



Carbon-supported Ru catalyst with lithium promoter for ammonia synthesis

Bingyu Lin^{*}, Kemei Wei

National Engineering Research Center of Chemical Fertilizer Catalyst, Fuzhou University, Fuzhou, Fujian 350002, PR China



ARTICLE INFO

Article history:

Received 16 May 2013

Received in revised form 28 June 2013

Accepted 1 July 2013

Available online 8 July 2013

Keywords:

Lithium

Ru catalyst

Ammonia synthesis

ABSTRACT

The electronegativity of Li is much higher than that of Na or K, but the ammonia synthesis activities of Li-promoted Ru/AC catalysts were comparable to the values of Ru catalyst promoted with K, which were much higher than those over Ru catalyst with Na promoter. The presence of Li increased the catalytic activity by changing the chemisorption properties such as hydrogen adsorption and nitrogen adsorption for carbon-supported Ru catalysts, rather than affecting the sizes of Ru particles or the electron density of Ru metal.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Catalytic synthesis of ammonia from hydrogen and nitrogen has been a subject of significant research dating back to the beginning of the 20th century. During the past decades, Ru catalysts supported on graphitized carbon were found to have higher ammonia synthesis activity than commercial iron catalyst. The promoters including of alkali or barium are necessary for obtaining the high catalytic activity of Ru catalyst. Although there are still doubts about barium is a structural promoter [1,2] or an electronic promoter [3,4], it is widely accepted that alkali is an electronic promoter, which can transfer electron from the alkali (cesium and potassium) to ruthenium surface [5,6]. The ammonia synthesis activity sequence was suggested to be in the order of the electronegativity of alkali [5,6], and Aika [6] found that the maximum activities for Ru/AC catalysts promoted with Cs, K and Na were 3.30, 1.28 and 0.12 mmol NH₃/g/h, respectively. Therefore, it can conclude that lithium is not a promising promoter because the electronegativity of lithium is higher than that of Na.

However, recently, we found that the change in the chemisorption properties of reactant gases was the main reason that K promoter enhanced the ammonia synthesis activity of Ru/AC catalyst [7]. It can therefore expect other alkalis with high electronegativity may be used as a promoter for a highly efficient Ru catalyst used in ammonia synthesis because they may effectively improved the chemisorption properties of reactant gases. Herein we prepared Ru/C catalysts promoted with different alkali promoters. The result showed lithium was an unexpected effective promoter of Ru catalyst for ammonia

synthesis, although the electronegativity of Li is much higher than that of Na or K.

2. Experimental

2.1. Catalyst preparation

Commercial carbon (Shanghai Carbon Co., Ltd.) was firstly graphitized according to the methods reported in previous literatures [8–10], that is, heating raw carbon in Ar at 1850 °C for 1 h and then oxidized in steam at 450 °C for 20 h. The as-obtained graphitized carbon (1110 m² g⁻¹) crushed and sieved to particles of size 0.30–0.56 mm. Ruthenium was introduced by the incipient wetness impregnation of support with RuCl₃ solution (Sino-Platinum Metals Co., Ltd. 0.05 g Ru metal per gram of carbon). After dried at 120 °C and then reduced in hydrogen at 450 °C for 6 h without calcination, the promoters were added by incipient wetness impregnation. Liang et al. [11] showed that KOH promoter was more effective than KNO₃ for ammonia synthesis over Ru/C catalysts, thus NaOH and KOH (analytical grade, Sinopharm Chemical Reagent Co., Ltd.) was selected as the promoter precursor, and Ru catalysts promoted with Li were prepared using LiNO₃ (analytical grade, Sinopharm Chemical Reagent Co., Ltd) as precursor. The catalysts were named as xM-Ru/AC, where x was the weight ratios of promoter to carbon, and M was the symbol of alkali promoters (M = Na, Li and K).

