Hydrogen Generation by Ammonia Cracking with Iron Metal-Rare Earth Oxide Composite Catalyst

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A series of fine powders of Fe–MOx (M = Ce, Al, Si, Sr, and Zr) composite were prepared by the conventional coprecipitation method from their nitrate solutions. The activity of hydrogen extraction from ammonia over these composite powders as ammonia cracking catalyst was characterized. The catalytic activity for ammonia decomposition observed on the composite powders of Fe–(Ce, Zr)O2 was high because of the electron donation to the iron metal from Ce3+ due to the reduction of CeO2 through the reaction. In addition to this effect, the additive (Ce, Zr)O2 solid solution supports worked as a solid acid to enhance the ammonia adsorption and reaction probability of Fe component. These were effective to generate hydrogen through the ammonia decomposition at relatively low temperature.

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1. Introduction

Hydrogen has been regarded as the new energy source because of its cleanliness, fast energy cycle, convenience of energy conversion, and so on. In the automobile industry, the polyelectrolyte membrane fuel cells car has been attractively developed. For the movable instruments, especially automobile, with on-board type, one of the main problems is of hydrogen supply. The ways of hydrogen supply to the fuel cell on the removable instruments are proposed by using liquid hydrogen directly, hydrogen storage materials, or reforming of chemical hydrides such as hydrocarbon. For the case of hydrocarbon reforming, there still remains the problem of the slow reaction rate between the metal surface and ammonia for ammonia decomposition. In our previous study, rare earth or transition metal-iron intermetallic compounds or Fe have little surface area due to the aggregation of powder particles during reactions, and there still remains the problem of the slow reaction rate between the metal surface and ammonia for ammonia decomposition. However, such intermetallic compounds or Fe have little surface area due to the aggregation of powder particles during reactions, and there still remains the problem of the slow reaction rate between the metal surface and ammonia for ammonia decomposition.

In this study, a series of composite powders between Fe and MOx (M = Ce, Al, Si, Sr, Zr) were prepared by coprecipitation method. The hybridization between Fe and MOx aims to suppress the aggregation of powders during reactions and to enhance the surface area, because the additive oxide is expected to retard the crystal growth of iron particle. Especially, CeO2 has been practically used as promoter of the automotive exhaust three-way catalyst for the ability of oxygen absorption and desorption due to its nonstoichiometry of oxygen. The catalytic activity of ammonia decomposition (hydrogen extraction from ammonia) was investigated from the viewpoint of the metal-support interaction and the solid acidity of additive oxides. Further, the nitrogen absorption-desorption properties on the Fe–MOx composite powders were also examined.

2. Experimental

The composite powder of Fe–CeO2 with a metal ratio of Fe/Ce = 5/1 was prepared by the coprecipitation method from their nitrate solution. The precipitant was collected by the centrifugal separator with washing by water five times, and then dried at 373 K for 86.4 ks. The powder after drying was finely pulverized and heated at 873 K in hydrogen gas flowing for 10.8 ks to reduce iron oxide. The other composite powders of Fe and MOx (M = Al, Si, Sr, Zr) were prepared by the same method mentioned above.

The composite powders prepared in this study were identified on the basis of the powder X-ray diffraction measurements by a MAC Science M18XHF-SHA diffractometer using CuKα radiation equipped with a curved graphite monochromator. The metal composition in the composite samples was quantified by ICP emission spectrometry. Spe-
cific surface area values for the composite powders were measured by a conventional (BET) nitrogen absorption method (Micrometrics Flow Sorb 2300II). The sample morphology was checked by the scanning electron microscope (HITACHI X-650).

Each composite powder was charged in a conventional fixed-bed quartz reaction tube, and the catalytic activity of composite powders for ammonia decomposition were evaluated by monitoring the integrated peak intensity ratio between NH$_3$ and its degradation product (N$_2$) measured on a gas chromatograph (Shimadzu GC-8A) in a temperature range of 373–973 K. The inlet gas composition of 5%NH$_3$ and He as a balance, or 100%NH$_3$ was used with a flow rate of 16.6 mm$^3$ s$^{-1}$ for 1 g of Fe. The nitrogen content after ammonia decomposition was determined by a nitrogen/oxygen analyzer (Horiba, EMGA 550).

