Molecular Catalysis 433 (2017) 235–241

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

Editor's choice paper

The effect of composition of the ruthenium precursors and heat treatment conditions on the activity of Ru-Ba/Sibunit catalysts for ammonia synthesis

N.S. Smirnova[c,*], K.N. Iost[a], V.L. Temerev[a], T.I. Gulyaeva[a], M.V. Trenikhin[a], I.V. Muromtsev[a], E.V. Khramov[b], Y.V. Zubavichus[b], D.A. Shlyapin[a], P.G. Tsyrul'nikov[a]

[a] Institute of Hydrocarbons Processing SB RAS, Neftezavodskaya st., 54, Omsk 644040, Russia
[b] National Research Center "Kurchatov Institute", pl. Kurchatova, 1, Moscow 123182, Russia
[c] Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Leninsky prospect, 31, Moscow 119991, Russia

ARTICLE INFO

Article history:
Received 2 August 2016
Received in revised form
20 December 2016
Accepted 21 December 2016

Keywords:
Ammonia synthesis
Supported ruthenium catalysts
Barium promoter
Sibunit

ABSTRACT

The effect of composition of the chlorine-containing precursors of ruthenium and heat treatment conditions on the preparation of catalysts supported on carbon composite Sibunit for the ammonia synthesis was studied. The activity of Ru-Ba/Sibunit samples was shown to depend on ruthenium dispersion and residual chlorine content in the catalyst. The removal of outer-sphere chloride ions from ammonia complexes of ruthenium via ionic exchange and the replacement of hydrogen reduction of the Ru precursor by calcination in an inert atmosphere prevent sintering and agglomeration of the active component particles, thus enhancing the catalyst activity.

1. Introduction

Molecular nitrogen fixation with the formation of ammonia is among the key industrial processes. Ammonia is commonly produced by the Haber-Bosch process, which is carried out at high pressures (20–30 MPA) and temperatures (620–820 K) [1]. Commercial catalysts for the process are represented by iron promoted with K_2O, Al_2O_3, SiO_2, CaO and other additives [2]. Ammonia production requires high equipment expenditures, which raise the cost of the final product.

Along with this, it is known that ruthenium is one of the most active catalysts for low-temperature synthesis of ammonia: its activity is five times higher as compared to iron at the same temperature and half as much pressure [3]. The use of carbon-supported ruthenium catalysts promoted with compounds of alkali (K, Cs) [4,5], alkaline earth (Ba) [6,7] or rare earth (Sm) [8] elements makes it possible to considerably decrease the process temperature (620–690 K) and pressure (6–8 MPa) [1].

The preparation of a supported ruthenium catalyst for low-temperature ammonia synthesis is a complicated multistep process in which the resulting activity of the sample is affected by various factors, in particular, the catalyst composition, type of promoter, structural and textural properties of the support, features of ruthenium precursors and a promoter, temperature and duration of heat treatments. Such factors commonly exert an effect on the size of particles and their resistance to sintering [9].

In a number of papers was stated that the ammonia synthesis on ruthenium-based catalysts is a structure-sensitive reaction [2,10]. The structure sensitivity is related with the presence of the ensembles of fifth ruthenium atoms (B5 sites), which are believed to be the active sites of the reaction. The quantity of these sites strongly depends on size and morphology of ruthenium particles [3]. In addition, it is known that chloride ions, which remain after decomposition and reduction of the active component, decrease the catalyst activity in ammonia synthesis. Catalysts are activated most often by a reducing heat treatment, so its duration, temperature mode and gas mixture composition also produce significant effects on the formation of catalyst particles, methanation of the carbon substrate and removal of chlorine ions [6].

This study aimed to reveal the effect of heat treatment condition and composition of chlorine-containing precursors of ruthenium during its deposition and fixation on the activity of Ru-Ba/Sibunit catalysts in ammonia synthesis.

---

* Corresponding author.
E-mail address: everinflame@gmail.com (N.S. Smirnova).

http://dx.doi.org/10.1016/j.mcat.2016.12.015
1381-1169/

2. Experimental

2.1. Preparation of ruthenium precursor

Complexes of divalent ruthenium $[Ru(NH_3)_nCl_m]Cl_p$ and $[Ru(NH_3)_nCl_m](OH)_p$ (n = 5–6; m = 0–1; p = 1–2) were used as the precursors [11]. The ammonia-chloride complex $[Ru(NH_3)_nCl_m]Cl_p$ was obtained by boiling of ruthenium (IV) hydroxochloride (0.5 g, reagent grade, «Reakhim») and hydroxylamine sulfate (0.71 g, p.a., «Omskreaktiv») with carbamide (1.2 g, p.a. «Omskreaktiv») and water (15 ml) for 3 h. To decrease the content of chlorine, the resulting ruthenium complex was passed through AB-17-8 anionite (ion exchange resin based on styrene with 8% divinylbenzene) in the OH form, as described in [11]. After obtaining a strongly colored solution of $[Ru(NH_3)_nCl_m](OH)_p$, the column was washed with water.

2.2. Catalysts synthesis

A mesoporous carbon composite Sibunit [12] with $S_{BET} = 300\ m^2/g$ was used as the support. The 0.4–0.8 mm fraction was preliminarily washed with distilled water to remove carbon dust and dried at 120 °C in air for 3 h.