2.2. Catalyst characterization

The X-ray diffraction (XRD) patterns of the catalysts were measured by a PANalytical X'Pert Pro X-ray diffractometer with a CoK α radiation operated at 40 kV and 40 mA. Transmission electron microscopy (TEM) analysis was performed on a FEI (Tecnai G2 F20) microscope

^{*} Corresponding author. Tel.: +86 591 83731234; fax: +86 591 83738808.
E-mail address: bylin@fzu.edu.cn (B. Lin).

with a field-emission gun operating at 200 kV, and the samples were prepared by putting a drop of particle suspension on a carbon coated copper grid. The dispersion was calculated from the average particle size based on the formulas of Borodzinski et al. [12]. X-ray photoelectron spectroscopy (XPS) was carried out with a Thermo Scientific ESCALAB 250 spectrometer with an Al K α X-ray source at 1486.6 eV.

Temperature-programmed desorption studies were measured on an AutoChem 2920 instrument (Micrometrics). The catalyst (ca. 100 mg) was reduced in H₂ at 450 °C for 1 h and then purged in Ar gas for 1 h. After cooled down to 50 °C in Ar, the sample adsorbed hydrogen for 1 h, and then flushed in Ar for 0.5 h. The H₂-TPD profiles were obtained with a heat rate of 10 °C/min. N₂-TPD profiles were obtained by a similar method using He as carried gas.

2.3. Activity measurements

The catalytic experiments were performed on a stainless steel reactor using samples. Details of the activity measurement were provided previously [7,13]. Briefly, Ru catalyst was diluted with quartz powder (catalyst/quartz volumetric ratio, 1/30) to prevent temperature gradients. The samples were activated in the gases mixture (H₂/N₂ = 3.0 v/v) at different temperatures (200, 300, 400, and 430 °C for 4 h, respectively). The activities were measured after the stabilization under various conditions (10 MPa, 10,000 h⁻¹, 2.4 × 10⁵ cm³ g_{cat}⁻¹ h⁻¹, 350–400 °C) for more than 4 h. The rates were obtained by analyzing the effluent gas with a known amount of diluted H₂SO₄.

3. Results and discussion

Ru catalysts without promoters were found to be completely inactive [8,14]. Fig. 1 shows the ammonia synthesis rates for Ru catalysts with different alkali promoters. The catalytic activities of Ru catalysts all increased with the increase of the reaction temperatures in the range of 350 to 400 °C, and the corresponding rates depended on the type and the quantity of alkali promoters. The rate orders for Li and Na promoted Ru catalysts were 2Li-Ru/AC > 1Li-Ru/AC > 4Li-Ru/AC and 8Na-Ru/AC > 4Na-Ru/AC > 12Na-Ru/AC, respectively. All Ru catalysts promoted with Li or Na had an appropriate loading. Based on the plots of the rates vs promoter loadings or the TORs vs the molar ratios of alkali promoter to Ru at 350 or 400 °C (Fig. S1 in Supplementary files), Li-promoted Ru catalysts showed similar catalytic activities as Ru catalysts with K promoter reported in our previous work [7], whereas the catalysts promoted with Na exhibited much lower catalytic activities. The rates stayed almost unchanged over approximately 100 h (Fig. 1), indicating the catalysts promoted

with Li, Na or K were stable during the ammonia synthesis reactions at 400 °C.

