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Influence of Ethylene Diamine Tetraacetic Acid on the Performance of Magnesia Supported Ru-based Catalysts for Ammonia Synthesis

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Huo Chao[1],   Cheng Xiangwei[1,2],   Du Yanlei[1]

[1] Zhejiang University of Technology, Hangzhou 310014, China; [2] Zhejiang Police College, Hangzhou 310053, China

Abstract: A series of barium doped nano-magnesia supports (Ba-MgO) modified with ethylene diamine tetraacetic acid (EDTA) were prepared by chemical co-precipitation with an ultrasonic method and were used as supports to prepare Ru-based catalysts. The surface texture and the matter phase of the supports and Ru catalysts were characterized by X-ray diffraction, scanning electron microscope, N_2 physical-adsorption, H_2 temperature-programmed reduction and inductively coupled plasma-atomic emission spectrometry. The results show that modification of EDTA increases the amount of barium promoter into the support and controls the formation state of barium in supports. The effects of barium promoter content and surface texture in supports achieve an equilibrium state when the molar ratio of EDTA to Ba is 1/2, and the highest activity of Ru/Ba-MgO catalyst is 69.31 mmol·$(g·h)^{-1}$ under the reaction conditions of 10 MPa, 10 000 h^{-1} and 698 K.

Key words: EDTA modification; barium doped nano-magnesia; ruthenium catalyst; ammonia synthesis; complexing agent effect

Ru-based catalysts are thought to be the next generation catalysts for ammonia synthesis since ammonia synthesis is generally carried out at lower temperatures and pressures compared to conventional multi-promoted magnetite-based iron catalysts. Ru-based catalysts exhibited much higher activity, less inhibition effect by ammonia and greater tolerance to poisons under quite moderate conditions[1]. The frequently-used supports of Ru-based catalysts mainly include activated carbon[2], MgO[3], Al_2O_3[4], $BaCeO_3$[5], lanthanide oxides (CeO_2, Sm_2O_3 and La_2O_3) and so on. Many researchers[1,6,7] have confirmed that the activities of ruthenium-based catalysts strongly depend on the properties of the supports as well as the nature of the promoters. Magnesium oxide is regarded as the most effective and stable support for ammonia synthesis. The basicity sites on the surface of MgO can facilitate the activation of dinitrogen over Ru atoms. Through comparing the influence of different promoters on Ru/MgO catalysts for ammonia synthesis, Szmigiel et al.[8] found that the doping of Ba promoter showed

a higher enhancement of basicity on MgO surface which made the Ru/Ba-MgO catalyst exhibit the higher activity of ammonia synthesis than other promoters. In the previous studies, MgO with high Ba dispersion supported ruthenium-based catalysts have been prepared by chemical co-precipitation with an ultrasonic method. The mechanism of how barium doping into MgO support can be seen in Fig.1a. $Mg(OH)_2$ taking positive charge in the co-precipitation solution system prevented Ba^{2+} adsorbing on $Mg(OH)_2$ precursor. Thus the doping amount of Ba could not be properly controlled, and large amounts of Ba^{2+} were dissolved in residual solution washing away during the preparation process. The key factor of the research is to find a method to enhance the interaction between Ba^{2+} and $Mg(OH)_2$ precursor.

Ethylene diamine tetraacetic acid (EDTA) is inclined to form stable $[M(EDTA)]^{x-}$ chelate with many alkali and lanthanide metal irons. Ryczkowski[9] investigated the adsorption of alkaline salts of EDTA on inorganic supports with different values of the isoelectric point of the surface

(IEPS) obtained by transmission and photoacoustic (PA) FT-IR. The results implied that the observed changes in the properties of adsorbed complexes are mainly due to interaction of the carboxyl groups of chelate molecule with hydroxyl groups of inorganic oxide. Al-Dalama et al.[10] studied the adsorption property of Ni^{2+} on Al_2O_3 support in the existence of EDTA. They found that EDTA could change the charge valence of Ni^{2+} ions by forming $[Ni(EDTA)]^{2-}$ chelate; as a result, the adsorbing capacity of Ni^{2+} ions on Al_2O_3 support increased. Thevenin et al.[11] reported that cerium-doped palladium catalysts exhibited a higher catalytic activity for catalytic combustion by introduction of EDTA to form $[Ce(EDTA)]^-$ complex during the preparation of the Ce-doped support. In the present paper, nano-magnesia supports and Ru-catalysts modified by different proportions of EDTA to barium were synthesized by ultrasound electrostatic adsorption, and the purpose of this work was to investigate the influence of EDTA modification on the Ba^{2+} doping into MgO support and the formation state of barium entering nano-magnesia supports. The catalytic activity of ruthenium-based catalysts for ammonia synthesis was also tested.

