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Synthesis of nanosized mesoporous Co–Al spinel and its application as solid base catalyst

Wenjie Xu, Xiaohui Liu, Jiawen Ren, Huihui Liu, Yichun Ma, Yanqin Wang *, Guanzhong Lu *

Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, People's Republic of China

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ABSTRACT

A novel mesoporous Co–Al spinel catalyst with high surface area and suitable basicity was prepared by the thermal decomposition of Co–Al hydrotalcite-like compound. The properties of the solid base catalyst were characterized by XRD, FTIR, TEM, nitrogen sorption and CO_2-TPD. The formation mechanism of the mesopores and the Co–Al spinel structure was also investigated by TG/DTA and mass-spectrometer, respectively. This is due to the partial oxidation of Co^{2+} ions and the dehydration of the interface OH groups in precursor. The formed Co^{3+} ions collapsed into the interlayer space, coordinated with the adjacent oxygen atoms (tetrahedral or octahedral), worked as pillars between layers and made the interlayer space to be almost opened (mesopores formed). The partial oxidation of Co^{2+} ions plays a critical role in the phase transformation and the formation of mesopores. The as-obtained mesoporous Co–Al spinel-type solid base catalyst was first used in the aldol condensation of furfural with acetone and the self-condensation of acetone and found that it had good activity and excellent selectivity in both reactions. The stability studies showed that the catalyst can be completely regenerated easily by calcination.

1. Introduction

Recently, mesoporous metal oxides as a kind of promising catalyst have attracted special attention because their high surface area can provide a large number of catalytically active sites [1,2]. Generally, metal oxides with surface acidity and basicity can be used as catalysts in a great variety of organic reactions [3]. However, only a few of references are available to deal with the synthesis and application of basic mesoporous materials in contrast to acidic or neutral mesoporous materials [4,5]. Thus, it is necessary to develop novel mesoporous materials with intrinsic basicity for promoting the performance of the traditional basic catalysts. The most commonly preparation method for basic mesoporous materials is the doping of host materials (mesoporous carbon, MCM-41, SBA-15) with basic guest species (alkali metal oxides, alkaline earth oxides, rare earth oxides). Several synthesis methods of ordered mesoporous metal oxides (MgO and ZrO_2) with high thermal stability have also been reported, which intrinsically possess strong basicity without the need of postfunctionalization. In this case, SBA-15 or CMK-3 was employed as hard templates to the synthesis of ordered metal oxides by the replica method [5–10]. Although the hard template method is a good way to synthesize nonsiliceous materials, but it is quite complicated and time consuming. So a facile and cheap synthesis route for mesoporous solid base with narrow pore size distribution and high surface area is required.

Cobalt aluminate adopts the spinel structure (space group *Fd*3*m*) with basicity and redox property. Co–Al spinels and the mixed oxides have been studied as a heterogeneous catalyst in the reforming of methane [11], capture and decomposition of nitrous oxide [12–15] and capture of carbon dioxide [16]. Usually, it can be synthesized by the solid-state chemistry method at high temperature. However, the high temperature synthesis always results in the sintering of the particles and the reduction of the surface area, which would lead to limitation in catalytic applications. Xu and coworkers [12–14,16], Sato et al. [17] and Kannan [18] synthesized a cobalt aluminate or the mixed oxides by calcining the Co–Al containing hydrotalcite-like precursors, which is an effective way to synthesize Co-containing spinels or mixed oxides with high surface area (including Co_3O_4 [19,20] and Co–Fe spinel [21]). But till now, there is no systemic research on the formation mechanism of the mesopores, the influence of reaction conditions on the thermal stability and its applications as a solid base.

So, in this paper, we present a facile approach for preparing nanosized mesoporous cobalt aluminate with narrow pore size distribution, uniform particle size and good thermal stability. We also investigate the influence of the preparation conditions on the surface area and thermal stability. A mechanism for the formation of nanosized mesoporous cobalt aluminate is also proposed. The as-synthesized material has unique acid–base properties and

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* Corresponding authors. Tel.: +86 21 64253824; fax: +86 21 64253703.
E-mail addresses: wangyanqin@ecust.edu.cn (Y. Wang), gzhlu@ecust.edu.cn (G. Lu).

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can be used as a solid base catalyst. The base-catalyzed aldol condensation is an important way to couple organic molecules via C–C bond formation in the fine chemical industry. The efficiency of this catalyst is tested towards two important reactions-aldol condensation of furfural with acetone and the self-condensation of acetone. The former reaction is a key step in an "aqueous phase reforming" (APR) process which was developed by Dumesic to convert the bio-mass derived compounds into fuels in order to tap renewable feedstocks instead of fossil fuels [22–24]. The latter reaction was normally used as a typical model reaction to detect the basicity of the new made catalyst with other typical solid base catalysts [25–28] and its product, diacetone alcohol (DAA) is an environmentally friendly solvent.