3. Results and Discussions

Figure 1 shows the X-ray diffraction pattern of the Fe–CeO$_2$ composite powder. It was found that this composite material consisted of Fe and CeO$_2$. The full width at half maximum (FWHM) of the respective peaks for Fe and CeO$_2$ was very fine. The crystalline size of the sample was determined from the X-ray line broadening using Scherrer’s equation:

$$D = 0.9\lambda/(\cos \theta)$$

where $D$ is the average diameter, $\lambda$ the wave lengths of the X-rays, $\theta$ the diffraction angle, and $\beta$ the FWHM of the peak. The crystalline sizes of the Fe and CeO$_2$ were 21 and 13 nm, respectively. The surface area of this composite material was 25 m$^2$ g$^{-1}$. The sole Fe powder prepared by the precipitation method had the surface area of only 0.6 m$^2$ g$^{-1}$. It was also observed by SEM measurements that the sole Fe powder heavily aggregated and sintered than the Fe–CeO$_2$ one (see Fig. 2). The respective secondary particle sizes were sub-$\mu$m and 10 $\mu$m for the composite powder and the sole Fe one. These results suggest that the addition of CeO$_2$ retards the aggregation of iron powder to enhance the surface area, because the existence of CeO$_2$ in the grain boundary of composite particles prevented the crystal growth of iron.

The ammonia cracking (extraction of hydrogen from ammonia) activities on the Fe–CeO$_2$ composite and the sole Fe powders were evaluated by the gas chromatograph. The inlet gas used here was 100% of ammonia with the flow rate of 16.6 mm$^3$ s$^{-1}$ for 1 g of Fe. Figure 3 shows the ammonia decomposition properties for these samples. The ammonia decomposition on the composite powder started at 473 K and the conversion of 100% was attained at 823 K. Meanwhile, the starting temperature of ammonia decomposition for the sole iron powder was delayed to 573 K and the 100% of conversion was obtained at 923 K. The ammonia decomposition over the composite powder was superior to the sole Fe due to the enhancement of surface area. CeO$_2$ is well known as a promoter of the automotive exhaust three-way catalysts as mentioned above, in which CeO$_2$ can control the oxygen partial pressure by absorbing and desorbing oxygen owing to its nonstoichiometric behavior. For the case of present study, hydrogen generated through the ammonia decomposition reaction. At high temperature, the product hydrogen could reduce CeO$_2$ to form the oxygen deficient fluorite-type compound CeO$_{2-x}$. The resulting Ce$^{3+}$ can be the electron donor to Fe. It is considered that Fe promoted by CeO$_{2-x}$ can decompose ammonia more easily than the sole one owing to the strong metal-support interaction between Fe and CeO$_{2-x}$. In fact, the similar behavior was reported on the ammonia synthesis catalyst of Ru/CeO$_{2}$.

Next, the ammonia decomposition properties for other composite powders between Fe and metal oxides were characterized to elucidate the effect of oxide addition. Figure 4 shows the ammonia decomposition properties on the Fe–MO$_x$ (M = Ce, Al, Si, Sr) composite powders in the temperature range form 373 to 773 K. The gas composition used here was 5 vol%NH$_3$ and He as a balance with a flow rate of 16.6 mm$^3$ s$^{-1}$ for 1 g of Fe. The surface areas for the respective Fe–CeO$_2$, Al$_2$O$_3$, SiO$_2$, and SrO composite powders were 25, 41, 48, and 8 m$^2$ g$^{-1}$. The highest activity for ammonia decomposition was observed on the Fe–CeO$_2$ composite powder. The lowest activity for the Fe–SrO composite powder was obtained because its surface area was smallest in the samples prepared here. Generally, a high valent metal ion with small ion radius tends to be solid acid, whereas a low valent metal ion with large ion radius is liable to be solid base. For the case of this study, the SrO acts as strong solid base, and SiO$_2$ as strong solid acid. The CeO$_2$ and Al$_2$O$_3$ are amphiphilic ones. The reactant gas of ammonia is well known as a basic gas, so that this gas species adsorb on the surface of solid acid such as CeO$_2$, Al$_2$O$_3$, and SiO$_2$. It is found from the results of ammonia decomposition properties over the composite powders that the acidity for CeO$_2$ and Al$_2$O$_3$ is more favorable than that for SiO$_2$, because the ammonia adhered on the strong acid oxide like silica cannot spill over the surface of oxide and cannot remove the active point of Fe for ammonia decomposition. The difference of ammonia decomposition activity above 673 K between Fe–CeO$_2$ and Fe–Al$_2$O$_3$ bears out the strong metal-support interaction. Therefore, Al$_2$O$_3$ dose not vary its valence in the hydrogen atmosphere even at high temperature, meanwhile CeO$_2$ can readily reduce by...
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4.3 μm

15 μm

Fig. 2 Scanning electron microscope photographs of a) the Fe–CeO$_2$ composite and b) the sole iron metal powders prepared by the precipitation method.