From the XPS spectra (Fig. S2 in Supplementary files), Ru 3d_{5/2} binding energy in Ru/AC catalyst was ca. 282.2 eV, and the presence of a low amount of Li did not affect the value of the Ru 3d_{5/2} binding energy (1Li-Ru/AC), but the values increased with the increase of Li loading. The Ru 3d_{5/2} binding energy of 4Na-Ru/AC was close to that of 4Li-Ru/AC, and similar value also was obtained for K promoted Ru catalysts [7]. The Li 1s binding energies in all Li promoted Ru/AC catalysts were found to be ca. 54.6 eV, such binding energies usually correspond to lithium metal. The Na 1s peaks were located at 1070.9 eV and 1072.6 eV, these values were comparable to the binding energy of sodium metal [15] and sodium oxide [16], respectively. On the other hand, the K 2p_{3/2} binding energy was ca. 292.8 eV while the K 2p_{1/2} component was found at 295.8 eV. These peaks were characteristic of K for containing-K ruthenate because the binding energy was close to those values for K in containing-K ruthenate or osmate [17]. Previous study on the chemical activation process of carbon with KOH [18,19] showed that K₂CO₃, K₂O and K gradually appeared with the increase of the heating temperature. Similar phenomenon might occur when Ru/C catalysts with alkali promoters were heated in mixed gases of nitrogen and hydrogen. However, only the reflections corresponding to lithium carbonate and sodium carbonate can be observed in the XRD patterns of Li- and Na-promoted Ru catalysts (Fig. S3). Before XPS study, all Ru catalysts were reduced in hydrogen and then transferred into analysis chamber without exposure to air. But XRD measurements were performed in ex-situ conditions, thus CO₂ was adsorbed to form carbonate. Thus the different existing forms of alkali promoters were obtained by different characterizations.

Representative TEM images with particle size distribution histograms (Fig. 2) show the change in the loadings or the types of alkali promoters had a limited influence on the size of Ru particles. Ru particles were finely dispersed on carbon support, most Ru particles exhibited a narrow size distribution in the range of 1.5–3.0 nm, and the average sizes of Ru for all samples were in the range of 1.7–2.3 nm. Similar results for K-promoted Ru/C catalysts have been reported by Liang et al. [11] and Lin et al. [7].

The H₂-TPD profiles (Fig. 3) showed that the addition of alkali to Ru catalysts significantly increased the amount of desorbed hydrogen. The H₂ uptake increased with the increase of Li loadings, whereas the change in Na contents did not significantly affect the intensity of the hydrogen desorption peak. Furthermore, for all Ru catalysts with an appropriate amount of alkali promoters, K-promoted Ru catalysts adsorbed the largest amount of hydrogen, the next was Li, whereas

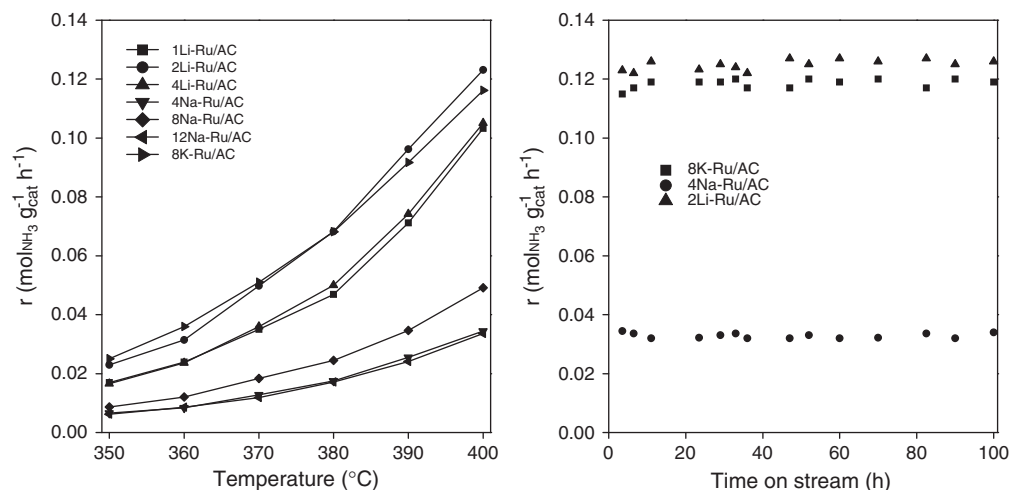


Fig. 1. (Left) The ammonia synthesis rates as a function of reaction temperatures over Ru catalysts with different alkali promoter contents and (Right) Dependences of catalytic performances on time on stream for ammonia synthesis at 400 °C.

Download English Version:

<https://daneshyari.com/en/article/6503562>

Download Persian Version:

<https://daneshyari.com/article/6503562>

[Daneshyari.com](https://daneshyari.com)