

Preparation and characterization of boron-doping ruthenium catalysts for ammonia synthesis

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Received 14 January 2004; revised 16 July 2004; accepted 16 July 2004
Available online 11 September 2004

Abstract

Boron-doping commercial magnesia-supported ruthenium catalysts for ammonia synthesis were conveniently prepared in a similar process of the preparation of supported amorphous alloy Ru–B catalysts using $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ as precursor. Activity evaluation results showed that the cesium-promoted catalyst exhibited significantly high activity for ammonia synthesis at atmospheric pressure, whereas the non-promoted catalyst had almost no activity in the same conditions. The catalysts were characterized by XRD, XPS and TEM.

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1. Introduction

Catalytic ammonia synthesis is one of the most important and the largest energy-consuming processes in the modern chemical industry. The relationship between it and other scientific areas is very close. Many new techniques, methods and theories developed in the field have been extended to other areas of catalysis, and meanwhile some new discoveries made in other areas also have been applied to the fundamental study or the industrial application of ammonia synthesis, making them further progress.

Promoted Ru/C catalysts have been commercialized since 1992, however recent researches have shown that promoted Ru/MgO catalysts should become the most promising second-generation ammonia synthesis catalysts [1–5]. The drawback of current preparation of promoted Ru/MgO catalysts is the high cost, mainly lying in the relatively expensive raw materials, i.e., chlorine-free Ru precursor and high purity magnesia with med-

ium surface area (around 50–100 $\text{m}^2 \text{g}^{-1}$) rather than commercial magnesia (usually about 20 $\text{m}^2 \text{g}^{-1}$) must be used, and in the troublesome preparation procedures and the severe conditions.

The amorphous alloy catalysts have been applied for over twenty years in the studies of electrolysis [6], hydrogenation [7,8], hydrogenolysis [9], oxidation [10], isomerization [11], and even ammonia synthesis [12]. The research emphases were mainly concentrated on the catalytic behaviors and properties of the amorphous alloy catalysts or the crystalline catalysts deriving from amorphous state ones. In the preparation process of amorphous alloy catalysts by chemical reduction, transition metallic ions (Ru^{3+} , Ni^{2+} , Co^{2+} and so on) are reduced into atomic state by hypophosphite (H_2PO_2^-) or borohydride (BH_4^-), resulting in the thorough separation of them with other anions (Cl^- , NO_3^- , SO_4^{2-} and so on). Thus one of our interesting questions is to know whether this method is superior to the conventional hydrogen reduction in removing poisonous chlorine, of which the result is not satisfactory when $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ is used as a precursor to prepare Ru/MgO catalysts for ammonia

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synthesis. Further more electronic transfer between transition metal and alloying metalloid B or P has been commonly found for amorphous alloy catalysts. While the most studied promoters for ammonia synthesis Ru catalysts were alkali oxides (or hydroxides), alkaline earth oxides or lanthanide oxides, and the report on the influence of boric or phosphoric compound on catalytic activity has not been seen. Thus our second interest is to investigate how the boric compound influences the catalytic performance of Ru catalyst for ammonia synthesis. Naturally, the third interest is to test whether a satisfactory result can be obtained when commercial magnesia is used as a support.

2. Experimental

Boron-doping cesium-promoted and non-promoted Ru/MgO catalysts were prepared in the following procedures. Commercial magnesia (2 g) was first pre-calcined at 773 K for 2 h ($15.5 \text{ m}^2 \text{ g}^{-1}$) and impregnated with 25 ml of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (0.162 g, $n = 1-3$ and 37 wt% of Ru content) aqueous solution for 4 h. Then 4 ml of KBH_4 (0.233 g, B:Ru = 7.2:1) aqueous solution was added to the slurry under stirring at room temperature until the completion of the reduction reaction. The obtained material was washed thoroughly with distilled water and then dried at 373 K for 6 h. The resulting solid was denoted as RuB/MgO, in which the content of Ru and B were detected by inductively coupled plasma (ICP) to be 2.89 and 0.34 wt%, respectively, suggesting the actual loaded molar ratio of Ru to B = 1:1.2. Partial the RuB/MgO was impregnated with aqueous solution of CsNO_3 , in the nominal molar ratio of Cs to Ru = 2.1:1 for 12 h, then dried at 373 K for 6 h, calcined at 703 K for 2 h and annealed in succession. As-obtained crystalline sample was labeled as Cs–RuB/MgO, in which the Ru content was detected to be 2.59 wt%. The Cs–RuB/MgO and other crystalline sample, which was labeled as T–RuB/MgO, obtained by treating the RuB/MgO in the same way as the Cs–RuB/MgO except impregnation with aqueous solution of CsNO_3 , were used as catalysts for ammonia synthesis.

X-ray diffraction (XRD) pattern measurements were carried out in a Rigakudmax instrument employing monochromated Cu $\text{K}\alpha$ radiation ($\lambda = 1.5148 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) spectra were measured with a PHI 5300 ESCA instrument in the condition of pass energy of 89.45 eV, vacuum of less than $1 \times 10^{-7} \text{ Pa}$, Mg X-ray as radioactive source and impurities of C_{1s} (284.6 eV) as internal reference. Transmission electron microscopy (TEM) micrographs were obtained on a TECNAI T20ST instrument with accelerating voltage of 200 keV.

