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Effects of solvent stabilizer in the preparation of highly active potassium-promoted Ru/MgO catalysts for ammonia synthesis

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Abstract

A method for the preparation of highly active potassium-promoted Ru/MgO catalyst (K–Ru/MgO-a(Eg)) has been designed. Ethylene glycol was used as reducing agent for the reduction of $RuCl_3$ at 433 K, simultaneously, as a solvent stabilizer for the size of ruthenium nanoparticles and the morphology of MgO. In the process of impregnating promoter, KNO_3 was used as promoter precursor and the ethylene glycol protected ruthenium nanoparticles from agglomeration. The ruthenium particle size of the K–Ru/MgO-a(Eg) was in the range of 1.5–2.8 nm. The highest activity of the nano-catalyst was 6342 μmol h^{-1} g_{-cat}^{-1} under 0.2 MPa at 658 K.

Keywords: Ammonia synthesis; Ruthenium; Ethylene glycol; Magnesia; Stabilizer

1. Introduction

Ruthenium-based catalysts, the second generation ammonia synthesis catalysts, have higher catalytic activities and allow much milder operating conditions than the conventional iron catalysts [1]. Among the well-developed ruthenium supports, magnesia is a stable carrier under ammonia synthesis conditions [2,3]. Up to present, great efforts have been paid to improve the catalytic activities of promoted Ru/MgO. It is reported that both ruthenium particle size and fraction of exposed ruthenium surface (FE) play important roles in ammonia synthesis activities. However, in the process of impregnating promoter, conventional techniques base on water impregnation often do not provide adequate control of the fraction of exposed ruthenium surface and the ruthenium particle size. Absolute ethanol or ethanol–water (EtOH–$H_2O = 50:50$) mixture was used as a solvent in the impregnating processes [2,4]. However, the ammonia synthesis activities were not satisfying yet. Cs_2CO_3 ethanol solution was also used as a promoter precursor in the impregnating process, but the decomposition temperature of Cs_2CO_3, above 880 K, may cause aggregation of ruthenium particles [4].

Ethylene glycol was supported to be an excellent reducing agent for the preparation of oxide-supported ruthenium catalysts [5,6]. In this work, $RuCl_3$ was also reduced by ethylene glycol to prepared Ru/MgO catalyst. To avoid the formation of $Mg(OH)_2$ and to give a deep insight into the effect of ethylene glycol in the process of impregnating promoter, the catalyst was heated in flowing hydrogen to eliminate Cl^-. Furthermore, in the process of impregnating KNO_3 on Ru/MgO catalyst, ethylene glycol was used as a solvent.

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2. Experimental

2.1. Preparation of the magnesia

The magnesia was prepared according to the procedure described by Choudhary et al. [7]. The size of MgO particles was approximately 14 nm.

2.2. Preparation of the ruthenium catalysts

0.27 g of $RuCl_3 \cdot nH_2O$ ($n = 1$–3, 37 wt% Ru) along with 2.00 g of MgO was added into 50 ml ethylene glycol under stirring at 433 K for 1.5 h in an oil bath, and then stirred for 3 h in an ice-water bath. Half part of suspension was evaporated by a rotary evaporator to eliminate ethylene glycol. Subsequently, the obtained solid was heated, in a microreactor, to 698 K under a stream of H_2 (99.999% purity, 30 ml/min) for 24 h to eliminate Cl^-. The obtained catalyst was marked as Ru/MgO-a. Another half part of suspension was washed with 0.3 M $NaNO_3$ aqueous solution and distilled water to remove ethylene glycol and Cl^-. Then the solid was dried in an oven at 373 K over night. The obtained catalyst was marked as Ru/MgO-w.

The prepared Ru/MgO-a catalyst was impregnated with a solution of KNO_3 (0.075 g KNO_3, mole ration K/Ru = 3:2) in ethylene glycol at ambient temperature for 6 h and, then, evaporated at 433 K by a rotary evaporator to obtain a dry solid. Subsequently, the solid was heated to 698 K under a stream of H_2 for 4 h to remove little residual ethylene glycol. The obtained catalyst was marked as K–Ru/MgO-a(Eg). K–Ru/MgO-a(water) was obtained by impregnating Ru/MgO-a with an aqueous solution of KNO_3 at ambient temperature for 6 h and, then, evaporated at 343 K by a rotary evaporator. Finally, the K–Ru/MgO-a(water) was dried in an oven at 373 K over night.