1 Experiment

All chemicals are of reagent grade and used without further purification. Ba-MgO supports modified by EDTA were synthesized by a wet homogeneous co-precipitation method in the presence of ultrasonic treatment. Certain amount of barium nitrate and different amounts of ethylene diamine tetraacetic acid disodium salt were dissolved in 25% ammonia aqueous solution, and the molar ratio of EDTA to Ba was 0, 1/4, 1/3, 1/2 and 1. Then certain amount of magnesium nitrate aqueous solution was added into the above solution instantly. After reacted by assistance of ultrasonic wave (25 kHz, 300 W) for 50 min, the resulted precipitation solution was further aged for 24 h, then filtered and washed with alcohol. Finally, the samples were dried in an oven at 383 K for 12 h and calcined in air at 873 K for 5 h.

In order to obtain Ru/Ba-MgO catalysts, the prepared Ba-MgO supports were impregnated with solutions of triruthenium dodecacarbonyl (Ru precursor) in THF. The Ru loading was fixed to 2 wt% by total mass of support. The solution was stirred under ambient conditions for 12 h, and then THF was removed by a rotary evaporator under vacuum at room temperature. After dried in air at 333 K for 6 h, the sample was treated in vacuum at 723K for 2 h to decompose $Ru_3(CO)_{12}$, then reduced in hydrogen stream and cooled to room temperature.

The crystalline structures of the samples were analyzed by X-ray diffraction (XRD) with a Thermo ARL X'TRA X-ray diffractometer, by the Cu Kα radiation (λ=0.154050 nm). All diffraction patterns were recorded in a 2θ range from 10° to 80° at a scanning rate of 4° min^{-1} in a step of 0.02°. Crystallite size can be calculated by Scherrer equation: $D =\lambda K/(\beta \cos\theta)$,

where D is average crystal size, K is the Scherrer constant (the calculation was performed with a value K=0.89), λ is the X-ray wavelength, β is the width of the X-ray peak (the height of the X-ray peak is half) and θ is the Bragg angle. The surface morphologies of the samples were investigated by scanning electron microscope (FESEM, Hitachi S-4700) at an accelerating voltage of 15 kV. BET surface area and the pore size of the samples were determined by Micromeritics ASAP 2010 Analyzer with N_2 as adsorbate at liquid nitrogen temperature. H_2 temperature-programmed reduction (H_2-TPR) of the samples was measured by a Micromeritics AutoChem 2910 Analyzer using a 20 mL·min^{-1} stream containing H_2 (>99.999%) at a linear heating ramp of 10 K min^{-1} from 323 K. The decomposition of barium carbonates was determined by temperature-programmed desorption (TPD) combined with mass spectrometry (MS). The sample was heated from 323 to 1,123 K at 10 K min^{-1} with an Ar stream of 20 mL·min^{-1}. The Ba content was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The catalytic activities in ammonia synthesis were evaluated by 2.3 g catalyst (particle size 80~140 um) in a fixed bed flow reactor (id=14 mm). Before measuring the catalytic activity, a reduction treatment was carried out with N_2+3H_2 for 6 h (723 K) and further 10 h (823 K) both at a heating rate of 10 K·min^{-1}. After being stabilized for 60 min at each reaction temperature, the catalyst was tested for ammonia synthesis at 648, 673, 698 and 723 K under 10 MPa with a space velocity of 10 000 h^{-1} of (N_2+3H_2). The concentration of the produced ammonia was determined by a chemical titration method using fixed amount of diluted sulfuric acid solution containing methyl red as indicator and the activities were expressed as mmol·(g·h)$^{-1}$.

2 Results and Discussion

Fig.1 presents the X-ray diffraction patterns of Ba-MgO supports modified by different amounts of EDTA. All supports show reflections corresponding to the formation of cubic MgO phase (2θ=36.89°, 42.85°, 62.21°, 74.58° and

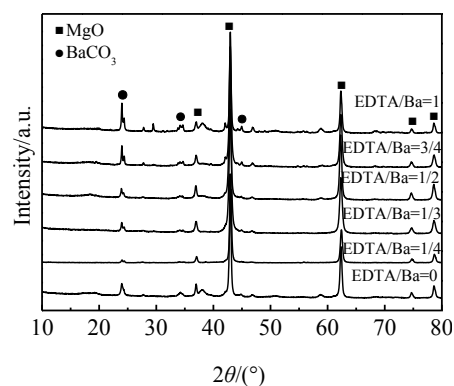Fig.1 XRD patterns of Ba-MgO supports modified by different amounts of EDTA (mol ratio)