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Synthesis, characterization, and activity in transesterification of mesoporous Mg–Al mixed-metal oxides

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ABSTRACT

In this work, a series of Mg–Al mixed-metal oxides with Mg/Al ratios of 0.125–8 were synthesized via a sol–gel method using cetyltrimethylammonium bromide as a template. All oxide samples were characterized by XRD, XRF, IR, DTA-TGA, TEM, and N_2 adsorption–desorption measurements. The phases of the Mg–Al mixed-metal oxides are the mixture of γ-Al_2O_3 and periclase (MgO) or the mixture of hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$) and periclase depending on the Mg/Al ratio. The Mg–Al oxides have mesoporous structure with surface areas in the range of 120–270 m^2/g. These oxides were also impregnated with KI to increase their base strength, and their activities for biodiesel production were tested via the transesterification of soybean oil with methanol. The KI impregnated Mg–Al mixed-metal oxide at Mg/Al ratio of 4:1 has base strength in the range of $9.8 \leqslant pK_{BH^+} \leqslant 15$ and, of all the catalysts tested, it is the most efficient catalyst for transesterification of soybean oil with methanol (>90% conversion after 8 h).

1. Introduction

Mesoporous metal oxides with narrow pore size distribution and good morphologies are interesting in a wide range of applications, especially in the field of heterogeneous catalysis. In a catalytic reaction, mesoporous materials enhance better interaction between substrates and surface of materials due to higher surface area and accessibility of pores. Among many metal oxides, Al_2O_3 is perhaps the most common material used as a catalyst or a support of catalysts, for example, in petroleum hydrodesulfurization, dehydration of alcohols to alkenes, and dehydrogenation of alkanes to alkenes.

The synthesis of Al_2O_3 with mesoporous structure, therefore, is of great importance for development of novel catalysts. Since the discovery of mesoporous M41S silica in 1992, many research groups have attempted to prepare a wide variety of mesoporous metal oxides via the template method. The templated mesoporous alumina was first synthesized using carboxylic acids as templates by Vaudry et al. [1]. Nonionic di/triblock copolymers have also been used as templates for the preparation of mesostructured alumina by Pinnavaia and coworkers [2–4]. The synthesis of ordered mesoporous alumina with high thermal stability was also achieved by a sol–gel process with block copolymer templates as reported by Yuan et al. [5]. In addition, mesoporous alumina has been prepared using cationic surfactants, such as cetyltrimethylammonium bromide (CTAB), as templating materials. Cabrera et al. [6] reported the surfactant-assisted synthesis of mesoporous alumina using CTAB as cationic template. Large mesopore alumina was synthesized by Zhang et al. [7] via a microemulsion method using CTAB as a template. Recently, sol–gel synthesis of mesostructured Al_2O_3 with CTAB template was reported by Aguado et al. [8].

Mixed-metal oxide systems can offer interesting properties, especially when each component differs remarkably from each other. For example, the acid–base properties of alumina depend very much on the synthesis conditions and post-synthesis treatment [9–11]. On the other hand, magnesia features a unique basic characteristic. The combination of these two oxides may establish new acid–base properties. Therefore, use of Mg–Al mixed-metal oxide as a support can introduce interesting range of properties. The Mg–Al mixed-metal oxide materials have been employed as supports in many reactions, such as Ru/MgO–Al_2O_3 in ammonia synthesis [12], Ni/MgO–Al_2O_3 in ethanol steam reforming [13], NiMo/Al_2O_3–MgO [14], and CoMo/Al_2O_3–MgO [15] in thiophene hydrodesulfurization. The catalysis was altered both positively and negatively, depending on the particular systems. Besides, due to the increase in basicity from the presence of MgO, the Mg–Al mixed-metal oxide itself has been utilized as a catalyst. Mg–Al mixed-metal oxides derived from thermal decomposition of crystalline hydrotalcite-like compounds (Mg/Al = 2–4) are widely stud-

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ied for many base-catalyzed organic transformations, including aldol condensations [16], alkylations [17], Claisen–Schmidt condensations [18], Michael additions [19], double-bond isomerization [20], and transesterification [21–23].

Research has been conducted on direct preparation and characterization of Mg–Al mixed-metal oxide systems, but only a narrow range of Mg/Al ratios was explored. Moreover, to our knowledge, only a few reports are available on mesoporous MgO–Al_2O_3 systems [24–28]. In this work, a series of Mg–Al mixed-metal oxides with Mg/Al ratios in the range of 0.125–8 were synthesized via a sol–gel method using CTAB as a template. All samples exhibit mesostructure and possess high specific surface areas. Furthermore, the Mg–Al mixed-metal oxides were examined as potential supports for KI in transesterification of soybean oil with methanol for biodiesel production.

2. Experimental

2.1. Preparation of Mg–Al mixed-metal oxides, MgAl(x) (x = 0.125–8)

The synthesis of the Mg–Al mixed-metal oxides was performed using the following molar ratio: $a\mathrm{Al(O^iPr)_3}$:$b\mathrm{Mg(NO_3)_2}$:0.8CTAB:22H_2O:17^{i}PrOH, where $a + b = 1$ and b/a was 0.125, 0.25, 0.5, 1, 2, 3, 4, or 8. In a typical synthesis, CTAB was dissolved with 2-propanol and water. The metal precursors were added to the CTAB solution and the mixture was stirred for 4 h at room temperature. The reaction mixture was then heated at 80 °C for 2 h and subsequently dried at 100 °C. The organic portion of the materials was extracted with 0.5 M n-butylamine in ethanol solution (100 mL/g of sample) at 80 °C. After extraction, the solid sample was calcined at 550 °C for 5 h at a heating rate of 1 °C/min under oxygen flow (80 mL/min). These samples were denoted MgAl(x), where x is the Mg/Al atomic ratio. In addition to the above mixed-metal oxides, two other samples, alumina (Al_2O_3) and magnesia (MgO), were also prepared under the same conditions.

