Low apparent activation energy of ammonia synthesis over Ru catalyst supported by hydrogen storage material

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Abstract

Ruthenium is an excellent catalyst for ammonia synthesis and recently shows quite high activity when supported on materials with high electron-donating and hydrogen-absorbing properties. The high activity is generally considered to originate from the two effects: the electron-donating property of the support, which reduces its apparent activation energy ($^{app}E_a$) to half of pure Ru's $^{app}E_a$, and the hydrogen-absorbing property, which increases the active site by suppressing hydrogen poisoning, a drawback of ruthenium catalysts. Here, we investigated the catalytic performance of ruthenium loaded on $TiMn_2$, a hydrogen storage material without electron-donating property to ruthenium. Ruthenium on $TiMn_2$ showed the $^{app}E_a$ reduced by half despite the lack of electron-donating property. It is plausible that the decreased $^{app}E_a$ is due to the elimination of hydrogen over Ru by $TiMn_2$. The hydrogen storage capacity is also an essential factor in discussing the $^{app}E_a$.

Introduction

Ammonia is indispensable for human beings as an artificial fertilizer and is one of the most produced chemicals. The amount of ammonia production is more than 182 million tonnes in 2019 and is expected to increase by 4% during the next four years[1]. Ammonia has been industrially synthesized at 400−500 °C and 10−30 MPa using an Fe-based catalyst for over 100 years[2,3]. However, these severe conditions require a large, robust, and expensive plant. Therefore, the business model is the synthesis at a large scale and distribution ammonia to each area. It results in scarce fertilizer in many countries that do not have sufficient transport infrastructures, such as Zambia, Tanzania, Ghana, and Nigeria[4,5]. The milder reaction condition would realize ammonia synthesis at a small scale and supply ammonia to local agricultural lands, making the fertilizer cost affordable, increasing food production, and reducing starvation.

Ru has been known to synthesize ammonia with high activity when the electropositive metal is added, although the fatal drawback of Ru is hydrogen poisoning[3,6-9]. It was recently reported that Ru supported on oxyhydride- and oxynitride-based materials are highly reactive even under mild conditions[10-14]. For example, Ru supported on electride $[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$ (Ru/C12A7:e$^-$) shows

high reactivity,[15] where C12A7:e⁻ has two characteristic properties: one is the hydrogen storage capacity, which suppresses hydrogen poisoning and increases the number of active Ru sites. The other is the high electron-donating property, which reduces the apparent activation energy ($^{app}E_a$) to half of Ru bulk's $^{app}E_a$ and enhances the reaction rate. There are many reports similar to this, and electron-donating properties are generally considered an important factor in lowering $^{app}E_a$.

Meanwhile, the coverage of hydrogen and nitrogen has a dependency on temperature [16]. For example, with the adsorption-desorption reaction of species A given by

$$A + * \rightarrow A^* \tag{1}$$

Where * means an unoccupied site. We can associate the reaction fraction, $\theta_A/p_A\theta_*$, where θ_A is a fractional coverage of the adsorbate A on the surface, p_A is a pressure of gas A, and a probability that a site is unoccupied, θ_*. At equilibrium, we have

$$\left.\frac{\theta_A}{p_A\theta_*}\right|_{Eq} = K_{ads} = e^{-\frac{\Delta G_{ads}}{k_B T}} \tag{2}$$

where K_{ads} is an equilibrium constant of the adsorption, ΔG_{ads} is the change of Gibbs free energy by the adsorption of A, k_B is Boltzmann constant, and T is temperature. Then, the coverage depends on temperature and directly determines reaction rates. In the case that the rate-determining step is the reaction, $A^* + B^* \rightarrow AB^{*} + ^*$, a reaction rate, r_{AB}, is described as follows

$$r_{AB} = k_{AB}\theta_A\theta_B \tag{3}$$

where k_{AB} is a reaction constant for the reaction. Therefore, $^{app}E_a$, estimated by the temperature dependence of k_{AB}, is influenced by the coverage through the equation below:

$$^{app}E_a = -\frac{\partial(ln r_{AB})}{\partial\left(1/k_B T\right)} = -\frac{\partial(ln k_{AB} + ln\theta_A + ln\theta_B)}{\partial\left(1/k_B T\right)} = E_a - \frac{\partial(ln\theta_A + ln\theta_B)}{\partial\left(1/k_B T\right)} \tag{4}$$