Catalyst performance was tested by feeding 40 ml min^{-1} of $\text{H}_2\text{-N}_2$ (3:1) synthesis gas mixture through

0.2 g of catalyst powder charged in a fixed bed stainless steel micro-reactor (i.d. = 8 mm) at atmospheric pressure. A catalyst was first activated in the stream of ammonia synthesis gas at 684 K for 2 h, and then cooled to desired reaction temperature. After a stable ammonia production was reached in about 1 h, a catalytic activity, expressed as $\mu\text{mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$, was determined by a chemical titration method using fixed amount of diluted sulfuric acid solution containing an indicator (methyl red) to absorb the produced ammonia. The dependence of catalytic activity on reaction temperature was plotted.

3. Results and discussion

The results showed that the T–RuB/MgO had almost no activity for ammonia synthesis at 684 K. Some activity values of non-promoted Ru/MgO catalysts prepared with $\text{Ru}_3(\text{CO})_{12}$ or $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ as precursor have been reported [1,5,13,14]. The reported different activities were attributed to the differences of the preparation of catalysts or the operation conditions. Based on these facts, it can be firmly inferred that the no activity of the T–RuB/MgO was due to the doping of boron. So the boric compound in the T–RuB/MgO actually acted as an inhibitor destroying the original activity of the Ru/MgO catalyst greatly. The possible reason may be ascribed to the acidity of the boric compound, as electron-deficient material is very disadvantageous to the dissociative chemisorption of N_2 on active Ru [15], which is accepted to be the rate-limiting step in ammonia synthesis. The dependence of the Cs–RuB/MgO catalytic activity for ammonia synthesis on reaction temperature is illustrated in Fig. 1. It is very interesting that the Cs–RuB/MgO catalyst exhibited unexpected high activity, and the highest activity reached to $2120 \mu\text{mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ at 662 K of reaction temperature. The catalytic performance of the Cs–RuB/MgO catalyst was similar to that of our recent reported Cs–Ru/MgO

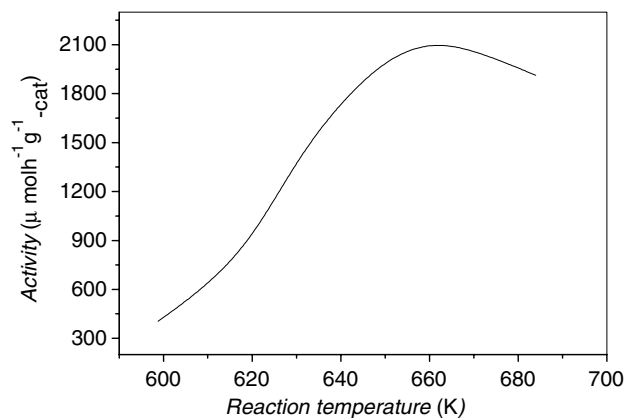


Fig. 1. Dependence of the Cs–RuB/MgO catalytic activity on reaction temperature at atmospheric pressure and 40 ml min^{-1} of ammonia synthesis gas flow rate.

catalyst [16], and no deactivation was observed in at least accumulative 40 h intermittent evaluation. Meanwhile the inhibition of the commercial magnesia to the catalytic reaction due to its low area could not be corroborated from above findings.

The boric compounds in the Cs–RuB/MgO and the T-RuB/MgO after reaction cannot be accurately identified from their corresponding XRD patterns presently. The very weak crystalline peaks of the boric compound in the curve of the Cs–RuB/MgO catalyst indicate that its content was very low compared to magnesia support, while the weak crystalline peaks of atomic Ru, which only observed in the curve of the T-RuB/MgO after reaction, indicate that cesium promoter (oxide or hydroxide) performed a better function than single boric compound to restrain metallic Ru from congregating. (see Fig. S1 in the Supplementary File).

The XPS spectrum of Ru3d of the RuB/MgO showed that Ru existed mainly in the oxidic state, because the amorphous alloy Ru–B was metastable and could be easily oxidized in air. The XPS spectrum of Cl3p_{3/2} of the RuB/MgO qualitatively showed that almost no appreciable chlorine signal was detected revealing the highly efficient removal of chlorine through this preparation process. The corresponding XPS spectrum of the Cs–RuB/MgO catalyst after catalytic reaction showed that the Ru was mainly in atomic state, meaning that the Ru species could be easily reduced to Ru metal, which is active in ammonia synthesis, in the course of catalytic reaction no matter what form or state it existed in after annealing at 703 K. (see Figs. S2 and S3 in the Supplementary File).

Some TEM images of the T-RuB/MgO after catalytic reaction showed that the surface of magnesia support was very uneven, some of the surface was stuck by some material of silk form, while other surface was almost clear. One of the micrographs was selected and shown in Fig. 2. The threadlike material, we thought according to the amount of Ru and B species in the T-RuB/MgO, should be composed of Ru metal and boric compound. Ru metal neighbored closely with electron-absorbing boric compound and its dispersion on the magnesia was poor, so its original activity for ammonia synthesis was lost and the existence of it was detected by XRD though its content was less than 3%.

