

# Enhanced catalytic activity of ammonia synthesis over Ru/CaH<sub>2</sub> by addition of oxygen

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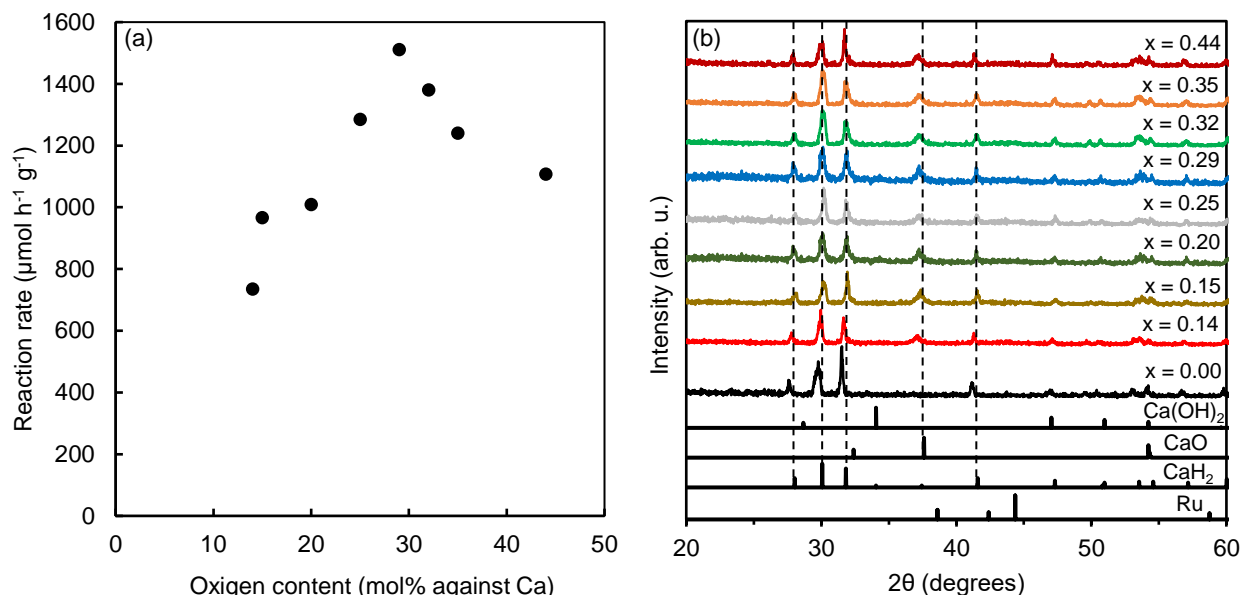
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We investigated the relationship between the catalytic activity of ammonia synthesis and the oxygen content of catalysts using Ru/CaH<sub>2-2x</sub>O<sub>x</sub> (x = 0.00–0.44). Ru/CaH<sub>2-2x</sub>O<sub>x</sub> were enhanced as the oxygen contents increased until x = 0.29 and decreased when x was over the threshold. The apparent activation energy also decreased up to x = 0.29. Based on the kinetic analysis, oxygen suppressed the excessive electron-donation from CaH<sub>2-x</sub>(e<sup>-</sup>)<sub>x</sub> to Ru and mitigated the hydrogen poisoning over Ru.

Ammonia is a promising renewable energy carrier because of its high energy density [1–4]. The reaction condition for the ammonia synthesis in the industry is severe, 400–500 °C and 10–30 MPa. It is difficult for time variability and thin density of renewable energy to achieve the harsh reaction condition [5,6]. Thus, high catalytic performance under mild conditions is inevitable for an energy-efficient synthesis. Catalysts (e.g., Ru) for ammonia synthesis generally employ electron-donating metals such as Ca enhance their activities[7-10], while oxygen is not preferable because of its electron-withdrawing ability. However, recent reports unraveled that oxygen (electrophilic species) addition enhances the activity of catalysts [11-13]. As plausible explanations, hydrogen-absorbing, electron-donating properties, and an increase in active sites have been proposed, but the reasons are unclear [8,13-23].

Here, we found that the addition of oxygen to Ru/CaH<sub>2</sub> enhanced the activity of ammonia synthesis. Through kinetic analysis and structural analysis, the reasons why the presence of oxygen enhances catalytic activity were evaluated.

Figure 1a shows the rate of ammonia synthesis over Ru/CaH<sub>2-2x</sub>O<sub>x</sub> at 0.1 MPa and 300°C. When the oxygen content was 29 mol% against Ca, the rate of ammonia synthesis reached a maximum and was about twice as high as that of 14 mol%. Too much oxygen, greater than 29 mol%, reduced the activity and raised the <sup>app</sup>E<sub>a</sub> (Figure 1b, Table 1). Figure 1b shows the XRD (Powder X-ray diffraction) patterns of Ru/CaH<sub>2-2x</sub>O<sub>x</sub> after ammonia synthesis. Ru-derived peaks were not identified, indicating Ru was loaded as amorphous. The catalyst Ru/CaH<sub>2</sub> (x = 0.00) showed only CaH<sub>2</sub>-derived peaks and no CaO-derived peaks. The catalysts exposed to oxygen (x = 0.14–0.44) showed a stronger peak around 2θ = 37.6° derived from CaO (2 0 0) as the oxygen content increased. The addition of oxygen shifts the CaH<sub>2</sub>-derived peak to the wide-angle side.