As well as the assumed reaction, the hydrogen storage ability itself can change θ_H, increasing the coverage of other species and changing the $^{app}E_a$. However, the influence of hydrogen storage ability on $^{app}E_a$ has not been discussed for the recent catalysts.

In this paper, we prepared Ru on hydrogen storage material, TiMn₂. The work functions of Ti, Mn, and Ru are 4.3, 4.1, and 4.7 eV, respectively, which are or similar values and hardly donates an electron to Ru from TiMn₂. Thus, the function of only hydrogen storage ability on $^{app}E_a$ can be estimated. The 1−10wt% of Ru on TiMn₂ catalysts were prepared to demonstrate the influence of the Ru/TiMn₂ ratio. For comparisons, Ru bulk and Ru dispersed on carbon and MgO were investigated. To discuss the effect of electron donation to Ru on $^{app}E_a$, K was added as an electropositive metal.

Experimental methods

The preparation of catalysts The powder of TiMn₂ (Mn:~51%, Ti:~29%, V:~14%, Fe, Cr, Zr: ~6%, Sigma-Aldrich Co. LLC) was prepared by only hand milling with an alumina mortar and pestle. The work function of V, Fe, Cr, and Zr are 4.3, 4.5, 4.5, and 4.1 eV, respectively, and are considered not to

donate electrons to Ru. Ruthenium (III) acetylacetonate (Ru(acac)$_3$, Strem Chemicals, Inc) was dissolved in pentane. The TiMn$_2$ powder was dispersed in the solution and evaporated in a vacuum at elevated temperature with staring. The amount of loaded Ru was 1, 3, 5 10 wt% (Xwt%Ru/TiMn$_2$ when Xwt% of Ru was loaded). 1wt% Ru on MgO (99.9%, Kojundo Chemical Lab. Co., Ltd., 1wt%Ru/MgO) and 10 wt% Ru on carbon (99.9%, Kojundo Chemical Lab. Co., Ltd., 10wt%Ru/C) were prepared in the same way using Ru(acac)$_3$, where MgO and C were employed not to have electron donation and hydrogen storage properties. When K was added to 10wt%Ru/TiMn$_2$ or Ru, 10wt%Ru/TiMn$_2$ or (Ru(acac)$_3$) were dispersed or dissolved in N,N-dimethylformamide, respectively. KNO$_3$ (99.9%, Fujifilm Wako Pure Chemical Corporation) was added to each solution and evaporated in a vacuum at elevated temperature with staring, adjusting the ratio of Ru and K to 1:1 (10wt%Ru+K/TiMn$_2$ or Ru+K, respectively). K was added to the TiMn$_2$ powder, in the same way, adjusting the K and TiMn$_2$ ratio to the same with 10wt%Ru+K/TiMn$_2$. For a comparison, Ru powder (Ru bulk, $\leq$ 0.3μm (TRU-300), Tokuriki-Honten CO. LTD) was tested as purchased. The temperature range of $^{app}E_a$ measurement was 340−420 °C.

The characterization of properties The Brunauer−Emmett−Teller (BET) specific surface areas of the samples were determined from nitrogen adsorption−desorption isotherms measured at −196 °C using an automatic gas-adsorption instrument: (Gemini VII 2390, Micromeritics)

The characterization of catalytic activity The reactivities of the catalysts were demonstrated in a stainless-steel flow set-up. Supplied gas is an extrapure (99.9999%) mixture of H$_2$, N$_2$, and Ar. Before the reactions, all the catalysts were treated in a stream of N$_2$:H$_2$ =1:3 under 0.1 MPa, raising reaction temperature by 200 °C h^{-1}. The concentration of ammonia in the stream that left the catalyst bed was monitored under steady-state temperature conditions. The ammonia produced was trapped in 5 mM sulfuric acid solution. The amount of NH$_4^+$ in the solution was determined using an ion chromatograph (Eco IC, Metrohm) equipped with a conductivity detector.

