

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

Huo Chao¹, Cheng Xiangwei^{1,2}, Du Yanlei¹

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, N₂ physical-adsorption, H₂ 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], Al₂O₃^[4], BaCeO₃^[5], lanthanide oxides (CeO₂, Sm₂O₃ and La₂O₃) 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 Ba²⁺ adsorbing on Mg(OH)₂ precursor. Thus the doping amount of Ba could not be properly controlled, and large amounts of Ba²⁺ 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 Ba²⁺ 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 ions. Ryczkowski^[9] investigated the adsorption of alkaline salts of EDTA on inorganic supports with different values of the isoelectric point of the surface

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Corresponding author: Huo Chao, Ph. D., Professor, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China, Tel: 0086-571-88320815, E-mail: chaohc@zjut.edu.cn

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(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 $[\text{Ni}(\text{EDTA})]^{2-}$ 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 $[\text{Ce}(\text{EDTA})]^-$ 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 $\text{Ru}_3(\text{CO})_{12}$, 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 $K\alpha$ radiation ($\lambda=0.154050$ 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 μm) 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 $10\,000 \text{ h}^{-1}$ 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 ($2\theta=36.89^\circ$, 42.85° , 62.21° , 74.58° and

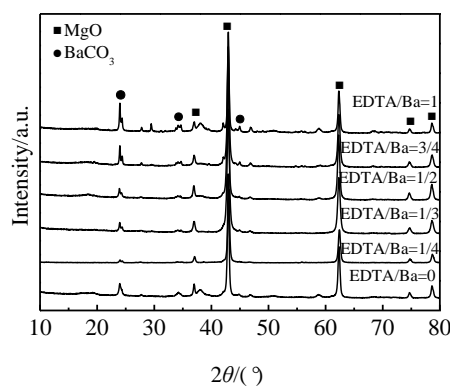


Fig.1 XRD patterns of Ba-MgO supports modified by different amounts of EDTA (mol ratio)

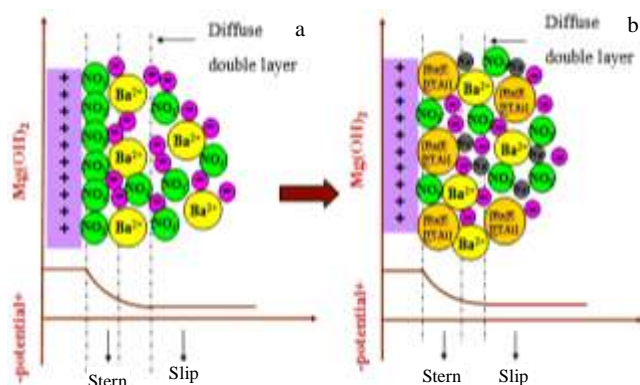


Fig.2 Schematic presentation of the interaction of EDTA modified Ba-MgO precursors: (a) without addition of EDTA and (b) appropriate addition of EDTA

78.51°) and orthorhombic BaCO_3 phase ($2\theta=23.98^\circ$ and 24.38°)^[12,13]. This indicates that barium containing species are decomposed into BaO when calcined at 873 K in air and BaO gradually reacts with CO_2 in air to form BaCO_3 which was the stable state of barium salt^[12-14]. It is observed clearly in XRD patterns that the strength of BaCO_3 phase characteristic diffraction peaks is enhanced gradually with increasing the amount of EDTA in Ba-MgO supports. But the peak width at half height narrows at the same time. The crystallite sizes of BaCO_3 were calculated from XRD peaks and Scherrer equation, and all parameters involved in Scherrer equation and the results are listed in Table 1. The crystallite size of BaCO_3 is 38 nm when the proportion of EDTA to Ba is 1/2, and the crystallite size decreases when a little amount of EDTA is added. The characteristic diffraction peaks of MgO change slightly after adding EDTA. It is well known that the isoelectric point of $\text{Mg}(\text{OH})_2$ particles in water is ca. pH 12^[15]. In this study, ammonia aqueous solution was used as the precipitator, and the pH value in final reaction system was about 10.5. Therefore, the electric charge on the surface of $\text{Mg}(\text{OH})_2$ precursor should be positive. Under this condition, HY^{2-} and HY^{4-} are the main forms of EDTA which react with Ba^{2+} to form $[\text{Ba}(\text{EDTA})]^{2-}$ ^[10]. There exist two forms of barium $[\text{Ba}(\text{EDTA})]^{2-}$ and Ba^{2+} in precipitation solution (Fig.2b). The positive surface of $\text{Mg}(\text{OH})_2$ adsorbs NO_3^- and $[\text{Ba}(\text{EDTA})]^{2-}$ ions when the amount of EDTA is little. Moreover, the ionic radius of $[\text{Ba}(\text{EDTA})]^{2-}$ is much larger than Ba^{2+} , and dimensional steric hindrance of EDTA disperses Ba^{2+} ion adsorbed on the surface of $\text{Mg}(\text{OH})_2$ precursor. With further increasing the amount of EDTA, however, $[\text{Ba}(\text{EDTA})]^{2-}$ becomes the major formation state of barium ions. The Ba content in Ba-MgO supports modified by different amounts of EDTA after calcined was measured by inductively coupled plasma-atomic emission spectrometry, which is shown in Table 1. The results show that the amount of Ba promoter entering MgO support increases a lot resulting in the growth of BaCO_3 crystalline grain. It is consistent with

