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An atom-economic reaction for synthesis of 1-phenoxy-2-propanol over Al_2O_3/MgO

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ABSTRACT

Al_2O_3/MgO materials with various Mg/Al molar ratios were prepared and characterized by XRD, FT-IR, SEM and BET analysis. These materials were used as catalysts for synthesis of 1-phenoxy-2-propanol (1-PhP) from phenol and propylene oxide as compared with some oxides, i.e. MgO, CaO, ZnO and Al_2O_3, etc. Al_2O_3/MgO with Al/Mg molar ratio of 1.5% exhibited outstanding catalytic performance with 98.2% conversion and 99.3% selectivity to 1-PhP at 120 °C for 5 h. This catalyst can be easily recovered and reused due to its heterogeneous catalytic nature.

1. Introduction

Glycol ether is an important chemical widely used as an industrial solvent for coating materials, printing ink, leather dyeing, etc. Because of the low toxicity of propylene glycol ether, it is expected as a safe substitute for toxic ethylene glycol ether. As one of the most important propylene glycol ethers, propanediol phenyl ether (or phenoxy propanol) is widely used as green coating assistant to remarkably modify the properties of leveling, gloss and richness due to its characteristics of nonvolatile, solvency for resins and good compactness of the formed coatings, etc., as well as a chemical building block for the manufacture of propylene glycol ether acetate. In addition, 1-phenoxy-2-propanol (1-PhP) is a useful anaesthetic for gastropods used in neurophysiology [1]. There are several methods for synthesis of propylene glycol ether. Among them, propylene oxide route is the most convenient and industrially feasible in terms of atom-economy and energy-efficiency. In this process, propylene oxide reacts with a substrate containing hydroxyl group to form propylene glycol ether catalyzed by acid or base catalysts, including earlier homogeneous acids or bases, such as NaOH, alcoholic sodium, H_2SO_4 and BF_3, etc., [2,3] and later solid acids or bases, e.g. acidic zeolites [4], Mg/Al Hydrotalcite [5], ZnMgAl-mixed oxides [6], MgO [7] and amine modified porous silica [8], etc. There are a few of investigations on synthesis of 1-PhP from phenol and propylene oxide [9,10]. In recent years, our group has disclosed highly selective synthesis of propylene glycol ether from methanol and propylene oxide catalyzed by basic ionic liquid [11]. As our continuous research work, here we wish to report the synthesis of 1-PhP over Al_2O_3/MgO via an atom-economic reaction. The simply prepared catalyst with low cost performed excellent catalytic performance for synthesis of 1-PhP and the results were reported in this paper.

2. Experimental

2.1. Catalyst preparation

MgO was purchased from Guangfu Institute of Fine Chemicals in Tianjin of China and directly used as catalyst in the reaction without any pretreatments.

20 g of MgO and aqueous solution containing 0.3 mol/L $Al(NO_3)_3$ (13–54 mL) were charged into a three-neck flask. The mixture was maintained at 80 °C for 1 h under stirring, and then aged statically at the same temperature for another 12 h. At that moment, the resultant mixture was changed to be viscous, followed by dried at 100 °C for 12 h. Thereafter, the solid was calcined at 300 °C for 4 h in a furnace and Al_2O_3/MgO with different molar ratios was obtained after cooling to room temperature.

MgO (s1) was synthesized as following procedure: ammonia (25%) was slowly dropped into 0.1 mol/L MgCl solution (6 g MgCl in 1 L H_2O) in a flask to reach at pH 10 of the solution with stirring. The mixture solution was continuously stirred for 30 min, and then aged for 2 h. The white solid obtained by filtration of the mixture

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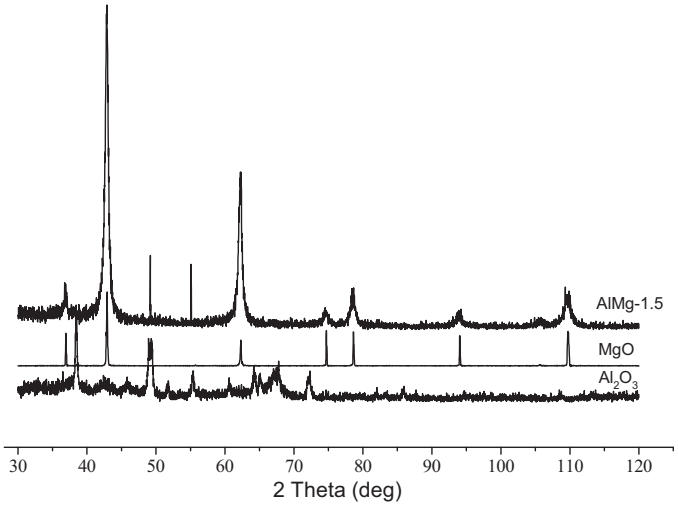

Fig. 1. XRD pattern of Al_2O_3-MgO composite.

solution was dried at 100 °C, followed by calcined at 300 °C for 4 h to afford MgO (s1).

MgO (s2) was synthesized through the same method for Al_2O_3/MgO preparation. 10 g of MgO was charged into 10 mL water in a three-neck flask. The mixture was stirred at 80 °C for 1 h, and then aged statically at the same temperature for 12 h, followed by dried at 100 °C for 12 h. Thereafter, the solid was calcined at 300 °C for 4 h in a furnace to afford MgO (s2).