Kinetic Analysis The reaction orders of N$_2$(α), H$_2$(β), and NH$_3$(γ) was determined by changing the flow ratio of H$_2$, N$_2$, and Ar in the similar way with previous publication[17] with the equation below.

$$r = kP_{N_2}{}^{\alpha}P_{H_2}{}^{\beta}P_{NH_3}{}^{\gamma} \tag{5}$$

The analysis was conducted at 0.1 MPa and 400 °C.

Results

The catalytic activities for ammonia synthesis were summarized in Table 1. The 1−10wt%Ru/TiMn$_2$ showed the reduced $^{app}E_a$, mostly the half of Ru bulk's $^{app}E_a$. TiMn$_2$ without Ru exhibited negligible activity. In addition, 1wt%Ru/MgO and 10wt%Ru/C did not possess such low $^{app}E_a$. Hence, the combination of TiMn$_2$ and Ru causes the low $^{app}E_a$. Interestingly, the less amount of Ru loading on TiMn$_2$ is, the less $^{app}E_a$ were detected. However, the reaction rate is high when the Ru amount is high. It should be reasonable that a low $^{app}E_a$ does not result in a high reaction rate.

Table 1 Performance of catalysts for ammonia synthesis

Catalyst	NH$_3$ synthesis rate[a] (μmol g^{-1} h^{-1})	BET surface area (m^2 g^{-1})	$^{app}E_a$ (kJ mol^{-1})
TiMn$_2$	Negligible	0.41	-
1wt%Ru/TiMn$_2$	25	1.64	44
3wt%Ru/TiMn$_2$	86	0.85	56
5wt%Ru/TiMn$_2$	130	0.73	68
10wt%Ru/TiMn$_2$	141	0.52	67
Ru bulk	564	18.02	128[b]
1wt%Ru/MgO	156	5.22	87
10wt%Ru/C	64	11.84	104
TiMn$_2$+K	21	0.18	78
10wt%Ru+K/TiMn$_2$	635	6.71	52
Ru+K	3828	4.35	80

[a]The catalytic activities at 0.1 MPa and 400 °C with N$_2$:H$_2$ =1:3 under 0.1 MPa. [b]The temperature range of measurement is 372−435 °C.

When K was added to TiMn$_2$, Ru, and Ru/TiMn$_2$ catalysts, the activities of all catalysts were enhanced. TiMn$_2$+K showed some reactivity, which is still negligible though and thus no need to be considered. For 10wt%Ru+K/TiMn$_2$, the improved activity is attributed to the enlarged surface area, although the $^{app}E_a$ decreased. Ru+K showed the highest activity among the catalysts tested in this paper even though $^{app}E_a$ is not the lowest. It is the same conclusion as the previous paragraph.

The reaction orders of 1wt%Ru/TiMn$_2$ and Ru+K were measured (Table 2). As we expected, the reaction order for hydrogen over 1wt%Ru/TiMn$_2$ was positive, which means TiMn$_2$ successfully suppressed hydrogen poisoning. In addition, Ru+K also showed a positive reaction order for hydrogen. It means K also has a role in disturbing hydrogen poisoning.