the crystallite size data of BaCO_3 calculated in Table 1.

The surface morphologies of the supports characterized by FE-SEM are shown in Fig.3. It can be seen that all the particles in Ba-MgO supports are in the degree of nanometer and nearly spherical after the introduction of EDTA during the preparation of supports. The sizes of particles become larger and limited aggregation is observed. The above phenomenon could be attributed to the moderate interaction between the carbonyl group of EDTA and the hydroxyl group on the surface of $\text{Mg}(\text{OH})_2$ precursor. The textural parameters of Ba-MgO supports modified by different amounts of EDTA are summarized in Table 2. The Ba-MgO support without adding EDTA exhibits a BET surface area of about $44.7 \text{ m}^2 \text{ g}^{-1}$. It could be noticed that the surface areas and the pore volumes of Ba-MgO supports decrease after modification by different amounts of EDTA. It is due to that EDTA modification increases the amount of Ba into support and the particles of BaCO_3 filled in the pores of the supports. The average pore sizes also decrease with the doping amount of EDTA. The diameters of all the pores in Ba-MgO mostly distribute from 4 to 10 nm. The introduction of EDTA causes Ba^{2+} , $[\text{Ba}(\text{EDTA})]^{2-}$ and $(\text{EDTA})^{4-}$ competing to adsorb on $\text{Mg}(\text{OH})_2$ precursor. EDTA doping amount could be regulated to control suitable surface area and pore size of Ba-MgO support for high activity of catalysts.

From the XRD patterns mentioned above, we know that barium is doped into the supports in the final form of BaCO_3 . Piacentini^[16] reported that BaCO_3 could be divided into two barium carbonate phases with different stability, low-temperature barium carbonate (LT- BaCO_3) and high-temperature barium carbonate (HT- BaCO_3). Fig.4 shows the H_2 -TPR patterns of Ba-MgO and EDTA-Ba-MgO supports (the molar ratio of EDTA to Ba is 1/2). Two small peaks of hydrogen consumption (753, 823 K) exist in Ba-MgO standing for the reduction of LT- BaCO_3 and HT- BaCO_3 , respectively^[17]. In comparison, only a broad peak of hydrogen consumption (673~803 K) is observed in EDTA-Ba-MgO supports. In the H_2 -TPR-MS patterns (Fig.5), the generated CO_2 and CH_4 peak both shift to lower temperature. The results indicate that BaCO_3 in EDTA-Ba-MgO support belongs to LT- BaCO_3 and decomposes to BaO absolutely at moderate

Table 1 Crystallite size of BaCO_3 in different supports calculated from the XRD measurement modified by different amounts of EDTA

Support	EDTA/Ba (mol ratio)	$\beta/\times 10^{-3} (^\circ)$	$2\theta/(^\circ)$	D/nm	Ba content/mol%
Ba-MgO-a	0	4.20	24.0	33	1.22
Ba-MgO-b	1/4	5.67	24.2	24	0.73
Ba-MgO-c	1/3	3.87	23.9	36	0.88
Ba-MgO-d	1/2	3.51	24.0	38	1.56
Ba-MgO-e	3/4	3.26	24.1	41	1.71
Ba-MgO-f	1	2.88	24.1	46	3.79