2. Experimental methods

2.1. Catalyst preparation

Co–Al hydrotalcite-like (Co–Al HT) precursors were prepared by the co-precipitation from an aqueous solution of cobalt and aluminum nitrate (solution A) and a basic solution (solution B). In this preparation, NaOH and Na_2CO_3 were used as the bases. First, an aqueous solution (100 ml) containing 0.027 mol $Co(NO_3)_2{\cdot}6H_2O$ and 0.018 mol $Al(NO_3)_3{\cdot}9H_2O$ with a molar composition of Co/Al = 1.5 (solution A) and another aqueous solution (100 ml) containing 0.13 mol NaOH and 0.065 mol Na_2CO_3 (solution B) were added dropwise into 250 ml of deionized water at room temperature under vigorous stirring to maintain the pH value between 10.7 and 11.2. Then the mixture was heated at 80 °C for 24 h under magnetic stirring. After cooling to room temperature, the solid precipitate was collected by centrifugation and washed several times with deionized water until the pH of the filtrate was ca. 7. The resulting Co–Al HT precursor was obtained after drying at 100 °C in air for 12 h. The molar ratios of Co/Al were also changed and the Co–Al HT precursors with different Co/Al molar ratios were labeled as CP-HT*n* (*n* denotes Co/Al ratio, *n* = 1, 1.5, 2 or 3).

The as-prepared precursors were calcined at required temperature for 4 h at a heating rate of 5 °C min^{-1} in air to get the corresponded cobalt aluminate, referred as to CP-SPn-m (*n* denotes Co/Al ratio and m denotes the calcination temperature, *m* = 300, 400, 500, 600 or 700).The Mg–Al mixed oxides were also prepared by calcining Mg–Al HT precursors [29] at 450 °C for 6 h at a heating rate of 5 °C min^{-1} in air.

Magnesia–zirconia ($MgO–ZrO_2$) catalyst was synthesized by using the sol–gel technique described by Aramendía et al. [30,31] starting with $Mg(NO_3)_2{\cdot}6H_2O$ and $ZrO(NO_3)_2$. The catalyst was prepared by dissolving 50.9 g of magnesium nitrate and 4.04 g of zirconyl nitrate in 1 L of deionized water. Then NaOH (25 wt.%) solution was added until the pH reached 10. The gel was aged at room temperature for 72 h and subsequently filtered. The precipitate was washed with deionized water until the pH of the filtrate was ca. 7. It was then dried in oven at 100 °C for 12 h. The calcination of the catalyst was carried out in air at 600 °C for 3 h.

Anion exchange resin (Amberlite IRA-900(Cl)) was purchased from Huachang Polymer Co., Ltd. of East China Univesity of Science and Technology.

2.2. Characterizations of catalysts

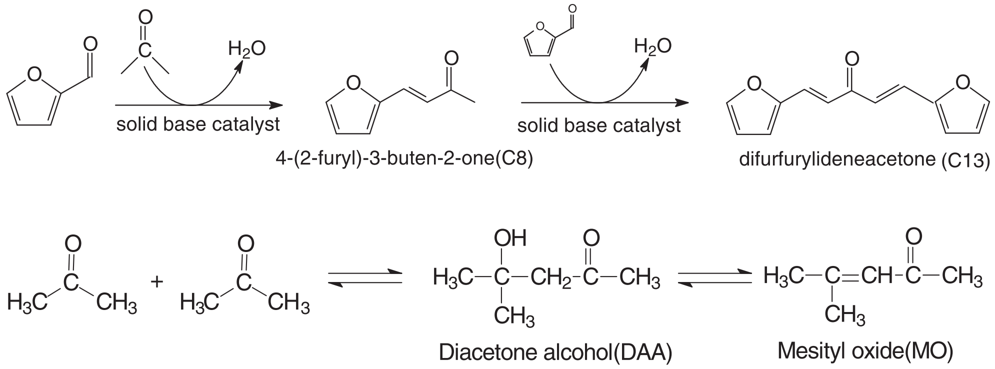
X-ray diffraction patterns (XRD) were recorded with a Rigaku D/max-2550VB/PC diffractometer using Cu Kα radiation operated at 100 mA and 40 kV. Chemical analysis of the samples was performed by using inductively coupled plasma atomic emission spectrometry (ICP-AES). FTIR spectra were recorded with a Nicolet Nexus 670 spectrophotometer. Nitrogen adsorption and desorption isotherms were measured at 77 K with an ASAP2020M sorption analyzer. Before the measurement, the samples were outgased at 280 °C for 6 h. Transmission electron microscopy (TEM) were carried out with TECNAI 20S-TWIN. Thermogravimetric studies were carried out using a PerkinElmer Pyris Diamond TG/DTA from room temperature to 800 °C at the rate of 10 °C min^{-1}.

The densities of the catalyst basic sites were measured by temperature-programmed desorption of CO_2 (CO_2-TPD). Sample (50 mg) was pretreated in N_2 flow at 300 °C for 2 h, cooled down to 50 °C, and then exposed to a flowing mixture of 25% of CO_2 in N_2 until the surface saturation was achieved (30 min). When the adsorption finished, the temperature was raised from 50 to 650 °C at a rate of 10 °C min^{-1} and the liberated CO_2 was detected by an on-line Quadrupole Mass Spectrometers (IPC400, INFICON Co. Ltd.).

2.3. Aldol condensation of furfural with acetone

The aldol condensation of furfural with acetone (Scheme 1) was carried out in a batch reactor at acetone/furfural = 10 (molar ratio) and furfural/catalyst = 6 (weight ratio). The batch reactor was heated up to the required temperature under magnetic stirring in an oil bath equipped with an automatic temperature control system. The liquid of reaction was analyzed by a PerkinElmer Clarus 500 gas chromatography with a SE-54 column. A flame ionization detector (FID) was used to analyze the final products. The response factors were calibrated for each reactive agent with pure chemicals.

The conversion of furfural, yields and selectivity to 4-(2-furyl)-3-buten-2-one (C_8) and difurfuryli–deneactone (C_{13}) were calculated as follows:



Scheme 1. The aldol condensation of furfural with acetone (upper) and the self-condensation of acetone (down).