Table 2 The reaction orders (see Eq. (5))

Catalyst	Reaction orders		
	α	β	γ
1wt%Ru/TiMn$_2$	0.95	1.19	-0.80
Ru+K	1.26	1.04	-0.55

Discussion

Eq. (2) indicates that θ_H decreases when the temperature is elevated, eliminating hydrogen poisoning and increasing θ_N. The large θ_N enhances r as well as Eq. (3), which leads to a high dependency of r on temperature. The reaction order of 1wt%Ru/TiMn$_2$ was positive, and thus the hydrogen poisoning

over the Ru supported by TiMn$_2$ was overcome. It can be interpreted that the θ_H was reduced not by temperature but by the TiMn$_2$. Then, the dependence on temperature of r was mitigated, which can result in low $^{app}E_a$. In fact, the $^{app}E_a$s of 1−10wtRu/TiMn$_2$ catalysts decreased to almost half of the Ru bulk's $^{app}E_a$. The lower $^{app}E_a$ can be explained by the hydrogen storage ability of support materials.

The density functional theory (DFT) calculation indicates the E_a for ammonia synthesis over Ru without electron donation is around 100 kJ/mol, which is higher than the $^{app}E_a$s of the tested catalysts. It is possible that over Ru supported on hydrogen storage materials, θ_* is dominant rather than θ_H and θ_N. Therefore, the raised temperature induces both lower θ_H and θ_N, which slowdowns r and mitigates the temperature dependency of r. It can decrease the $^{app}E_a$ than the actual E_a.

The tendency of the $^{app}E_a$ among 1−10wt%Ru/TiMn$_2$ is also explained by the role of the hydrogen storage ability. In the case of the large amount of Ru on TiMn$_2$, the amount of hydrogen stored in TiMn$_2$ per Ru is less, and thus the hydrogen poisoning is not fully suppressed. Therefore, the large amount of Ru on TiMn$_2$ results in the relatively high $^{app}E_a$. However, the reaction rate is faster on the catalysts with a larger Ru-loading amount but a smaller surface area. Besides, Ru+K shows the highest activity among the tested catalysts even though its $^{app}E_a$ is not smaller than 1−10wt%Ru/TiMn$_2$. We should conclude that the discussion on $^{app}E_a$ is not suitable to associate with the reaction rate directly.

The hydrogen poisoning over Ru+K was suppressed, as shown by the reaction order of hydrogen over Ru+K. In addition, the 10wt%Ru+K/TiMn$_2$ exhibits the less $^{app}E_a$ than that of 10wt%Ru/TiMn$_2$. Then, the reduced $^{app}E_a$ of Ru+K can be explained by electron donation from K and storing hydrogen. It would be concluded that both electro-donating and hydrogen storage properties have an enormous influence on an $^{app}E_a$. According to the XANES spectrum in the previous report[18], the K-edge of Ru on C12A7:e$^-$ did not shift to lower energy, which means electrons were not donated to Ru from C12A7:e$^-$ although the N≡N bonding on Ru/C12A7:e$^-$ is weakened at −170°C under 5 kPa of N$_2$ [15]. The $^{app}E_a$ of Ru/C12A7:e$^-$ is around 40 kJ/mol at the lowest, similar to the $^{app}E_a$ of 1wt%Ru/TiMn$_2$. Recent progress of catalysts associated with much-reduced $^{app}E_a$ of ammonia synthesis might be explained by the influence of the hydrogen storage ability.

Conclusion

The catalytic performance of ammonia synthesis over Ru supported by hydrogen storage alloy, TiMn$_2$, was examined to estimate the influence of only hydrogen storage property on $^{app}E_a$. The positive reaction orders of hydrogen on Ru/TiMn$_2$ indicate that the hydrogen poisoning over the Ru on TiMn$_2$ is suppressed. Ru/TiMn$_2$ catalysts exhibit low $^{app}E_a$, almost half of Ru bulk's $^{app}E_a$. The decreased θ_{HS} over Ru derived from hydrogen storage properties are considered to reduce their $^{app}E_a$. Besides, even if the $^{app}E_a$ is not low, the reaction rate can be high according to the results of 1−10wt%Ru/TiMn$_2$ and

Ru+K. Hydrogen storage properties should be included to discuss reduced $^{app}E_a$, which would give the correct direction to design a new catalyst of ammonia synthesis.

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