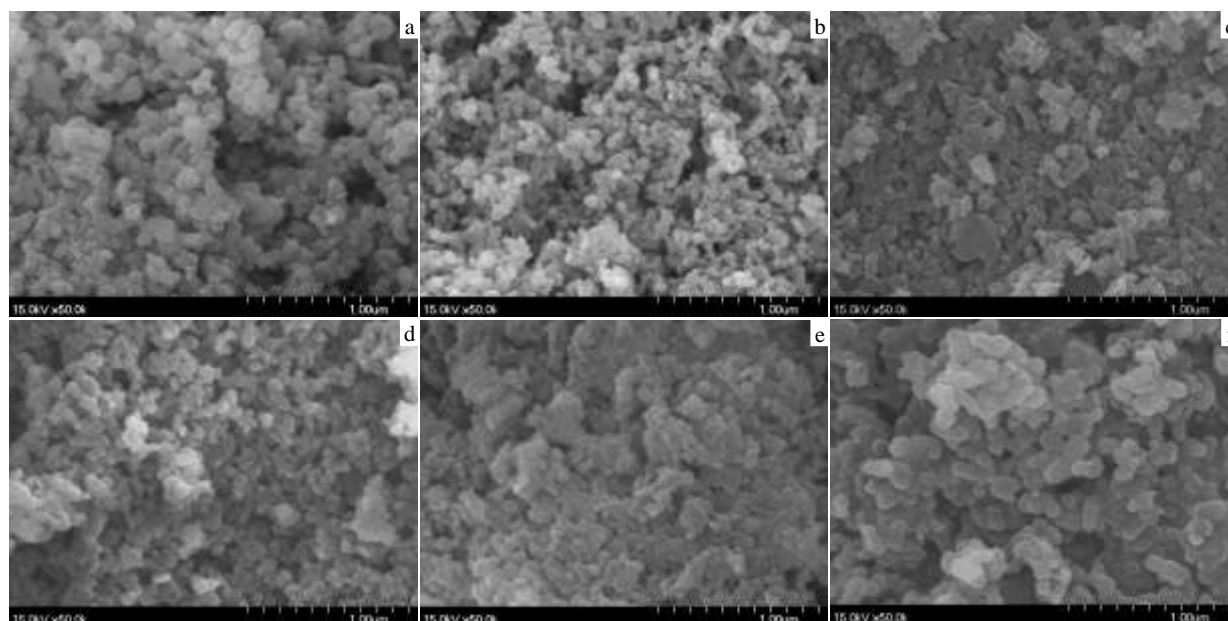


Fig.3 FE-SEM images of Ba-MgO supports modified by different amounts of EDTA: (a) EDTA/Ba=0; (b) EDTA/Ba=1/4; (c) EDTA/Ba=1/3; (d) EDTA/Ba=1/2; (e) EDTA/Ba=3/4; (f) EDTA/Ba=1

Table 2 Textural parameters of Ba-MgO supports modified by different amounts of EDTA

EDTA/Ba (mol ratio)	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	$V_p/\text{cm}^3 \text{ g}^{-1}$	Average pore diameter/nm
0	44.7	0.16	21.7
1/4	38.6	0.24	23.9
1/3	37.7	0.19	17.4
1/2	37.1	0.16	14.6
3/4	32.4	0.13	14.4
1	24.8	0.12	14.4

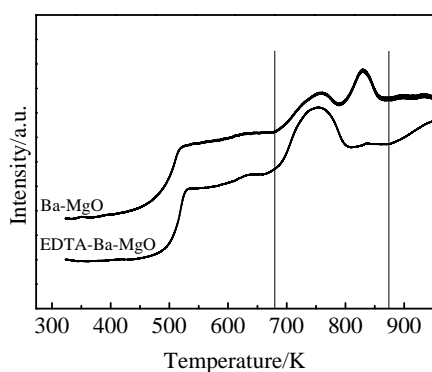


Fig.4 H_2 -TPR patterns of Ba-MgO and EDTA-Ba-MgO (the molar ratio of EDTA to Ba is 1/2)

temperature. Since amorphous BaO is the most effective promoter to ruthenium based catalyst^[18], the activity of the catalysts modified by EDTA improves after heat-resisting.

