at 600 °C for 5 h under a flow of air (100 mL min^{-1}). A pure MCM-41 to be tested in blank reactions was prepared by the same procedure without the addition of ferrous sulfate or ferric nitrate. A supported iron catalyst to be tested for comparison was prepared by a simple impregnation via incipient wetness technique of the MCM-41 with aqueous iron nitrate solution ($Fe(NO_3)_3{\cdot}9H_2O$) (Aldrich). The sample was dried in air oven at 110 °C and then calcined in air at 600 °C for 4 h at a heating rate of 10 °C/min. The impregnated material was designated as the Fe/MCM-41 catalyst.

The catalysts were characterized by nitrogen adsorption (−196 °C) in an AUTOSORB 1-Quantachrome system. The surface area was calculated using the BET model; the total pore volume was estimated from the amount of nitrogen adsorbed at $P/P_0 = 0.95$; and the pore size distribution was calculated based on the BJH theory. Energy dispersive X-ray spectroscopy (EDS) data were collected using an EDS/INCA 350 equipment. Mössbauer spectra were collected in constant acceleration transmission mode with a 10 mCi $^{57}Co/Rh$ source at 25 and −193 °C. The data were stored in a 1024-channel MCS memory unit and were fitted using Lorentzian line shapes with a least-squares fitting procedure using the NORMOS program. Isomer shifts were calculated relatively to α-Fe.

The content of Fe was determined by atomic absorption analyses on an (Carl Zeiss Jena AAS) instrument equipped with a background corrector for Zeeman polarization.

The samples were characterized by scanning electron microscopy (SEM) using a JEOL analyzer coupled to an Oxford (EDS/INCA 350) energy dispersive X-ray analyzer with an acceleration potential of 200 kV.

The powder X-ray diffractometry (XRD) measurements were performed on a Rigaku model Geigerflex-3034 equipment using a Cu Kα radiation scanning from 2° to 10° (2θ). Silicon was used as an external standard.

The acidic properties of solids were determined by temperature-programmed desorption using ammonia as probe molecule. The NH_3-TPD profiles were obtained using a Chembet-3000 (Quantachrome) equipment (TCD detector, current of 150 mA, attenuation of 32). About 0.2 g of each solid was treated at 400 °C for 50 min in a continuous flow of helium (80 mL min^{-1}) prior to adsorption of NH_3 at 50 °C. After the sample has been purged, the profiles obtained from heating rate of 10°/min up to 500 °C.

2.2. Catalytic tests

The reactions were carried out in a glass reactor equipped with a magnetic stirrer and a condensor. In a typical run, a mixture (total volume of 5.0 mL) of α-pinene oxide (0.75–3.0 mmol, 0.15–0.6 M), dodecane (0.5 mmol, 0.1 M, GC internal standard) and the solid catalyst (25–50 mg of MCM-41, Fe^{3+}-MCM or Fe^{2+}-MCM) in a specified solvent was intensely stirred under air at a specified temperature (40–60 °C). The reactions were followed by gas chromatography (GC) using a Shimadzu 17 instrument fitted with a Carbowax 20 M capillary column and a flame ionization detector. At indicated time intervals, stirring was stopped and after catalyst settling down aliquots were taken and analyzed by GC. The calculations of the mass balance, product selectivity and yield were based on the reacted substrate using dodecane as an internal standard. Any difference in mass balance was attributed to the formation of unidentified minor products and oligomers, which were GC unobservable.

To control metal leaching and the possibility of a homogeneous reaction, the catalyst was removed by centrifugation of the reaction mixture at the reaction temperature to avoid re-adsorption of active components onto silica. No further reaction was observed in such experiments, indicating the absence of Fe leaching.

The structures of products **2**–**5** were identified by GC/MS (Shimadzu QP2010-PLUS instrument, 70 eV) by comparison with authentic samples.

Spectroscopic data for *trans*-sobrerol (**2**), campholenic aldehyde (**3**) and *trans*-carveol (**4**) have been reported in our previous works [23,24].

Mass-spectroscopic data for 2-hydroxy-p-mentha-1(7),8-diene (**5**) (m/z/rel.int.): 152/11, 134/56, 137/30, 119/89, 109/100, 95/33, 93/30, 91/55, 81/36, 79/33, 67/35 and 55/34.

3. Results and discussion

3.1. Characterization of the catalysts

The results of the elemental analysis of the prepared samples, their BET surface areas and pore volumes are presented in Table 1. Nitrogen adsorption–desorption isotherms and corresponding BJH pore size distributions are shown in Fig. 1. The MCM-41, Fe^{2+}-MCM and Fe^{3+}-MCM materials showed high specific surface areas of 1406, 911, and 676 $m^2\,g^{-1}$, respectively. The samples exhibited a type IV isotherm, characteristic of mesoporous materials and a type H1 hysteresis loop (Fig. 1a) related to the filling of the mesopores due to capillary condensation [28,29]. However, considering the values of average pore diameter the presence of some pores in the microporous region, especially in the non-modified sample, cannot be excluded. The pore size distribution in the MCM-41 sample is narrow and monomodal, showing a peak pore diameter at ca. 1.7 nm (Fig. 1b). Both iron-containing MCM samples exhibited bimodal distributions of porous sizes with two distinguishable peaks (Fig. 1b). The first peaks (centered at about 1.7 nm) are narrow and weak, whereas the second peaks (centered at ca. 3–4 nm in Fe^{3+}-MCM and ca. 5–9 nm in Fe^{2+}-MCM) are much broader and much intense than the first one. These results indicate much higher structural disorder of the modified materials compared to the pure MCM-41.

Thus, the incorporation of iron species decreases the BET surface area of the silicate and increases the average pore diameter. However, the presence of larger pores in the modified materials can enhance their mass transfer properties, which is highly important for the conversion of bulky natural substrates. Probably, the strong modification of textural properties of the mesoporous material at the incorporation of iron was due to the significant differences