To prepare the supported ruthenium catalyst, Sibunit was impregnated with an aqueous solution of the ruthenium complex, dried at 120 °C in air for 3 h, and then reduced in hydrogen (purity = 99.98%) or calcined in flowing argon (initial purity 99.997%, additional cleaning from oxygen content was performed by passing Ar through copper shavings at 300 °C) at 450 °C for 4 h at a heating/cooling rate of 10 °C/min. The synthesized catalyst 4%Ru/Sibunit was impregnated with an aqueous solution of $Ba(CH_3COO)_2$ (p.a., «Omskreaktiv») assuming the molar ratio Ba: Ru = 2.5 and dried at 120 °C in air for 3 h; this was followed by activation of the catalyst, first in flowing Ar at 350 °C for 2 h, and then in flowing H_2 at 350 °C for 2 h at a heating/cooling rate of 5 °C/min. Both the barium-free 4%Ru/Sibunit samples and the 4%Ru–13.7%Ba/Sibunit catalysts were examined (Table 1).

2.3. Determination of dispersion from CO chemisorption

Ruthenium dispersion in 4%Ru/Sibunit catalysts was estimated using pulse chemisorption of CO. The study was performed on an AutoChem II 2920 (Micromeritics) analyzer. CO chemisorption was carried out after reduction of the samples with a $10\%H_2/Ar$ (puriss.) mixture by heating to 450 °C and holding at this temperature for 60 min, with subsequent purging with helium at 450 °C for 30 min and cooling the sample to room temperature. A 10 vol.% CO/He mixture (puriss.) was fed in pulses at equal time intervals into a flow of inert carrier gas (helium). The dispersion and particle size values were calculated according protocol described in [13] with regard to linear chemisorption of CO on ruthenium (the stoichiometric coefficient CO: Ru = 1:1) [13,14].

2.4. Electron microscopy

A transmission electron microscopy study of the samples was performed using a JEM-2100 (JEOL) electron microscope (accelerating voltage 200 kV and lattice resolution 0.145 nm) with an INCA-250 (Oxford Instruments) energy dispersive X-ray spectrometer. Alcohol suspensions of the samples were subjected to ultrasonic dispersion (UZDN-2T) followed by deposition onto the holey carbon film supported on a copper grid. When measuring diameter of the particles, linear dimensions were calibrated against the crystal lattice of gold particles. Therewith, the measurement error for the linear dimensions on electron microscopy images did not exceed 0.02 nm. The particle size distribution was obtained by measuring 150–200 particles in each case.

The surface morphology and composition of the samples were examined on a JSM-6610LV (JEOL) scanning electron microscope equipped with an INCAx-Act (Oxford Instruments) spectrometer for X-ray microanalysis.

2.5. X-ray diffraction analysis

X-ray diffraction analysis was carried out with a Bruker D8 Advance (Germany) powder X-ray diffractometer using a monochromatic Cu K_α source (a wavelength of 0.15418 nm). The following measurement modes were employed: scanning step 0.05°, signal accumulation time 2 s, voltage and filament current 40 kV and 40 mA, respectively, and 2θ scanning range 10–80°.

The obtained diffraction patterns were interpreted using the powder diffraction database ICDD PDF-2, 2006.

2.6. XAFS spectroscopy

Synchrotron radiation measurements were performed at the Structural Materials Science experimental station of the synchrotron radiation source Sibir-2 at the National Research Center "Kurchatov Institute" [15]. The X-ray beam with an energy resolution $\Delta E/E \approx 2 \cdot 10^{-4}$ was monochromatized using a (220) silicon single crystal channel-cut monochromator. The Ru K-edge XAFS absorption spectra were recorded in a transmission mode using two ionization chambers that were filled with Ar and attached to Keithley picoammeters. The spectra were processed using IFEFFIT (Athena, Artemis, FEFF 6) software package [16,17]. The Fourier transforms of EXAFS oscillations were taken in a range of $k = 2.0 \div 12.5\ Å^{-1}$ with the weight coefficient k^3 and approximated in a range of $R = 1.0 \div 3.0$ Å.

2.7. Catalytic testing

The activity of 4%Ru–13.7%Ba/Sibunit catalysts in low-temperature synthesis of ammonia was measured in a fixed-bed flow reactor under a 7 atm pressure of the gas mixture $H_2:N_2$ (3:1) (N_2 purity = 99.9991%) at a temperature of 350 °C. Contact time was 1.3 s, and volume of the loaded catalyst, 2 cm^3. Prior to catalytic measurements, the samples were purged with flowing hydrogen (40 ml/min) at 350 °C for 12 h.

Gas mixture at the reactor outlet was analyzed titrimetrically. To this end, 25 ml of a 0.1 H sulfuric acid solution prepared from analytical standard («Omskreaktiv») was placed in a bubbling flask to absorb ammonia at the reactor outlet. The gas mixture evolved at a flow rate of 42 ± 3 ml/min was bubbled for 60 min; after that, an aliquot was taken from the solution and titrated against a solution of NaOH (analytical standard, «Omskreaktiv») with methyl red. The amount of NaOH consumed for titration was used to calculate the volume flow rate of NH_3 (ml/min) and the volumetric concentration of NH_3 at the reactor outlet (vol.%). The catalytic activity was expressed in terms of ammonia amount formed per gram of catalyst per unit time ($ml_{\ NH3}\ g_{cat}{}^{-1}\ h^{-1}$) and relative percents from equilibrium yield (5.33 vol.%) at current conditions. Data of equilibrium yields were obtained from [18].

3. Results and discussion

3.1. CO chemisorption

The dispersion and average size of ruthenium particles were determined from CO chemisorption data for 4%Ru/Sibunit catalysts. The determination was made for non-modified samples since the presence of barium compounds in the catalyst substantially underrates the dispersion of supported metal [1].