The reducibility of ruthenium catalysts supported on

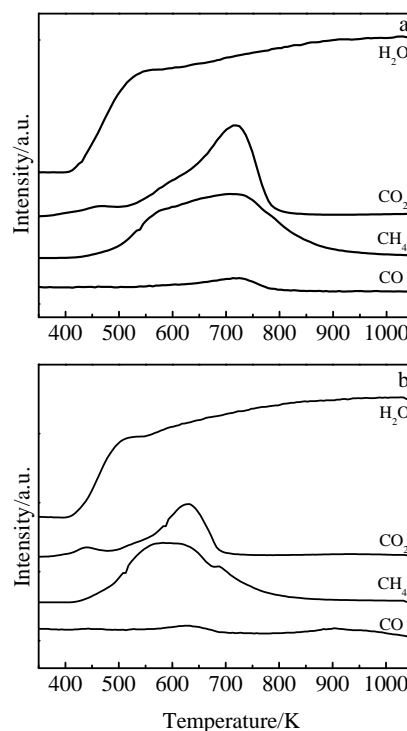


Fig.5 H_2 -TPR-MS patterns of Ba-MgO supports modified by EDTA: (a) EDTA/Ba=0 and (b) EDTA/Ba=1/2

Ba-MgO modified by EDTA was studied by hydrogen temperature-programmed reduction. Fig.6 shows the H_2 -TPR patterns measured from 323 to 1073 K. Two typical reduction peaks could be observed. The peak at 423~523 K corresponds

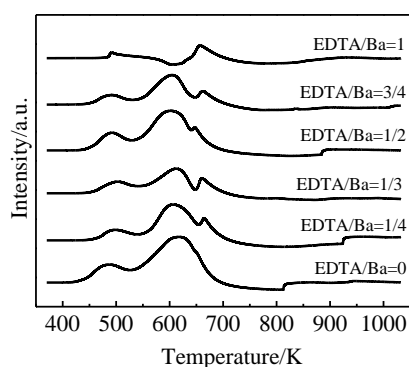


Fig.6 H₂-TPR patterns of Ru/Ba-MgO catalysts modified by different amounts of EDTA

to the reduction of highly decentralized Ru particles and RuO_x species on the surface of catalysts, and the peak in 550~650 K corresponded to the reduction of Ru particles and RuO₂ species in the phase. It is worth noting that in Ru/Ba-MgO catalysts modified by EDTA a shoulder reduction peak at 650~700 K, which corresponds to the hydrogen consumption of carbonyl group decomposed from EDTA. Payne et al.^[19,20] had certificated that the decomposition of EDTA consisted of several steps: Firstly, EDTA degraded to EDTA by losing carbonyl group, and then EDDA-N, N' or EDDA-N, N decomposed to EDMA at last. The decomposition of EDTA facilitates distribution of ruthenium oxides on Ba-MgO supports and then improves the activities of catalysts.

The catalytic activities of the catalyst system (Ru/EDTA-Ba-MgO) were measured to determine the promoting effect of EDTA. The initial catalytic activities increase with the addition of a little amount of EDTA as shown in Fig.7. When the molar ratio of EDTA to Ba is 1/2, the Ru/Ba-MgO catalyst exhibits the highest catalytic activity for ammonia synthesis with a reaction rate of 69.31 mmol (g h)⁻¹ at 698 K, 10 MPa and 10 000 h⁻¹. It is 13.73% higher than the initial activity of catalyst without EDTA. Then the activities of the catalysts decrease on the contrary with further increasing the doping amount of EDTA. Its reason is that when the content of EDTA is low, the main existing form of Ba is Ba²⁺ and NO³⁻ is the main surface adsorption on Mg(OH)₂ precursor, and it causes the low adsorption of Ba promoter. When the content of EDTA is proper, the main existing form of Ba is [Ba(EDTA)]²⁻ which could be absorbed on the negatively charged surface of supports directly, and could effectively increase the amount of Ba promoter into the support (Fig.3d) and control the formation state of barium in supports. The appropriate addition of EDTA and Ba²⁺ could form [Ba(EDTA)]²⁻ which could decompose to LT-BaCO₃ promoting catalytic activity (Fig.4). And the steric repulsion of EDTA makes the reduction of Ba promoter easier which could increase the activity of catalysts. When the content of EDTA is high, [Ba(EDTA)]²⁻ and (EDTA)⁴⁻ compete to absorb on Mg(OH)₂ precursor which causes low