Catalysts with different K/Ru mole ratios were prepared under the same preparing method of K–Ru/MgO-a(Eg). All catalysts were crushed and sieved to the size between 250 and 425 μm.

2.3. Measurements of catalytic activities

The ammonia synthesis activities were evaluated over 0.15 g of the catalyst powders in a fixed bed flow reactor (id = 8 mm). The catalytic activity measurements were carried out with a stoichiometric mixture of purified $3H_2$ and N_2 at a pressure of 0.2 MPa. The flow rate of the gas mixture was maintained constant at 2100 ml/h in all experiments. The catalysts were stabilized in the flowing reactants at 698 K for 24 h. The activity was measured after the catalyst was stabilized at each reaction temperature for 30 min and expressed as $\mu mol\ h^{-1}\ g^{-1}_{-cat}$. The produced ammonia was determined by a chemical titration method using fixed amount of diluted sulfuric acid solution containing methyl red as indicator.

2.4. Characterization of catalysts

X-ray powder diffraction analysis (XRD) was carried out by a Philips PW1010 X-ray diffractometer with Cu K_α radiation. XRD pattern was recorded with a scan step of 0.016° (2θ) for 10 s in the range from 20° to 90°. The XRD pattern of Ru/MgO-a and Ru/MgO-w were shown in Fig. 1.

To better characterize the dispersion of ruthenium particles, temperature-programmed desorption of hydrogen (TPD-H_2) on ruthenium particles was measured [7–9].

Surface images and sizes of ruthenium nanoparticles were investigated by a TECNAL F30 high-resolution transmission electron microscopy (HRTEM).

3. Results and discussion

3.1. Catalysts characterization

As we can see from Fig. 1, there is no any clear peak attributed to ruthenium particles for the Ru/MgO-a. This may be due to that the size of ruthenium particle is out of the detection limit of the diffractometer or the dispersion of ruthenium particle is satisfying. As shown in Fig. 1, there are clear peaks attributed to $Mg(OH)_2$ (2θ: 32.86°, 37.93°, 50.72°, 58.64°, 62.07°, 38.17°, 72.02°, 81.24°). It indicates that hydroxide is formed when the reduced Ru/MgO is washed with aqueous solution of KNO_3 or distilled water.

The HRTEM images of Ru/MgO-a, K–Ru/MgO-a(Eg) and K–Ru/MgO-a(water) are shown in Fig. 2. Fig. 2A and B exhibit that the presence of small and uniform ruthenium particles on the MgO. The ruthenium particles dispersed on the MgO are approximately 1.3–2.5 nm and 1.5–2.8 nm in size, respectively. However, ruthenium particles of K–Ru/MgO-a(water) are approximately 1.5–5.5 nm in size which is much larger than that of Ru/MgO-a and K–Ru/MgO-a(Eg). Additionally, ruthenium particles of K–Ru/MgO-a(water) do not disperse on the MgO uniformly. It is suggested that impregnation of Ru/MgO-a in KNO_3 aqueous solution will cause the aggregation of ruthenium nanoparticles. This opinion is supported by Siporin and Davis

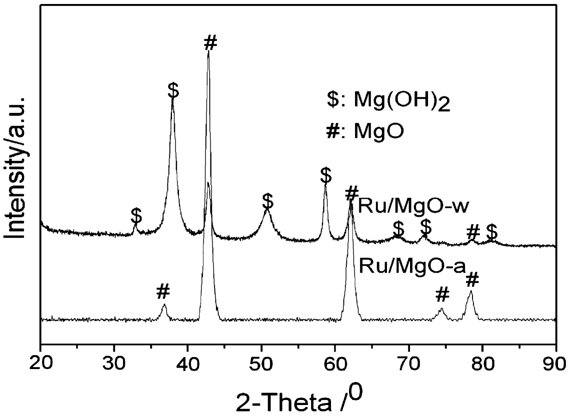

Fig. 1. XRD pattern of the Ru/MgO-a and Ru/MgO-w.