![Fig. 2](image)

The following important roles for the ammonia decomposition reaction:

1. CeO$_2$ as solid acid adsorbs ammonia suitably to increase the reaction probability through the spill over of ammonia to the reaction point of Fe.
2. The trivalent cerium metal ion in CeO$_{2-x}$ promotes Fe by electron donation from Ce$^{3+}$ to Fe.
3. CeO$_2$ in the grain boundary of composite particles prevents the powder aggregation to enhance the reaction area.

To accelerate the electron donation from CeO$_2$ to Fe, the composite powders between Fe–(Ce,Zr)O$_2$ (Fe:Ce:Zr = 30:1:5 and 10:1:1 in molar ratio) were prepared. The addition of ZrO$_2$ into CeO$_2$ improves the catalytic property since oxygen removes from the lattice more easily than that from the sole CeO$_2$ due to the formation of pyrochlore-type structure Ce$_2$Zr$_2$O$_{7+x}$. It was confirmed from the XRD measurements that both composite samples (Fe:Ce:Zr = 30:1:5 and 10:1:1 in molar ratio) were consisted of the iron metal and cerium zirconium oxide solid solutions and no super lattice reflection derived from pyrochlore structure was detected.

Fig. 3 Ammonia decomposition properties over the Fe–CeO$_2$ composite and the sole Fe powders.

![Fig. 3](image)

Fig. 4 Ammonia decomposition properties over the Fe–MO$_x$ (M = Ce, Al, Si, Sr) composite powders.

![Fig. 4](image)
Fe–(Ce, Zr)O$_2$ composite with the ratio of Ce/Zr was higher than that on the Fe–ZrO$_2$ composite powder (see Fig. 5).

To distinguish the solid acidity between them, the temperature programmed desorption (TPD) for both samples was conducted by gas chromatograph. We let ammonia adsorb the surface of samples at room temperature in a flow of ammonia gas and then the samples was slowly heated (heating rate of 16.6 mK·s$^{-1}$) in helium gas flow to detect ammonia desorbed from the samples by gas chromatograph. Figure 6 shows the TPD profiles for the Fe–(Ce, Zr)O$_2$ composite powders with the ratio of Ce/Zr = 1/5 and 1/0. The composite with the ratio of Ce/Zr = 1/0 desorbed ammonia at 383 and 463 K, whereas the composite with the ratio of Ce/Zr = 1/5 desorbed ammonia at higher temperature than the former. As obviously seen from the desorption temperature of ammonia and the amount of ammonia desorption, the Fe–(Ce, Zr)O$_2$ composite with the ratio of Ce/Zr = 1/5 was stronger acid than that with the ratio of Ce/Zr = 1/0. The size of Zr$^{4+}$ with coordination number VIII (84 pm) is smaller than that of Ce$^{4+}$ (97 pm), resulting that ZrO$_2$ is stronger acid than CeO$_2$. From these results, it is concluded that the degree of effect for additive oxide to the ammonia decomposition activity on the Fe–MO$_x$ composite powder is pre-dominant as following, the enhancement of surface area > the solid acidity for ammonia adsorption > electron donation from oxide to Fe.

Figure 7 shows the Arrhenius plot for the ammonia decomposition rate ($\mu$mol·s$^{-1}$·g$^{-1}$) observed on the Fe–(Ce, Zr)O$_2$ composite powders with the ratio of Ce/Zr = 1/5. The ammonia decomposition rate was determined from the peak area of gas chromatograph profiles for the residual ammonia gas during reaction. The activation energy was evaluated to be 21 kJ/mol. This value is considerably lower than the Ru/CeO$_2$/Y-zeorite catalyst reported previously (67 kJ/mol). The ammonia decomposition rate in the Fe–(Ce, Zr)O$_2$ composite powder at 623 K is $4.8 \times 10^{-1} \mu$mol·s$^{-1}$·g$^{-1}$ whereas $5 \times 10^{-2} \mu$mol·s$^{-1}$·g$^{-1}$ for Ru/CeO$_2$/Y-zeorite catalyst at the same temperature. The reaction rate over composite powder is about 10 times higher than that over the Ru/CeO$_2$/Y-zeorite catalyst. (Ce, Zr)O$_2$ solid solution added into Fe adsorbs ammonia suitably and the ammonia spills over the surface of the oxide, so that this composite powder can crack ammonia at lower temperature around 673 K than the usual supported catalyst in accordance with the low activation energy.

