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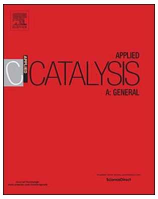

Ammonia synthesis over Cs- or Ba-promoted ruthenium catalyst supported on strontium niobate

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ABSTRACT

Strontium niobates with different crystalline structure and morphology have been prepared via a hydrothermal method and applied as a support for ruthenium catalyst in ammonia synthesis. The sample synthesized with a nominal Sr/Nb = 2.0, having a pure $Sr_2Nb_2O_7$ crystalline phase and specific surface area of 87 $m^2\,g^{-1}$, exhibits the best performance as support for Ru catalyst. The flake-structured $Sr_2Nb_2O_7$ substrate induced epitaxial growth of truncated pyramid shaped ruthenium nanoparticles with a dispersion as high as 93%, which have abundant steps and B_5 sites playing a key role in ammonia synthesis catalysis. Adding Cs- or Ba-promoter enhanced the activity of $Ru/Sr_2Nb_2O_7$ catalyst drastically. The highest ammonia synthesis rate over 8Cs- or 4Ba-2 wt%$Ru/Sr_2Nb_2O_7$ was 4986 and 2317 ($\mu mol\, g_{cat}^{-1}\, h^{-1}$) at 0.1 MPa and 673 K, respectively. In addition, both catalysts were stable over reaction for 72 h at 673 K and 0.1 MPa. Thus, the synthesized $Sr_2Nb_2O_7$ is expected to be a practically promising oxide support for ruthenium ammonia synthesis catalsyts.

1. Introduction

Ammonia is an important commodity chemical manufactured globally at a scale of 170 million metric tons per year in 2016 [1]. So far, more than 80% of the synthesized ammonia is utilized to produce fertilizers for food crop's growth [2]. Thus, ammonia synthesis is an effective artificial nitrogen-fixation technique, which supplies 40–60% of nitrogen source for human bodies [3]. Additionally, ammonia is recently attracting extensive research interests as a potential carrier for renewable energies or hydrogen due to its characteristics of (1) carbon-free, (2) high hydrogen content (17.8 wt %), (3) easy liquification (0.86 MPa at 293 K or 239.7 K at 0.1 MPa) and (4) mature technologies and infrastructures for production, transportation and storage [4–6]. Currently, ammonia is mainly synthesized from N_2 and H_2 via Haber-Bosch process using fused iron (Fe-Al_2O_3-K_2O) catalysts. Since dinitrogen molecule has extremely high dissociation energy (945 $kJ\,mol^{-1}$) [7,8] of its triple bond, the Haber-Bosch process must be operated at high temperatures (673–873 K) and high pressures (20–40 MPa) to achieve a reasonable performance [9,10]. Due to such stringent operational conditions, the Haber-Bosch synthesis becomes one of the most energy-intensive industrialized processes; it is estimated to consume approximately 1% of the world's power production [11]. Moreover, the H_2 feed of the present ammonia synthesis plants are mostly obtained from steam reforming of natural gas (one type of fossile resource), which is unsustainable and will be substituted by renewable H_2 souceses, such as biomass gasification or water electrolysis (electricity is generated from renewable energies). These renewable low-pressure H_2 sources are relatively dispersive, which demands catalysts that are more efficient to accelerate ammonia synthesis at milder reaction conditions. For these reasons, searching for noval catalysts that have reasonable performance at moderate reaction conditions is one of the key challenges for promoting the traditional Haber-Bosch process and for applying ammonia as a carrier for sustainable energies or hydrogen in the future.

Ruthenium-based catalysts have been extensively investigated as the second-generation ammonia synthesis catalysts because they exhibit higher activity at mild reaction conditions and less sensitivity to NH_3 concentration in gas phase as compared to the traditional fused iron catalysts [12–17]. Ru catalysts supported on high surface area graphite (HSAG) have been industrially applied in the KBR advanced ammonia synthesis process (KAAP) since 1992 [18]. However, carbon supports react readily with H_2 to form methane at ammonia synthesis conditions in the presence of Ru. Methanation in this manner causes gradual degradation of the carbon support, limiting the lifetime of Ru/C catalyst [19–21]. It is thus still of importance to find a suitable oxide support for ruthenium catalyst. So far, a variety of metal oxides, such as MgO [22–27], Al_2O_3 [28–33],Co_3O_4 [15],barium hexaaluminate [13], zeolite [34–36], mayenite electride [37–40], Pr_2O_3 [17], CeO_2 [41] and