**Figure 1.** (a) Catalytic performance of Ru/CaH<sub>2-2x</sub>O<sub>x</sub> ( $x = 0.14-0.44$ ). Reaction conditions are as follows: weight of catalysts (500 mg), total flow rate (60 mL min<sup>-1</sup>, N<sub>2</sub>/H<sub>2</sub> = 1:3), temperature (300°C), pressure (0.1 MPa). (b) XRD patterns for Ru/CaH<sub>2-2x</sub>O<sub>x</sub> ( $x = 0.00-0.44$ ) after ammonia synthesis (reaction conditions: total flow rate (60 mL min<sup>-1</sup>, N<sub>2</sub>/H<sub>2</sub> = 1:3), temperature (300°C), pressure (0.1 MPa)).

**Table 1.** Catalytic performance of Ru/CaH<sub>2-2x</sub>O<sub>x</sub> ( $x = 0.14, 0.25, 0.44$ ) at 0.1 MPa.

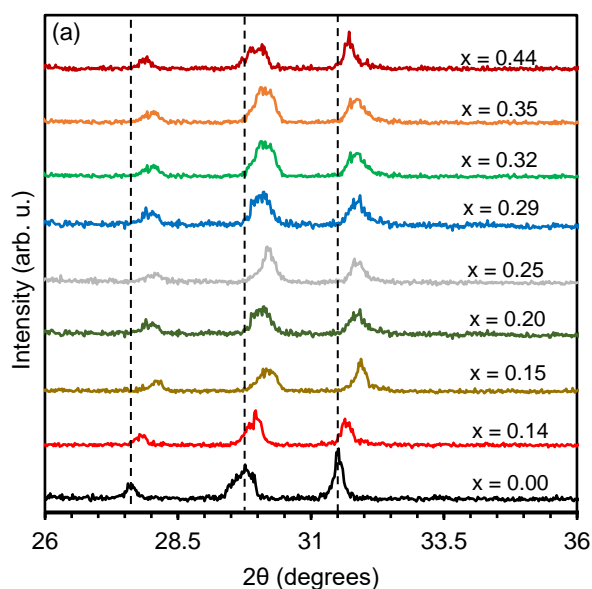
| Catalyst                                 | $r_{\text{NH}_3}$ ( $\mu\text{mol g}^{-1} \text{h}^{-1}$ ) <sup>a</sup> | $S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ ) <sup>b</sup> | ${}^{\text{app}}E_a$ ( $\text{kJ mol}^{-1}$ ) <sup>c</sup> | $\alpha^d$ | $\beta^d$ | $\gamma^d$ |
|--|---|--|--|------------|-----------|------------|
| Ru/CaH <sub>1.72</sub> O <sub>0.14</sub> | 734.8   | 27.3   | 69   | 0.98       | -0.85     | -1.24      |
| Ru/CaH <sub>1.50</sub> O <sub>0.25</sub> | 1285.0  | 22.6   | 59   | 0.98       | -0.29     | -1.00      |
| Ru/CaH <sub>1.12</sub> O <sub>0.44</sub> | 1107.4  | 22.9   | 80   | 1.31       | 0.05      | -1.11      |

<sup>a</sup> $r_{\text{NH}_3}$  is ammonia synthesis reaction rate at 300°C, total flow rate; 60 mL min<sup>-1</sup> (N<sub>2</sub>/H<sub>2</sub> = 1:3). <sup>b</sup> $S_{\text{BET}}$  is BET specific area. <sup>c</sup>Apparent activation energy ( ${}^{\text{app}}E_a$ ) was measured at 280–320°C, 0.1 MPa, total flow rate; 60 mL min<sup>-1</sup> (N<sub>2</sub>/H<sub>2</sub> = 1:3). <sup>d</sup> $\alpha$ ,  $\beta$ , and  $\gamma$  are the parameters (reaction orders) in the equation,  $r_{\text{NH}_3} = kP_{\text{N}_2}^\alpha P_{\text{H}_2}^\beta P_{\text{NH}_3}^\gamma$ , where  $P_i$  is the partial pressure of the gas,  $i$ , and  $k$  is the rate constant.

