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Effect of Ru crystal phase on the catalytic activity of hydrolytic dehydrogenation of ammonia borane

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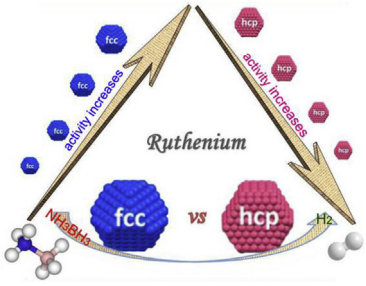
HIGHLIGHTS

- The crystal phase effect of Ru on the hydrolysis of ammonia borane was studied.
- The *hcp* Ru/γ-Al_2O_3 exhibits higher activity than that of *fcc* Ru with similar Ru size.
- The variation trend of activity is opposite with the *fcc* and *hcp* Ru size change.
- DFT was used to understand the activity difference between *fcc* and *hcp* Ru.

GRAPHICAL ABSTRACT



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ABSTRACT

Ruthenium (Ru) is one of the most attractive catalysts in the hydrolytic dehygrogenation of ammonia borane. So far, the employed Ru-based catalysts are mainly focusing on hexagonal close packed structured Ru. In this work, we study the crystal phase effect of Ru on the hydrolytic dehygrogenation of ammonia borane, using face-centered cubic structured and hexagonal close packed structured Ru nanoparticles supported on γ-Al_2O_3. The results show that the catalytic activity is different even these two kinds of Ru nanoparticles hold similar size. Impressively, with the Ru particle size change, the variation trend of activity is opposite for face-centered cubic and hexagonal close packed structured Ru/γ-Al_2O_3. Finally, some possible reasons for their difference are proposed based on density functional theory calculations.

1. Introduction

Metal-based catalysts, especially for noble metals, are widely studied in various kinds of heterogeneous catalysis reactions. To achieve high-efficient catalysts, one may tune the size, composition, morphology or employed supports of the noble metals to optimize their catalytic activities [1–8]. For example, Pt with surfaces enclosed by facets with Miller index of {100} yields only cyclohexane in the hydrogenation of benzene, while Pt enclosed by facets with Miller index of {111} leads to both cyclohexene and cyclohexane [9]. Since the catalytic reaction is indeed surface reaction, it is generally acknowledged that this difference in catalytic selectivity is mainly resulting from the different space packing pattern of the metal atoms in different exposed crystal planes. As we know, there are three basic crystal structures for

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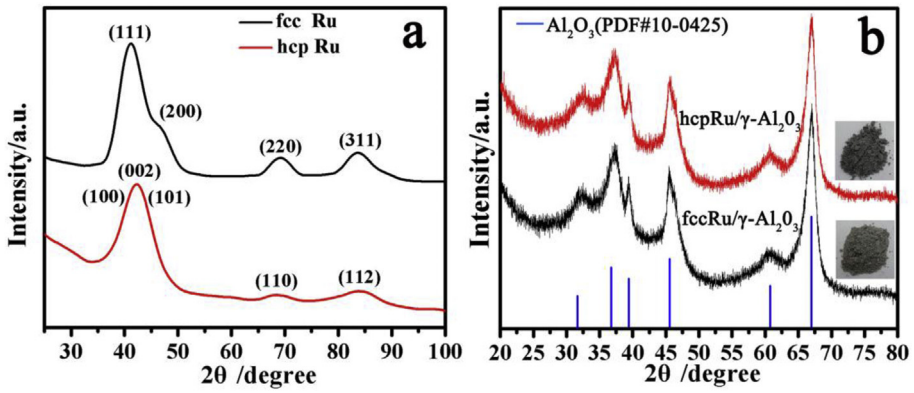

Fig. 1. XRD patterns of *fcc* and *hcp* structured Ru nanoparticles (a) and Ru/γ-Al_2O_3 (b). Insets in (b) are the corresponding photographs of *fcc* Ru//γ-Al_2O_3 and *hcp* Ru/γ-Al_2O_3.

