



Kinetic enhancement of ammonia decomposition as a chemical hydrogen carrier in palladium membrane reactor



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ARTICLE INFO

Article history:

Available online 29 March 2014

Keywords:

Ammonia
Decomposition
Hydrogen
Palladium
Hydrogen carrier

ABSTRACT

Decomposition of ammonia as a promising chemical hydrogen carrier is carried out at low temperatures using a ruthenium supported catalyst, where a highly efficient hydrogen recovery from ammonia is being desired. The equilibrium conversion is almost 100% in the range of 623–723 K but the decomposition remains in a low conversion, so that insufficient activity of present catalysts should be improved. This study attempts to prove that this kinetically limited decomposition can be enhanced in the palladium membrane reactor, while in most of membrane reactor applications the equilibrium limited reactions can be shifted to the product side by selective hydrogen separation.

The Langmuir–Hinshelwood types of rate equations, seven reaction models, for ammonia decomposition using a Ru/SiO₂ catalyst were derived and compared with experimental results. As the result, the combinative desorption of nitrogen atom was found to be the rate determining step in the range of 623–723 K. One dimensional model for a palladium membrane reactor could show that the kinetic enhancement differed considerably according to the reaction model (rate expression).

In the ammonia decomposition employing a membrane reactor with a 200 μm-thick palladium tube, 15% increase in conversion compared with the conventional packed reactor and 60% of the hydrogen recovery at 723 K could be obtained. Simulation showed that further enhancement would be achievable by using thinner palladium membrane.

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1. Introduction

Ammonia (NH₃) has been concerned as a liquid chemical hydrogen carrier together with cyclohexane, methylcyclohexane and methanol since 1990s, which are dealt in the Euro-Quebec Hydro-Hydrogen Project (EQHHP) carried out between EC and Canada [1] as well as in the World Energy Network (WE-NET) project (Japan) [2]. In these projects, it was planned that water was converted to hydrogen utilizing the hydropower overseas via electrolysis and then the hydrogen was shipped in the form of liquid hydrogen or chemical carriers. Ammonia as hydrogen carrier having a high hydrogen storage capacity of 17.6 wt% can be easily stored and transported in liquid because ammonia gas is liquefied by pressurizing up to 8.57 MPa at 20 °C. However, in order to use ammonia as a H₂ carrier, the research and development of the catalyst for the decomposition at lower temperatures and the separator for the purification of hydrogen from the mixture (H₂, N₂ and NH₃) is needed.

There is a long history in the catalyst development for ammonia synthesis since the finding by BASF in the early 19th century. Many improvements have been made for triiron tetraoxide (Fe₃O₄, magnetite) based catalyst. On the other hand, not so many decomposition catalysts of ammonia have been known, where supported metal catalyst like Ni/Al₂O₃ are commonly used in a comparatively higher temperatures above 500 °C. Recently, it was reported that 40 wt% Ni/La₂O₃ show a higher activity at 550 °C based on its high dispersion of nickel particles over the support [3]. Nevertheless, ruthenium catalyst is believed to be the most active particularly at lower temperatures below 500 °C. Even if active Ru supported catalysts are used, the decomposition rate seems to remain low in a low temperature range, while according to the decomposition equilibrium, as will be shown below, the equilibrium conversion close to 100% can be obtained in the range of 300–500 °C but below 300 °C the conversion drops significantly. More attention should be paid to endothermic heat that must be supplied from the outside of reactor, suggesting that the reactor performance will strongly depend on the heat transfer rate to the packed catalyst layer, so that the reactor with high heat transfer efficiency, even in membrane reactors [4], should be designed.

It is required to remove ammonia as much as possible in polymer fuel cell system since ammonia should be detrimental for the

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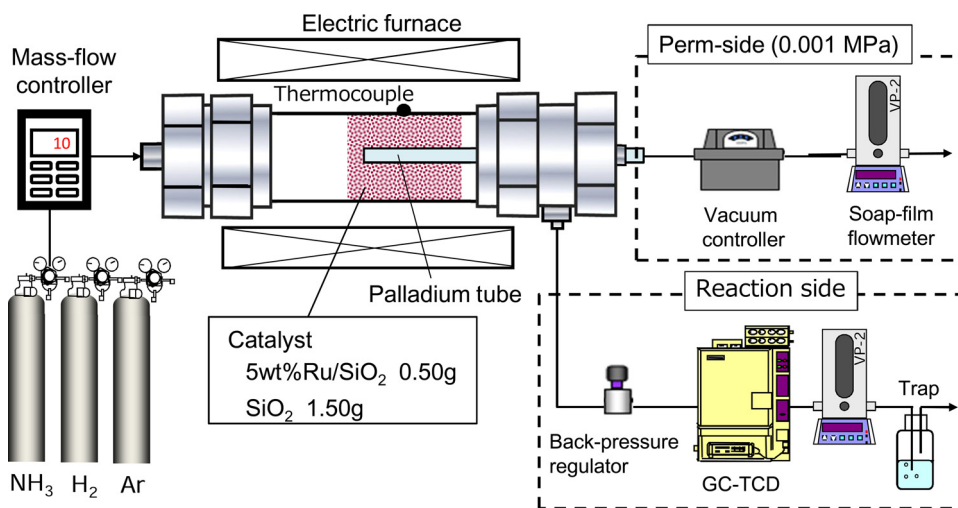