2.2. Impregnation of MgAl(x)

The mixed oxide MgAl(x) was loaded with KI by the incipient wetness method. The resulting solid sample was dried and heated in a muffle furnace to 550 °C at a heating rate of 1 °C/min and kept at that temperature for 5 h. These samples were denoted KI_MgAl(x), where x is the Mg/Al atomic ratio.

2.3. Characterization

Powder X-ray diffraction was carried out on a Bruker D8 Advance diffractometer with filtered Cu Kα radiation ($\lambda = 1.54060$ Å) operating at 40 kV and 40 mA; measurements were conducted using step size of 0.02° and counting time of 1 s. FTIR measurements were carried out on a Perkin–Elmer system 2000 spectrometer (KBr pellet). Thermal analyses were preformed on a TA instrument STD 2690 simultaneous DTA-TGA; samples were heated at a heating rate of 10 °C/min up to 1000 °C in flowing air.

Nitrogen physisorption was conducted at −196 °C on a Micromeritics ASAP 2020 surface area and porosimetry system; samples were outgassed at 90 °C for 60 min and then at 350 °C for 240 min prior to measurement. The TEM images were obtained using a Phillips Tecnai-20 microscope, operating at 25 and 50 kV. The elemental analysis was determined by wavelength dispersive X-ray fluorescence spectrometer. The measurements were performed by using Bruker AXS model S4 Explorer equipped with Rh K radiation operating at 50 kV and 20 mA.

The base strength of samples was determined using Hammett indicator method, according to literature protocols [29]. The Hammett indicators used were bromothymol blue ($\mathrm{p}K_a \sim 7.2$), phenolthalein ($\mathrm{p}K_a \sim 9.8$), 2,4-dinitroaniline ($\mathrm{p}K_a \sim 15$), and 4-nitroaniline ($\mathrm{p}K_a \sim 18.4$). Methanol was used as the solvent.

2.4. Catalytic activity tests

The transesterification reactions were performed at 70 °C in a 100 mL two-neck reaction flask equipped with a condenser by refluxing 10 mL of methanol (247 mmol) with 11.23 g of soybean oil (commercial edible grade, acid value < 0.4 mg KOH/g, saponification index = 185.6 mg KOH/g, and average molecular weight = 909 g/mol) and 0.56 g of catalyst (5 wt.%). The catalyst was dried at 120 °C overnight prior to use. A 0.5 mL aliquot was taken from the reaction mixture at various times in order to follow the product yield. Each aliquot was extracted in a hexane/water system. The hexane layer was then dried with anhydrous Na_2SO_4 and was purged with N_2 to remove hexane. Then the sample was submitted to NMR analysis (Bruker 300 MHz) in $CDCl_3$. The oil conversion was determined by the integration ratio of the ^{1}H NMR signal of the methoxy protons of fatty acid methyl ester (FAME, at 3.7 ppm) and the signal of the α-carbon protons (at 2.3 ppm) of all fatty acid derivatives [30].

3. Results and discussion

3.1. Characterization of Mg–Al mixed-metal oxides, MgAl(x)

A series of Mg–Al mixed-metal oxides were synthesized in an acidic medium using CTAB as a structure directing agent. The powder XRD patterns for MgAl(x) (x = 0.125–8) are presented in Fig. 1. After calcination, the XRD patterns of MgAl(0.125), MgAl(0.25), and MgAl(0.5) reveal the phase of γ-Al_2O_3 with low crystallinity as is evidenced by the broad diffraction peaks. MgAl(1), MgAl(2), MgAl(3), MgAl(4), and MgAl(8) are the mixture of hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$) and periclase (MgO). The formation of the hydrotalcite may be caused by the absorption of CO_2 and moisture from the atmosphere during the synthesis procedure. The relative amount of the hydrotalcite phase in the mixed-metal oxides is the highest at the Mg/Al ratio of 4, which is close to the ratio of Mg/Al in the hydrotalcite phase identified. The relative hydrotalcite content decreases as the Mg/Al ratio deviates from four. Even though, hydrotalcite easily decomposes at temperature above 400 °C, our synthetic conditions (specifically the presence of CTAB) may prevent complete thermal conversion of crystalline hydrotalcite to Mg(Al)O. From the thermal analysis, we found that the decomposition of pure CTAB occurs at temperature lower than that of CTAB in the as-synthesized oxide samples. The interaction between the oxides and CTAB may cause the slower CTAB decomposition [31] and prolong the phase transformation of the oxide samples; therefore, the hydrotalcite phase was observed. In addition, the mixed-metal oxides have higher relative amount and larger crystallite size of periclase as the Mg content increases. The change in the relative amount of each phase is consistent with the atomic ratio of Mg/Al in the samples. The XRD results also suggest that the homogeneous atomic distribution of Mg and Al was not achieved since MgO and Al_2O_3 formations have been observed, and only the hydrotalcite has the atomic mixing of Mg and Al. This may be attributed to the differences in the hydrolysis rate of $Mg(NO_3)_2$ and $\mathrm{Al(O^iPr)_3}$, as well as the condensation rate of Mg and Al intermediates. Even though the phase segregation was observed in our Mg–Al mixed-metal oxides, Klabunde and coworkers [27,28,32] have revealed the synthesis of nanocrystalline Al_2O_3/MgO with intimately intermingled mixed-metal oxide structure. The nanocrystalline Al_2O_3/MgO was prepared by a cogelation aerogel procedure with quite a complex apparatus setup; however,