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etc., have been proposed as supports for Ru ammonia synthesis catalysts. Among these oxides, magnesia, barium hexaaluminate, praseodymium oxide and electride are currently promising oxide supports for Ru catalysts due to their electronic and/or structural promotion to the activity of Ru nanoparticles for ammonia synthesis [13,17,37,42]. However, the high reactivity to H_2O of MgO and electride inhibit their widespread use in industry.

The rate-determing step in ammonia synthesis is dissociation of N_2 molecules on the surface of Ru crystallites [29,43]. The dissociation rate has been reported to depend significantly on the morphology (size and shape) and electronic state of Ru crystallites, which can be modified by the supports and/or promoters [44,45]. Previous studies have proved that: (1) flat Ru crystallites epitaxially grown on layered substrates show better performance than round Ru particles because more abundant B_5 sites can be found on the surface of the former [13,45,46]; and (2) compounds such as alkali, alkaline earth, or electrides that can donate electrons to Ru metal, resulting in a decreased ionization potential of Ru, thereby allowing electron transfers from the metal to the antibonding orbitals of the N atom and reducing the activation energy for the dissociative adsorption of N_2 molecules [47]. Therefore, an ideal support for Ru catalysts should modify the shape and size of Ru crystallites to achieve abundant B_5 sites on their surface and have ability to donate electron to Ru metallic atoms.

Rencently, strontium niobates are widely investigated as photocatalyts because they have special optical, ferroelectric and piezoelectric properties [48–51]. It has been reported that the morphology of strontium niobates can be tailored by changing synthetic parameters during preparation [52]. Based on the previous knowledge, we expect that niobates with layered structure may influence the shape and size of Ru crystallites and thus work as promising supports for Ru catalysts. Herein, we demonstrate that Ba- or Cs-promoted Ru supported on $Sr_2Nb_2O_7$ substrate exhibits superior activity and stablibity for ammonia synthesis.

2. Experimental

2.1. Preparation of $Sr_2Nb_2O_7$ support

The $Sr_2Nb_2O_7$ support was synthesized via a hydrothermal method. First, a precursor of niobium ($Nb_2O_5{\cdot}nH_2O$) was synthesized from $NbCl_5$ via a hydrothermal method as previously reported work [53]. An alcohol solution of $NbCl_5$ (0.37 mol L^{-1}) was prepared by dissolving appropriate amount of $NbCl_5$ (Aldrich, 99.0%) in ethanol (Sinopharm Chemical Reagent, analytical purity). Then, the pH of the solution was adjusted to around 10.5 by adding 4 wt% NH_4OH aqueous solution with stirring. After 4 h-stirring at room temperature, the mixture was transferred into a Teflon-lined autoclave and treated at 473 K for 24 h. Subsequently, the solid product was recovered by centrifugation at 8000 rpm for 30 min and washed repeatedly with distilled water until the filtrate was confirmed to be free of chloride anions using $AgNO_3$. Finally, the product was dried at 353 K under a vacuum of around 1.0 KPa.

Second, the resultant $Nb_2O_5{\cdot}nH_2O$ and $Sr(OH)_2{\cdot}8H_2O$ (aldrich, 99.5%) with different molar ratio were mixed in 45 ml distilled water. After stiring for 30 min, the pH of supernatant was in the range of 12.85–13.50; the mixture was transferred into a Teflon-lined autoclave and heated at 473 K for 24 h. The resultant product was filtered, washed thoroughly with deionized water until the pH of the filtrate was nearly 7. The product was dried in vacuum (~ 1.0 KPa) at 353 K for 10 h.