2.2. Catalyst characterization

The XRD of the samples was performed on a Bruker-D8 Advance X-ray diffractometer with Cu Kα radiation (40 kV and 36 mA). The morphologies of the samples were observed by a Hitachi S-4800 scanning electron microscopy (SEM). FT-IR spectra of the samples were recorded on vertex 80 infrared spectrometer (Brucker Company). The surface area of the catalyst was determined by N_2 adsorption–desorption using NOVA 2000e surface area and pore size analyzer. The elemental analysis of the Al_2O_3-MgO was made on ICP-MS (Angilent Company).

2.3. Catalysis test

All the reactions were carried out in a sealed stainless-steel autoclave (500 mL) equipped with a mechanical stirrer and an electric heater. In a typical procedure, 30.1 g (0.32 mol) of phenol, 30 mL (0.5 mol) of propylene oxide and 1.5 g of catalyst were added into the reactor. After purging for 5 min with N_2 flow, the mixture was heated to the desired temperature under stirring. After the reaction was completed, the reaction mixture was cooled down to room temperature and filtered to remove the catalyst. The liquid samples were analyzed by GC and GC-MS. The catalyst was washed with ethanol, then dried and used for the next run. The conversion and yield was calculated on the basis of phenol.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 illustrates XRD patterns of Al_2O_3/MgO, MgO and Al_2O_3. As compared with that of MgO and Al_2O_3, the composite material prepared from magnesium and aluminum salts is mainly composed of MgO and Al_2O_3 as shown in the figure and the characteristic diffraction peaks of Al_2O_3 at $2\theta = 48.9°$ and 55.2° were observed, although there is a little content of Al in the composite (1.5% mol/mol, denoted as AlMg-1.5). Therefore, this material was confirmed to be mixed phase of MgO and Al_2O_3 with a higher crystalline.

In order to investigate the surface properties for the Al_2O_3/MgO composite, the morphology of the composites with different calcined temperatures was observed with SEM (Fig. 2). A mixture of thin flat and needle-like crystals was formed. The size in needle width was less than 100 nm and it was uniformly dispersed as shown in Fig. 2a and d, which is beneficial to its catalytic performance for the addition reaction. With the increase in calcination temperature the surface morphology was obviously changed. The crystalline was reduced and the thin flat and needle crystals began to aggregate at calcination temperature of 400 and 500 °C (Fig. 2b and c). As a result, the surface area of the composite AlMg-1.5 was remarkably decreased from 84.6 to 66.7 m^2/g with increase in calcination temperature from 300 to 500 °C. This dropped area may cause the decline of the catalytic performance.

IR spectrum of AlMg-1.5 was recorded with pressed KBr pellet in the 4000–400 cm^{-1} region (Fig. 3). The high frequency region showed a broad band at about 3431.0 cm^{-1} and a narrow band at 3699.8 cm^{-1}, which are likely assigned to hydrogen stretching mode of hydroxyl groups in M–OH or M–H_2O. Especially, the narrow band is attributed to stretching vibration of the isolated surface OH groups. The vibration of the isolated OH groups on the Al_2O_3/MgO composite was almost disappeared in the FT-IR spectrum of the sample after being calcined at 500 °C. Since the band positions in the infrared spectrum are reciprocally related to the bond strength of the cation to oxygen and the influence of divalent and trivalent metal on hydroxyl group is very different, therefore, the broad and narrow band can be predominantly assigned to stretching vibration of Mg–OH and Al–OH, respectively [12]. The bands observed at 1636.9 and 1381.8 cm^{-1} are respectively ascribed to bending vibration mode of these two groups. The shoulder bands at 567.0 and 652.6 cm^{-1} could be assigned to translation modes of the hydroxyl groups mainly influenced by the trivalent aluminum but probably influenced by Mg^{2+} in its coordination [12]. Besides, the appearance of absorption band at 422.6 cm^{-1} is characteristic of lattice vibrations of Mg or Al octahedral (δ O–M–O) [5].

3.2. Catalytic performance

3.2.1. Catalytic performances of various catalysts

Table 1 summarized the catalytic activities of various oxides and their composites, such as MgO, CaO, ZnO, Al_2O_3, KCl-KOH-MgO, CaO-ZnO, Al_2O_3-ZnO and Al_2O_3-MgO with different BET surface area for the reaction of PO with phenol at 120 °C for 5 h. As can be seen, MgO exhibited a good activity for the reaction, giving 84.4% conversion and 98.5% selectivity to 1-PhP (entry 1). The synthesized MgO (s1) and MgO (s2) basically presented similar catalytic performance to the purchased MgO (entries 2 and 3). KCl-KOH-MgO showed nearly the same activity as MgO although it possesses stronger basicity than MgO (entry 4). Conversely, CaO and its composite CaO-ZnO represented very low activity for the reaction, suggesting that the strong basicity is suppressive for the reaction (entries 5 and 6). However, the oxides ZnO, Al_2O_3 and their composite Al_2O_3-ZnO with approaching neutrality or weak acidity exhibited lower activity (entries 7–9). It was known that few weak basic sites were presented on Al_2O_3, while a large amount of moderate basic sites were presented on MgO and strong basic sites on CaO [4]. This implied that the moderate basic sites on the catalyst surface played a key role for the reaction. Furthermore, the composite oxides Al_2O_3/MgO with different Al/Mg molar ratios were found to have high activity and selectivity for the addition reaction. The composite Al_2O_3/MgO with Al/Mg molar ratio 1.5%, denoted as AlMg-1.5, exhibited highest activity (entry 10), but when the Al/Mg molar ratio was above 1.5% the catalytic activity was slightly