Table 1 shows the catalytic performance, surface area ( $S_{\text{BET}}$ ), apparent activation energy ( ${}^{\text{app}}E_a$ ), and reaction orders of N<sub>2</sub> ( $\alpha$ ), H<sub>2</sub> ( $\beta$ ), and NH<sub>3</sub> ( $\gamma$ ) of Ru/CaH<sub>2-2x</sub>O<sub>x</sub>, where  $x$  is 0.14, 0.25, and 0.44. The surface area of the catalysts did not change so much as the oxygen content changed. Among the three, the reaction rate was the maximum value (Figure 1a), and  ${}^{\text{app}}E_a$  showed the minimum (59 kJ mol<sup>-1</sup>) in Ru/H<sub>1.50</sub>O<sub>0.25</sub>. NH<sub>3</sub> order ( $\gamma$ ) was unchanged even as oxygen increased. On the other hand, H<sub>2</sub> order ( $\beta$ ) increased as the oxygen amount was raised. It means the oxygen suppressed the hydrogen poisoning over Ru and enhanced the activity.

The increase in ammonia synthesis activity due to an increase in the oxygen content of CaH<sub>2</sub> can be explained as follows. During the reaction, CaH<sub>2</sub> became CaH<sub>2-x</sub>(e<sup>-</sup>)<sub>x</sub> [16,24], resulting in intense electron donation to Ru [24]. Too much electron donation can induce more severe hydrogen poisoning [7]. The oxygen in Ru/CaH<sub>2-2x</sub>O<sub>x</sub> weakened the electron donation and facilitated the release of hydrogen, as well as the previous report that the electronegative element, F facilitates the release of H in CaFH [13]. Therefore, the introduction of oxygen improved hydrogen poisoning and enhanced activity. It is evidenced by the larger reaction order of hydrogen as the oxygen content increased in Ru/CaH<sub>2-2x</sub>O<sub>x</sub>. However, excessive oxygen caused the lower electron donation and decreased the activity found in Ru/CaH<sub>1.12</sub>O<sub>0.44</sub>, indicated by the high  ${}^{\text{app}}E_a$ . It matches that the N<sub>2</sub> order is high, and N<sub>2</sub> dissociation is more difficult when the oxygen content is  $x = 0.44$ . Therefore, Ru/CaH<sub>2-2x</sub>O<sub>x</sub> had the plateau of catalytic activity against the oxygen amount.

When we focus on the XRD patterns around  $2\theta = 27\text{--}33^\circ$ , the  $\text{CaH}_2$ -derived peak shifts to a wider angle with increasing CaO content (Figure 1b, Figure 2). The plausible explanations are given below. The increase in CaO means an increase in electrophilic O relative to  $\text{CaH}_2$ : O prefers electrons rather than H. Therefore, the increase in CaO weakens the ionic bonds between  $\text{Ca}^{2+}$  and  $\text{H}^-$ , which facilitates the replacement of  $\text{H}^-$  in  $\text{CaH}_2$  by  $\text{O}^{2-}$  and the release of hydrogen. The defects in the crystal structure due to the release of hydrogen cause Ca to attract H more strongly, shortening the bond lengths and shrinking the crystal lattice, and the  $\text{CaH}_2$ -derived peak shifts to the wide-angle (Figure 1b, Figure 2). When the oxygen content exceeds  $x = 0.15$ , the peak conversely shifts to a narrower angle because the oxygen itself expands the unit lattice. The introduction of oxygen to  $\text{Ru}/\text{CaH}_2$  enhanced the catalytic activity, in the same way that  $\text{Ru}/\text{MH}_3$  ( $\text{M} = \text{La}, \text{Ce}$ ) was activated by oxygen in the previous study [12]. In  $\text{Ru}/\text{CaH}_{2-2x}\text{O}_x$ , the  $\text{CaH}_2$ -derived unit lattice shrank; in  $\text{Ru}/\text{MH}_{3-2x}\text{O}_x$  the  $\text{MH}_3$ -derived unit lattice expanded. These differences in unit lattice when oxygen is introduced can be explained as follows.  $\text{MH}_3$  is in the same space group ( $\text{Fm}\bar{3}\text{m}$ ) as  $\text{MH}_2$ , but the lattice is larger for the dihydrides than for trihydrides. Therefore, in the case of  $\text{Ru}/\text{LaH}_{3-2x}\text{O}_x$  and  $\text{Ru}/\text{CeH}_{3-2x}\text{O}_x$ , the crystal lattice is more extensive as the hydrogen is more easily released by oxygen. Because of this different behavior of crystal lattice stretching, the origin of activity increased by oxygen in  $\text{Ru}/\text{LaH}_{3-2x}\text{O}_x$  and  $\text{Ru}/\text{CeH}_{3-2x}\text{O}_x$  can be different from the mechanism in  $\text{Ru}/\text{CaH}_{2-x}\text{O}_2$ .



**Figure 2.** XRD patterns for  $\text{Ru}/\text{CaH}_{2-2x}\text{O}_x$  in the range of  $26\text{--}34^\circ$ .

In conclusion, we found that oxygen can enhance  $\text{Ru}/\text{CaH}_2$ , whereas oxygen is generally considered unfavorable for ammonia synthesis catalysts. The enhancement mechanism was discussed based on kinetics and structures. The oxygen suppresses the hydrogen poisoning on Ru surface and seems to make optimal electron donation to Ru, resulting in high activity.

#### Author Contributions

<sup>†</sup>R. M. and T. O. contributed equally to this work

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