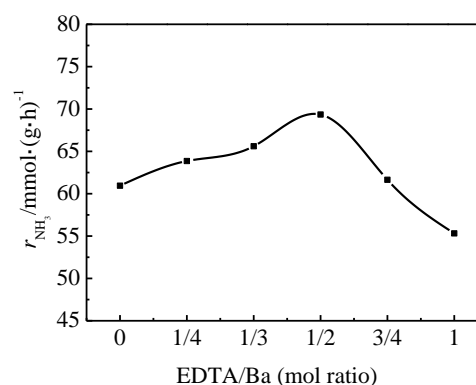


Fig.7 Catalytic activities (r_{NH_3}) of Ru/Ba-MgO catalysts modified by different amounts of EDTA

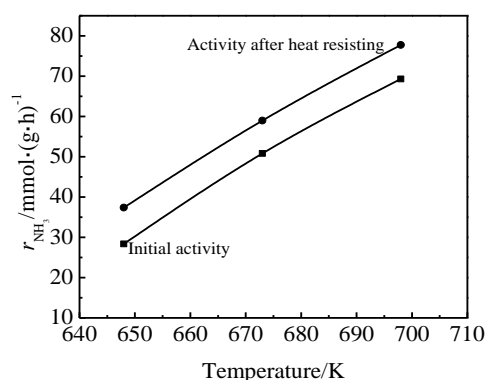


Fig.8 Catalytic activities (r_{NH_3}) of Ru/Ba-MgO catalysts modified by EDTA (EDTA/Ba=1/2)

surface absorption of Ba promoter on the supports. The catalytic activity of Ru/Ba-MgO catalyst modified by EDTA (EDTA/Ba=1/2) increases a lot as shown in Fig.8. After heat-resisting for 12 h under the condition of 823 K, 5 MPa and 30 000 h⁻¹. The results are consistent with the H₂-TPR analysis mentioned above.

3 Conclusions

1) During the preparation of Ba-doped nano-magnesia by ultrasound electrostatic adsorption method, barium promoter could be adsorbed on the surface of the supports directly due to the formation of [Ba(EDTA)]²⁻ chelate when EDTA modifier is added. The introduction of EDTA not only changes the chemical and textural properties of Ba-MgO supports for high distribution of ruthenium, but also controls the growth and size of BaCO₃ crystalline grain.

2) The catalytic activities for ammonia synthesis are higher when LT-BaCO₃ occupies the main formation state. The Ru/Ba-MgO catalyst with the molar ratio of EDTA/Ba= 1/2 shows the highest catalytic activity for ammonia synthesis with a reaction rate of 69.31 mmol (g h)⁻¹ at 698 K, 10 MPa and 10 000 h⁻¹.

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EDTA 修饰对 Ru/Ba-MgO 氨合成催化剂性能的影响及作用机理

霍超¹, 程向炜^{1,2}, 杜彦磊¹

(1. 浙江工业大学, 浙江 杭州 310014)

(2. 浙江警察学院, 浙江 杭州 310053)

摘要: 利用超声-共沉淀技术制备了一系列 EDTA 修饰的掺钡纳米氧化镁载体 (EDTA-Ba-MgO) 及其负载的钌基氨合成催化剂 (Ru/EDTA-Ba-MgO)。通过场发射扫描电镜、X 射线粉末衍射仪、氮物理吸附、热重分析仪及 H₂ 程序升温还原等方法对载体/催化剂进行表征。结果表明: EDTA 的修饰作用改变了钡助剂与载体的作用方式, 通过与 Ba 助剂发生络合作用形成了 [Ba(EDTA)]²⁺, 改变了 Ba²⁺ 的带电性质, 使钡助剂在带正电荷的载体表面实现了直接吸附, 从而更有利于对钡助剂在 Ba-MgO 中掺杂量及掺杂形式的调控, 最终达到提高催化剂活性的目的。在 10 MPa, 10 000 h⁻¹ 和 698 K 的反应条件下, Ru/EDTA-Ba-MgO 催化剂上氨合成速率达到 69.31 mmol (g h)⁻¹, 比 Ru/Ba-MgO 提高了 7.4%。

关键词: EDTA 修饰; 掺钡纳米氧化镁; 钌基催化剂; 氨合成; 络合作用

作者简介: 霍超, 女, 1971 年生, 博士, 教授, 浙江工业大学化学工程学院, 浙江 杭州 310014, 电话: 0571-88320815, E-mail: chaohc@zjut.edu.cn