2.2. Preparation of supported Ru catalyst

Ruthenium catalysts were prepared by impregnation method. The dried $Sr_2Nb_2O_7$ samples were ground with an agate morta and pestle, and dispersed in a tetrahydrofuran (THF) solution of $Ru_3(CO)_{12}$ (Aldrich, 99.0%) with stirring at room temperature for 12 h. Then the solvent was removed using a rotary evaporator (313 K, 10 KPa). The dried samples were treated in an Ar (99.999%) flow of 5 mL min^{-1} at 723 K for 3 h. The catalysts obtained had a nominal Ru loading of 2 wt %. The Cs- or Ba-promoted Ru/$Sr_2Nb_2O_7$ catalysts were prepared by impregating the treated Ru/$Sr_2Nb_2O_7$ samples in an aqueous solution of $CsNO_3$ or $Ba(NO_3)_2$, respectively.

2.3. Ammonia synthesis

The dried catalyst samples were gound, pelletized, crushed and sieved. The fractions from 220 to 450 μm were collected and loaded into a quartz tubular reactor (I.D. = 7 mm). Before activity measurements, the catalysts were treated in a H_2 (99.999%) flow at 573–873 K for 3 h to reduce ruthenium cations to metallic state and to decompose $CsNO_3$ or $Ba(NO_3)_2$. The catalytic activities were measured in a synthesis gas ($H_2/N_2 = 3/1$, 99.999%) flow of 60 mL (STP) min^{-1} over 0.10 g sample. The reaction temperature was varied from 573 to 773 K at 0.1 MPa. The produced ammonia was absorbed by a 1×10^{-3} mol L^{-1} solution of sulfuric acid, and the rate of ammonia formation was determined from the decreasing rate in the conductivity of the sulfuric acid solution for measurement after a 30-min stabilization at appropriate reaction conditions.

2.4. Characterization

The crystalline structure of the samples was analyzed by a X-ray diffraction (XRD) technique performed on a PANalytical X'Pert Pro diffractometer equipped with a Cu-Kα radiation source (λ = 1.5405 Å). All diffraction patterns were recorded in a 2θ range of 10–70∘ at a scan speed of 2∘/min.

The N_2 adsorption-desorption isotherm data collected at 77.3 K using an automatic specific surface area/pore size distribution measurement apparatus (BELSORPmini II, BEL, Japan) was applied for evaluating Brunauer-Emmett-Teller (BET) surface area of the prepared samples. Pior to analysis, the samples were degassed at 473 K under 10^{-2} KPa for 2 h. The specific surface areas were calculated from the linear part of the BET plot where P/P_0 ratios are 0.05–0.25.

The content of Nb and Sr in the products were measured by an inductively coupled plasma-atomic emission spectrum (ICP-AES, IRIS Intrepid II XSP, Thermo Fisher Scientific Inc., USA).

The morphology of the synthesized $Sr_2Nb_2O_7$ samples was observed on a Zeiss Sigma scanning electron microscopy (SEM) at an acceleration voltage of 20 kV. The images of Ru nanocrystallites on the supports were recorded on a transmission electron microscope (TEM, JEM-2100, JEOL, Japan) at an acceleration voltage of 200 kV.

The acidity of the supports was evaluated by a temperature-programmed desorption (TPD) of ammonia technique carried on a laboratoray-made flow system connected to a gas chromatograph (GC) (GC-2020, Trustworthy, China) equipped with a thermal conductivity detector (TCD). Before the desorption test, the catalyst (100.0 mg) was pretreated in a N_2 (99.999%) flow of 15 mL min^{-1} at 773 K for 3 h, then cooled to 373 K, and finally exposed to a flow of 5 vol% NH_3 (balanced by 99.999% N_2) of 10 mL min^{-1} for 30 min, to allow the sample to reach adsorption equilibrium. The physically adsorbed ammonia molecules were then removed by purging the catalyst with a N_2 (99.999%) flow of 15 mL min^{-1} at 373 K for 30 min. In the desorption test, the catalyst was heated from 373 to 1073 K at 10 K min^{-1}, and the desorbed ammonia was carried in N_2 flow (15 mL min^{-1}) into the GC for quantification.

The density of exposed Ru atoms on the catalysts was determined by a H_2-pulse titration method performed at 323 K assuming chemisorption stoichiometry of H:Ru = 1:1 [25,54]. Before measurements, the catalyst (100.0 mg) was first reduced in a H_2 (99.999%) flow of 45 mL min^{-1} at 573 − 823 K for 3 h, and then kept at the same temperature under a Ar (99.999%) flow of 15 mL min^{-1} for 1 h to remove the adsorbed H atoms on reduced samples. After cooling to 323 K under