Ruthenium loaded 12CaO·7Al₂O₃ as a chlorine-tolerant catalyst for ammonia synthesis

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Abstract: Poisoning is the strong adsorption of reactants, products, or impurities on active sites, which limits the catalytic activity. For example, the activity of ruthenium (Ru) catalyst is significantly degraded by chlorine in ammonia synthesis. Here we demonstrate that 12CaO·7Al₂O₃ with subnanometer-sized cages prevents the poisoning of Ru catalyst by chlorine ions in ammonia synthesis. The catalytic activity of Ru/C12A7 is not influenced by chlorine ions even though the amount of chlorine in Ru/C12A7 is up to 2wt%. Such chlorine resistance of Ru/C12A7 is attributed to the unique anion-exchange properties of C12A7; i.e., the chlorine ions are preferentially trapped in the positively charged sub-nanometer-sized cages of C12A7 instead of OH⁻ ions under ammonia synthesis conditions.

Keywords: Chlorine-tolerance, C12A7, hydrothermal synthesis.

1. Introduction

Small amounts of impurities such as SO₄²⁻, Cl⁻, F⁻, and PO₄³⁻ are known to be poison of Ru catalysts for ammonia synthesis and decomposition.¹ The removal of chlorine ions from Ru catalyst should be performed at high temperature in the range from 450 to 700 °C,² which leads to the growth of Ru particles and decrease in the activity. As a result, chlorine-free Ru precursors provide catalysts with higher activity than the RuCl₃ precursor.³ Therefore, the development of highly efficient support materials that are not subject to chlorine poisoning is important for both fundamental research and the industrial application of RuCl₃.

Recently, we have reported a Ru-loaded 12CaO·7Al₂O₃ electride (C12A7⁺e⁻) that exhibits excellent catalytic activity for ammonia synthesis with lower activation energy.⁴,⁵ C12A7 is the component of alumina cement and composed of the ubiquitous elements (Ca, Al and O), i.e., it is one of the most cheapest material. In addition, the C12A7 has unique anion-exchange properties, where O²⁻ ions encapsulated as counter anions in the nanocages of C12A7 can be replaced by various anions such as e⁻, H⁺, OH⁻, F⁻, Cl⁻, and NH₂⁻. Inspired by this, we have determined that C12A7 prepared by a hydrothermal method (hereafter abbreviated as HT-C12A7) is also an excellent support for ammonia synthesis with high catalytic activity. Most importantly, HT-C12A7 support could prevent the chlorine poisoning of Ru when RuCl₃·xH₂O is used as the precursor.

2. Experimental

HT-C12A7 was synthesized by the calcination of Ca-Al mixed hydroxide produced hydrothermally.⁶ RuCl₃·xH₂O, was used as a precursor for preparing a Ru-loaded catalyst by the impregnation method. For comparison, chlorine-free Ru catalyst was prepared by the chemical vapor deposition (CVD) process using Ru₅(CO)₁₂ precursor.⁴

Ammonia synthesis reactions were conducted in a silica tube reactor supplied with an ultrapure mixture of N₂/H₂ = 1/3. The concentration of ammonia in the stream that left the catalyst bed (0.1 g catalyst) was monitored under steady-state conditions of temperature (400 °C), gas flow rate (60 mL·min⁻¹) and...
pressure (0.1 MPa). The produced ammonia was trapped in 5 mM sulfuric acid solution and the amount of NH$_4^+$ generated in the solution was determined using ion chromatography.

3. Results and discussion

The catalytic activity for ammonia synthesis over various supports loaded with 2 wt% Ru was investigated. As shown in Fig. 1, most Ru catalysts prepared using RuCl$_3$·xH$_2$O exhibit much lower activity than the chlorine-free catalysts prepared using Ru$_3$(CO)$_{12}$. In contrast, the catalytic activity of Ru(Cl)/HT-C12A7 remains almost the same as that of Ru(CO)/HT-C12A7 together with high sustainability.

Detailed characterizations were conducted to evaluate the catalytic performance of Ru(Cl)/HT-C12A7. HAADF-STEM measurement shows that the size of the Ru nanoparticles of Ru(Cl)/HT-C12A7 was distributed in the range of 1.0 to 4.0 nm and the mean particle size was estimated to be approximately 2 nm, which is the optimum size for ammonia synthesis. XRF, XPS and H$_2$-TPR measurements show that the chlorine content in Ru(Cl)/HT-C12A7 did not change during reduction and ammonia synthesis process. Moreover, the chlorine species were not located on the surface, but migrated into bulk to replace the extra-framework Cl$^-$ ions via the reaction of 2RuCl$_3$·xH$_2$O + 3H$_2$ + 6OH$^-$ (cage) → 2Ru + 6Cl$^-$ (cage) + (6+x)H$_2$O. This reaction process is schematically described in Fig. 2.

![Fig. 1](image1.png) Catalytic activities for ammonia synthesis over 2wt% Ru-loaded catalysts.

![Fig. 2](image2.png) Schematic diagram for the plausible formation of Ru(Cl)/HT-C12A7 catalyst and the ammonia formation process over the Ru catalyst.

4. Conclusions

In summary, Ru-loaded HT-C12A7 was demonstrated to function as an efficient chlorine-tolerant catalyst for ammonia synthesis, whereas conventional Ru catalysts exhibit low activity in the presence of chlorine on the catalyst surface. The unique chlorine resistance of Ru/HT-C12A7 is attributed to the anion exchange properties of C12A7; i.e., OH$^-$ ions in the cages of C12A7 can be exchanged for Cl$^-$ ions during the reduction treatment. These results demonstrate a new approach to avoid chlorine poisoning on the catalyst surface, and indicate that C12A7 can be applied as catalyst supports of various metal catalysts such as Pt, Pd, Cu, Ni, and so on through the use of inexpensive metal chlorides.

References