The TEM images of the Cs–RuB/MgO after catalytic reaction were almost unanimous and one of them was shown in Fig. 3. It was seen that the dispersion of metallic Ru over the support was enhanced greatly in the presence of cesium promoter compared to the T-RuB/MgO, thus no crystalline Ru peaks were detected in its XRD pattern. But the spherical Ru particles were still uneven, which is of the character of impregnation process. Though the weak crystalline peaks were assigned to boric compound, it is not easy to identify it in the TEM image. Interestingly, sporadic rodlike support with around

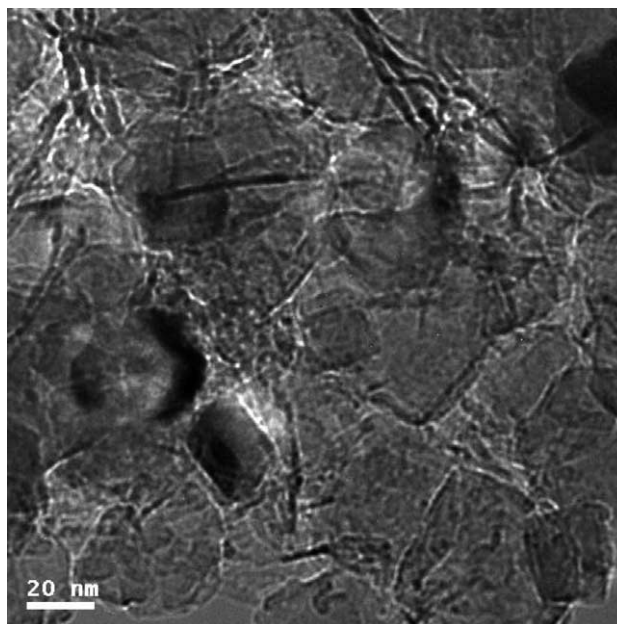


Fig. 2. Selected TEM micrograph of the T-RuB/MgO after catalytic reaction.

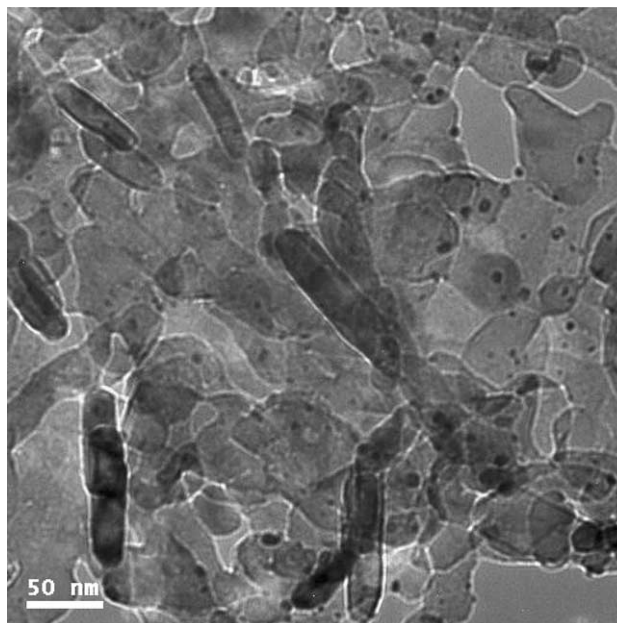


Fig. 3. TEM micrograph of the Cs–RuB/MgO after catalytic reaction.

20 nm of diameter and 70–100 nm of length was observed in Fig. 3. How it was formed is still not clear now, however the conclusion that the transformation of some support morphology was due to the coexistence of cesium and boron species can be authentically drawn. As the catalyst was stable after activation for 2 h at 684 K, it is reasonable to infer that the transformation mainly completed at the first activation stage of catalyst. Cesium (CsOH or Cs₂O) is an excellent promoter for Ru catalyst for ammonia synthesis, the negative function of

boric compound to the reaction was counteracted by cesium, thus the Cs–RuB/MgO catalyst exhibited high activity for ammonia synthesis.

4. Conclusion

This method was convenient in preparing magnesia-supported Ru catalyst for ammonia synthesis, showed superiority over conventional hydrogen reduction method in removing chlorine of Ru precursor, and obtained satisfactorily high activity at atmospheric pressure for the cesium promoted catalyst. The findings showed that $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and commercial magnesia could be used as raw materials to reduce the preparation cost of promoted Ru/MgO catalysts with high activity for ammonia synthesis. Studies on the influence factors of promoted RuB/MgO catalysts, such as pH value of solution, amount of added borohydride, annealing temperature, content and type of promoter, activity and lifetime of catalysts under high pressure and so on, are in process.

Acknowledgements

This work was a Joint Project between Nankai University and Tianjin University sponsored by the Ministry of Education, PR China and was also financially supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.catcom.2004.07.009](https://doi.org/10.1016/j.catcom.2004.07.009).

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