For the Fe–(Ce, Zr)O$_2$ composite powder with the ratio of Fe/Ce/Zr = 30/1/5 which shows the highest catalytic activity, the nitrogen absorption properties was characterized by heating in pure ammonia flow (flow rate: 16.6 mm$^3$·s$^{-1}$ for 1 g of Fe) at the temperature of 100% conversion for ammonia decomposition (698 K) for 3.6 ks. The nitrogen content after the ammonia decomposition for this composite was determined to be FeN$_{0.08}$(Ce, Zr)O$_2$ from nitrogen analysis for the sample. On the other hand, the nitrogen concentration in the Fe–CeO$_2$ (Fe/Ce = 5/1) composite powder after the ammonia decomposition at 823 K (the temperature of 100% conversion) under the same reaction conditions was only FeN$_{0.003}$. The nitrogen absorption reactions on these samples proceed via the ammonia decomposition. The reaction equilibrium of ammonia decomposition is indicated:

$$3/2\text{H}_2 + \text{N}_2 \rightleftharpoons \text{NH}_3$$

$$\Delta G^0 = -98450 + 42.3T$$

$\Delta G^0$ is the partial Gibbs free energy, $T$ the absolute temperature. The activity of nitrogen atom while nitriding in NH$_3$.
atmosphere can be calculated from eq. (3) as
\[
an_N = \frac{P_{NH_3}}{P_{H_2}} \frac{3}{2} \exp(\Delta G^0 / RT)
\]  
(4)

\( R \) is the gas constant. From eq. (4), increasing reaction temperature and decreasing hydrogen concentration result in the increase of the activity of nitrogen atom. The ammonia decomposition at higher temperature is favorable for nitriding reaction due to the activity of nitrogen atom according to the term \( \exp(\Delta G^0 / RT) \) in above eq. (4) with the constant hydrogen concentration. However, nitrogen content after ammonia decomposition of the Fe–(Ce, Zr)O_2 (Fe/Ce/Zr = 30/1/5) composite powder was higher than that of Fe–CeO_2 (Fe/Ce = 5/1). The temperatures for 100% of ammonia decomposition were 698 K and 823 K for the respective Fe–(Ce, Zr)O_2 and Fe–CeO_2 composite powders. From these results, it is considered that the iron nitride was readily reduced by the product hydrogen gas at high temperature of 823 K and that the nitrogen absorption reaction for Fe and the ammonia decomposition reaction on Fe are competitive. The ammonia decomposition reaction over Fe is consequently assumed to be following reaction equations:

\[
Fe + NH_3 \rightleftharpoons xFeN_y + (1 - x)/2N_2 + 3(1 - x)/2H_2 
\]  
at low temp.  
(5)

\[
FeN_y + H_2 \rightarrow Fe + y/2N_2 + H_2 
\]  
at high temp.  
(6)

From above reaction equations, the ammonia decomposition at lower temperature allows the Fe–(Ce, Zr)O_2 composite powder to absorb nitrogen up to FeN_{0.08}. This nitrogen content is comparable that Fe trapped 37% of the nitrogen atom to the total amount of nitrogen atom supplied from ammonia during decomposition reaction. The resulting hydrogen concentration in the product gas passed from the Fe–(Ce, Zr)O_2 catalyst is higher than that on the usual supported Ru catalyst since about 40% of nitrogen atom was stored in the iron metal as iron nitride, namely the hydrogen concentration in the product gas for the present composite catalyst is 83% and 75% for the usual catalyst.

The sample after ammonia decomposition FeN_{0.08}–(Ce, Zr)O_2 was heated in pure hydrogen flow at 573 K and the product nitrogen species were monitored by gas chromatograph in the course of reaction. No molecular nitrogen could be detected and only ammonia generation was observed by gas chromatograph, and the nitrogen content in the composite powder after reaction was zero from nitrogen analysis. These results are ascribable to the high reactivity of atomic nitrogen liberated form the metal nitride and indicate that one can regenerate ammonia readily by using the present catalyst system. Figure 8 shows a schematic model for hydrogen generation method by cracking ammonia on the Fe–(Ce, Zr)O_2 catalyst as proposed in this study.

4. Conclusions

The fine composite powders between Fe and some oxides were prepared by coprecipitation method. In a series of composite powders, the Fe–(Ce, Zr)O_2 composite powder with the ratio of Ce/Zr = 1/5 could catalytically decompose ammonia at low temperature to generate hydrogen and nitrogen because of its high surface area and the additive oxide acting as ammonia adsorbent for its solid acidity. About 40% of the nitrogen atom generated through the ammonia decomposition was stored in Fe as metal nitride, so that the resulting hydrogen concentration after ammonia decomposition by the present catalyst was higher than that by the usual supported catalyst due to preventing the hydrogen dilution by nitrogen. The nitrogen captured in the iron metal could easily be regenerated at about 100% of yield as ammonia by the subsequent reaction with hydrogen. Consequently, one can construct a new hydrogen supplying system in which ammonia is used as a hydrogen source and 40% of ammonia wasted is easily regenerated by using the above composite material.

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REFERENCES