Fig. 1. Apparatus for ammonia decomposition in palladium membrane reactor.

anode catalyst and the acidic membrane of the fuel cell. Therefore establishing a low-temperature ammonia decomposition process is considered to have the highest-priority. By taking advantage of a simultaneous reaction and separation principle using membrane reactors, some attempts have been made not only to lower the decomposition temperature but also to enhance the conversion [5–10]. In the case that a nickel supported catalyst was used [5,7], 5–10% increase in conversion was observed in palladium membrane reactors at 500 °C [7], and 15–25% increase in the range of 427–477 °C [5]. Ruthenium catalyst, on the other hand, was devoted exclusively to the low temperature decomposition below 450 °C [6,8], where the decomposition rate was small. Improvements in the conversion were observed as 18–36% at 352 °C in a palladium membrane reactor [6] and 45% at 450 °C in a porous silica membrane reactor [8]. One-dimensional and two-dimensional simulation were also carried out to evaluate the reactor performance of the catalytic membrane reactor using porous silica [10] and the palladium membrane reactor [7] respectively. Those models employed the Temkin-Pyzhev model for the decomposition kinetics, which was originally postulated for describing the rate expression of ammonia synthesis. The Temkin-Pyzhev model may be applied well both for synthesis and decomposition of ammonia, but it will be preferred that a more precise rate formula is presented, in particular, at lower temperature, where the backward reaction term should be taken into account and incorporated into the formula because the equilibrium conversion drops with decreasing reaction temperature.

In this study, therefore, thermodynamic and kinetic analysis of ammonia decomposition in the low-temperature range is conducted using a supported Ru catalyst prepared by ourselves, which is known as a highly active one, whereby acquiring the fundamental information about the decomposition reaction and then postulating the rate formula in a low temperature range. Furthermore, the kinetic acceleration effect of the ammonia decomposition by removing hydrogen using a palladium membrane reactor will be examined and discussed.

2. Experimental

2.1. Ru/SiO₂ catalyst preparation

Ruthenium (Ru) supported on porous silica for low-temperature decomposition of ammonia was employed as catalyst in this study because Ru was known as more active metal species than other ones [3] and porous silica had a large specific surface area. 5 wt% Ru/SiO₂

catalyst was prepared by impregnating method as follows. Spherical silica particles were immersed in RuCl₃·nH₂O aqueous solution for 10 h, where the amount of Ru salt was added as to become 5 wt% Ru on the dry basis. Then water was all evaporated in an oven at 60 °C overnight. The catalyst precursor (RuCl₃/silica) was decomposed to remove chlorine at 450 °C in a nitrogen flow, followed by reduction in 30% H₂-Ar flow. Thus obtained granules being crushed and sieved; 0.71–1.0 mm of the particles were employed as catalyst.

2.2. Ammonia decomposition rate and kinetic analysis

The catalyst performance was examined using an integration type of catalyst-packed bed reactor, in which Ru/SiO₂ catalyst particles of 0.5 g mixed with 1.5 g of quartz particles (0.71–1.0 mm) were packed in a 1/2 inch stainless-steel tube reactor. The ammonia decomposition rate was measured with changing temperature (350–450 °C), pressure (1–2 bar) and feed rate (10–100 cm³/min).

Using the experimental data obtained, kinetic analysis based on the Langmuir-Hinshelwood mechanism was conducted to obtain the decomposition rate formula.

2.3. Palladium membrane reactor

Fig. 1 shows the experimental set-up with a palladium membrane tube (thickness: 200 μm, outer diameter: 3 mm, length: 65 mm). The pressure of inside of the palladium membrane tube was controlled at 0.001 MPa with a vacuum pump. The flow rate of hydrogen permeated was measured by a soap-film flow meter. On the reaction side, the total flow rate was measured with a soap-film flow meter and the composition of gas mixture was analyzed with a gas chromatograph (TCD detector).

3. Results and discussion

3.1. Ru/SiO₂ catalyst characterization

Fig. 2 shows the powder X-ray diffraction (XRD) pattern for the Ru/SiO₂ catalyst in comparison with those for the silica support and as prepared, confirming that the ruthenium supported silica catalyst for ammonia decomposition has been prepared. From the result for characterization of the catalyst in Table 1, it becomes clear that the catalyst has as large as surface area as 109 m²/g and 4.1 wt% of Ru loading, where the Ru particles are well dispersed with 15.3 nm of an average diameter.

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