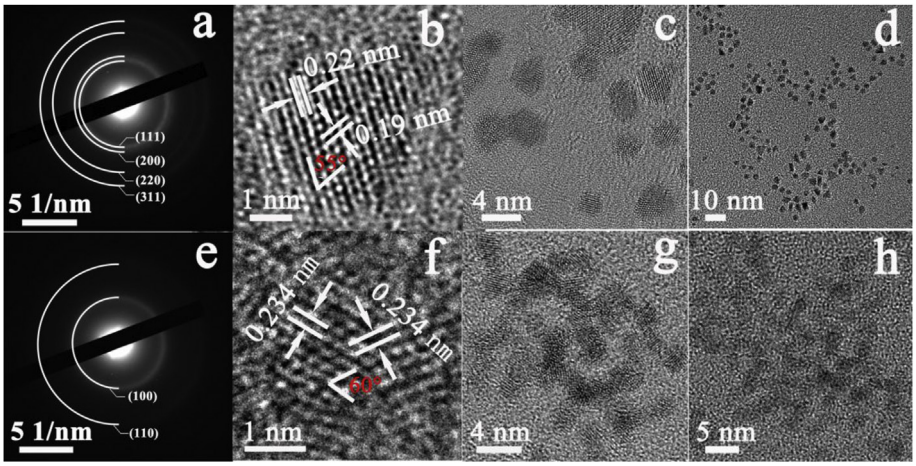

Fig. 2. SAED (a, e), TEM and HRTEM images of *fcc* Ru (b–d) and *hcp* Ru (f–h).

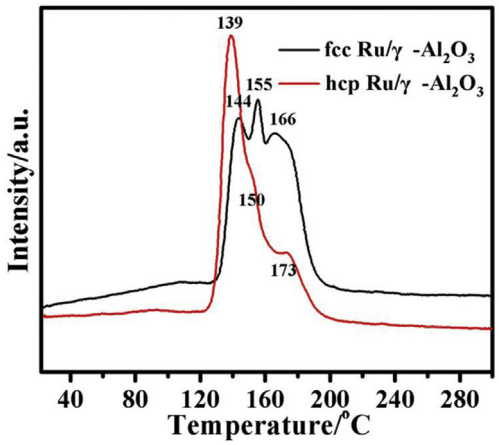

Fig. 3. H_2-TPR profiles of *fcc* Ru/γ-Al_2O_3 and *hcp* Ru/γ-Al_2O_3.

the majority of metals, body-centered cubic (*bcc*), hexagonal close packed (*hcp*) and face-centered cubic (*fcc*). The coordination environment and the spatial distribution of the metal atoms vary significantly in these crystal phases [10,11]. Keeping in mind this understanding, the crystal phase of the metals is also expected to induce the catalytic performance difference.

Ru is a 4d transition metal that in the bulk adopts an *hcp* structure at all temperatures. Similar to metallic Co, except stable *hcp* phase, Ru can exist in crystallographic *fcc* structure. Thanks for the nanotechnology, *fcc* Ru can be stabilized during the synthesis process and even under reaction conditions. Recently, the crystal phase effect of Ru towards different catalytic reactions were studied [12–17]. For example, Ye et al. prepared hollow *fcc* Ru by means of preferentially epitaxial growth of Ru on the corners and edges of Pd truncated octahedral, followed by the selective removal of Pd. They found the *fcc* Ru nanoframes showed higher catalytic activities towards the reduction of p-nitrophenol compared with *hcp* Ru nanowires [12]. Kusada et al. found the *fcc* structured Ru nanoparticles (> 3 nm) were more reactive towards CO oxidation than the conventional *hcp* Ru nanoparticles with similar size, partially because the *fcc* Ru nanoparticles generally tend to be enclosed by (111) facet with lowest surface energy. In addition, they also found that the *fcc* and *hcp* Ru showed different trend in CO conversion at T_{50} [13]. Considering the catalytic performance is dependent on the metal particle size, the crystal phase effect of Ru with similar particle size is therefore of importance and interest to further understand Ru-involved catalytic reaction mechanisms.

Nowadays, the ever-increasing demand for energy provokes effective, renewable and clean alternative energy strategy, *e.g.* the polymer electrolyte membrane fuel cell (PEMFC). However, the hydrogen supply including hydrogen transport and storage has been a bottleneck to the application of PEMFC as portable power sources. PEM fuel cells require stable and high-capacity hydrogen generator at ambient condition [18]. Recently, ammonia borane (NH_3-BH_3, AB for short) with high hydrogen storage density and high stability has been identified as one of the leading molecular candidates for hydrogen storage in future. The hydrolysis of AB is considered more promising because it provides 3 mol of hydrogen per AB mol at room temperature, in the presence of suitable metal catalysts (as shown in Eq. (1)). Among the metal catalysts reported, Ru is the most widely studied catalyst due to its high