Rate-determining Step Examination of Ammonia Synthesis over Electride-supported Ru Catalysts by Kinetics Analysis

Yasukazu Kobayashi, Masaaki Kitano, Shigeki Kawamura, Toshiharu Yokoyama, Hideo Hosono*
Materials Research Center for Element Strategy, Tokyo Institute of Technology, 226-8503, Japan
**Corresponding author: 045-924-5339, hosono@msl.titech.ac.jp*

Abstract: Using kinetic analysis, we demonstrate that the rate-determining step (RDS) for ammonia synthesis over Ru catalysts supported by electrides, such as $[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$ and $Ca_2N:e^-$, is not the N_2 dissociation step but subsequent surface reactions of N and H adatoms. In this case, conventional modified Temkin rate equations derived with the RDS assumption of N_2 dissociation step can be not used any more to describe the kinetics, and instead of this, Langmuir-Hinshelwood model-based rate equations should be used.

Keywords: Rate-determining step, Ammonia synthesis, Electride.

1. Introduction

The RDS of catalytic ammonia synthesis has been acknowledged of N_2 dissociation adsorption step for a long time, due to the large bonding energy of N_2 (945 kJ/mol). This concept is successfully applied in the Temkin rate equation describing the kinetics of industrial-scale ammonia synthesis [1].

Recently, our research group reported that Ru catalysts supported by electrides, such as $[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$ (C12A7:e$^-$) and $Ca_2N:e^-$, exhibit much higher activities than conventional Ru catalysts [2]. Due to their low intrinsic work function, these electrides are unique in their ability to donate anionic electrons confined within them while maintaining chemical and thermal stability. In addition, surface hydrogen can be reversibly stored as hydride ions (H^-) in the electride cages, so that hydrogen poisoning reported as a serious obstacle with Ru catalysts is not observed for Ru/electride catalysts at elevated pressures. These results suggested that ammonia synthesis over Ru/electride catalysts proceeded through a different mechanism from the conventionally accepted mechanism. In this work, kinetic analysis was performed to examine the RDS of ammonia synthesis over electride-supported Ru catalysts [3].

2. Experimental

Experimental rates of ammonia synthesis were acquired with Ru catalysts supported on electrides (C12A7:e$^-$, $Ca_2N:e^-$) and non-electrides (C12A7:O^{2-}, $CaO-Al_2O_3$, MgO, CaNH). Ammonia synthesis was conducted in a silica glass reactor under flow of a $N_2/H_2/Ar$ mixture at 0.1 MPa. The reaction gas composition was varied at a constant temperature to acquire a variety of reaction rates for comparison with model equations. The reaction temperature was selected to ensure that the obtained rates were sufficiently distant from the equilibrium values so that the influence of the reverse reaction was negligible.

Step 1	$H_2(g) \rightarrow H_2(ad)$
Step 2	$N_2(g) \rightarrow N_2(ad)$
Step 3	$H_2(ad) \rightarrow 2H(ad)$
Step 4	$N_2(ad) \rightarrow 2N(ad)$
Step 5	$N(ad) + H(ad) \rightarrow NH(ad)$
Step 6	$NH(ad) + H(ad) \rightarrow NH_2(ad)$
Step 7	$NH_2(ad) + H(ad) \rightarrow NH_3(ad)$
Step 8	$NH_3(ad) \rightarrow NH_3(g)$

The RDS for ammonia synthesis with each catalyst was examined by fitting the model rate equations to a set of obtained reaction rates. The rate equations were expressed by the Langmuir-Hinshelwood mechanism, and it was assumed that the catalytic ammonia synthesis reaction can be divided into 8 elementary steps and that any of steps 4-7 controls the overall rate of reaction due to the large E_a barrier.

For example, in the case that step 4 is the RDS, the other steps quickly reach equilibrium during the reaction and the overall rate of reaction (*r*) is approximated to the rate of step 4. When the partial pressure of ammonia at the outlet is sufficiently low enough that the influences of the reverse reaction of step 4 and

NH_3 adsorption can be ignored, the modelled rate equation can be expressed as a function of only the partial pressures of H_2 (P_{H2}) and N_2 (P_{N2}):

$$r = \frac{\overrightarrow{k_4} K_2 P_{N2}}{\left(1 + K_1 P_{H2} + K_2 P_{N2} + \sqrt{K_1 K_3 P_{H2}}\right)^2}$$

where $\overrightarrow{k_4}$ is the rate constant of the forward reaction in step 4 and K_i is the equilibrium constant in step i. In the same manner, rate equations that correspond to steps 5-7 as the RDS are given, and finally derived equations were separately fitted into the sets of experimental data using a least squares method and evaluated to determine which equations best described the data.

3. Results and discussion

Table 1 summarizes the R^2 values obtained by fitting each model equation of step 4-7 to a set of experimental data over various Ru catalysts supported by electrides or non-electrides, and also activation energies (E_a) of ammonia synthesis for reference. As the results, the model rates derived from the RDS assumptions of steps 5-7 give better fits to the experimental rates than that for step 4 for Ru/C12A7:e^- and Ru/Ca_2N:e^-, whereas, for the non-electride-supported catalysts of Ru-Cs/MgO and Ru/C12A7:O^{2-}, Ru/CaO-Al_2O_3, Ru/MgO, and Ru/CaNH, the best fits to the model rates were derived from the conventional RDS of step 4. These results kinetically indicated that the RDS for ammonia synthesis over Ru catalysts supported by electrides is not the N_2 dissociation step but subsequent surface reactions of N and H adatoms.

Table 1. R^2 values obtained from best-fit results and E_a values of ammonia synthesis.

Sample	Coefficient of determination, R^2 [-]				E_a [kJ/mol]
	Step 4	Step 5	Step 6	Step 7	
Ru/C12A7:e^-	0.514	0.873	0.977	0.981	51
Ru/C12A7:O^{2-}	0.967	0.796	0.752	0.797	104
Ru/CaO-Al_2O_3	0.986	0.818	0.808	0.807	118
Ru/MgO	0.989	0.846	0.765	0.812	80
Ru-Cs/MgO	0.994	0.850	0.850	0.844	120
Ru/Ca_2N:e^-	0.548	0.886	0.955	0.954	60
Ru/CaNH	0.838	0.593	0.596	0.569	110

4. Conclusions

We have previously reported that electride-supported Ru catalysts exhibited higher catalytic activity for ammonia synthesis with a lower E_a as listed on Table 1. Therefore, taking into consideration the quite low E_a values observed only in electride-supported catalysts with the distinctive features of electride materials, we conclude that adsorbed N_2 molecules dissociate more smoothly on the catalyst surface by electron donation from the electrides, while any of the subsequent steps can be the RDS for surface reactions of dissociated N and H. In this case, conventional rate equations derived from the Temkin model no longer describe the kinetics of ammonia synthesis over electride-supported Ru catalysts. Therefore, a new rate equation based on the newly determined RDS should be developed for industrial applications.

References

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