Self-promoted LaCoSi Catalyst for N_2 Activation and the Mechanism

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Abstract: In the presentation, we show that ternary intermetallic LaCoSi is an efficient catalyst for N_2 activation to produce NH_3. The reaction is remarkably promoted by shifting the rate-determining step from the sluggish N_2 dissociation to NH_x formation, which few catalysts have achieved. The activity is 60 times higher than those of supported Co catalysts under mild conditions (400°C, 0.1 MPa). We show that the N_2 dissociation is significantly enhanced via the negatively charged Co, which mediates electrons from La to the adsorbed N_2, and a strong exothermic effect of N_2 adsorption due to the specific crystal structure of LaCoSi.

Keywords: Intermetallics, Catalyst, N_2 activation.

1. Introduction

Transition metals (TM) often show good catalytic ability due to their ability to temporarily exchange electrons with reacting species. Such ability can be largely promoted by electron donation from a material with low work function, such as alkali, alkaline earth and rear earth metals as well as electrides [1,2]. Intermetallics provide a wide platform to regulate the activity of TM because the chemical environment can modify the electronic structure of TM via crystallographic structure and peculiar mixed bonding of the constituent elements.

In our previous study, we have shown that the electride concept can be well applied to LaScSi, a member of RTX intermetallics (R = rare earth, T = transition metal, X = p-block element) with more than 1,000 analogues [3]. When loaded with Ru, LaScSi shows excellent catalytic activity for ammonia synthesis under mild conditions (400°C, 0.1 MPa); however without Ru, there is no activity, because there is no activation center (active TM) in LaScSi. In order to combine the electride concept and TM in one compound, in the presentation, we show that it is a good idea to replace Sc with active TM to realize an effective catalyst for N_2 activation to produce NH_3 [4].

2. Experimental and Theoretical

Intermetallic LaCoSi was prepared by arc melting followed by annealing, the pure-phase sample was ground into powder in a glovebox and directly applied as catalyst without further treatment. The purity of the compound was checked by powder XRD and SEM-EDX measurements. The charge state in bulk and the crystal structure were checked by XAFS measurement. The surface state was measured by UPS, XPS and AES, and hydrogen desorption behavior was measured using TDS. The catalytic reaction was performed under mild conditions with temperature varying from 250 to 400°C and pressure from 0.1 MPa to 1 MPa.

The structure relaxation and electronic structure calculations were performed using the density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP). The generalized gradient Perdew-Burke-Ernzerhof functional was adopted in the DFT calculations and the core electrons were described using the projector augmented wave method.

3. Results and discussion

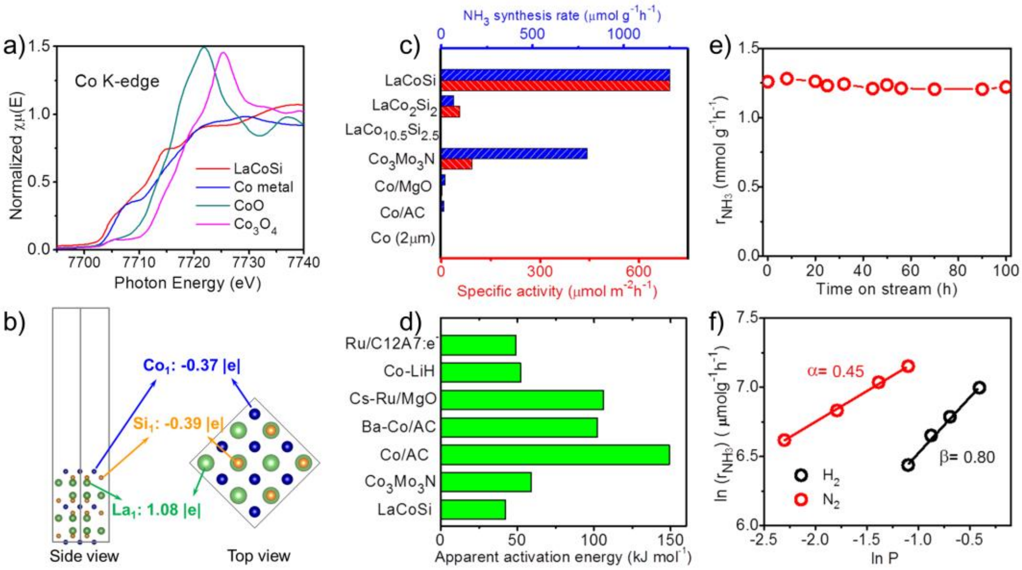

Figure 1. Characterization and catalytic performance of LaCoSi and other Co-based catalysts.

As shown in Fig. 1a,b, the negatively charged Co was confirmed by Co K-edge XANES spectra of LaCoSi, Co, CoO, and Co_3O_4, and a theoretical analysis. A consistent surface charge state was also checked by AES and XPS measurements. The catalytic activity for ammonia synthesis is 60 times higher than those for 10 wt% Co/MgO and 10 wt% Co/AC under mild conditions (400°C, 0.1 MPa, Fig. 1c). The apparent activation energy of LaCoSi is estimated to be 42 kJ mol^{-1} (Fig 1d), which is around half of that for the well-studied catalysts, indicating that N_2 dissociation over LaCoSi is highly promoted. This value is close to that of Ru-loaded C12A7:e^- and Co-LiH [1,2], implying the similarity in reaction mechanism, where formation of NH_x species is the rate-determining step of the overall reaction. The catalytic ability is very stable (Fig 1e), in contrast to the supported catalysts which often show a decline of activity due to the aggregation of the supported TM nano-particles. N_2 reaction order is measured to be 0.45, almost half of the conventional heterogeneous catalysts (0.8-1.0), indicating that N_2 dissociation is sufficiently fast and the surface is continuously populated with activated N, in agreement with the Ru-loaded electrides [1]. H_2 reaction order in this reaction is positive for LaCoSi, showing that the problem of hydrogen poisoning with Co/AC is prevented by the hydrogen absorption ability of LaCoSi.

The mechanism of N_2 activation is further studied by theoretical calculations over Co terminated surface of Co metal and LaCoSi. The specific crystal structure of LaCoSi enables a strong exothermic effect of N_2 adsorption, which dramatically decreases the apparent energy barrier of N_2 activation.

4. Conclusions

We showed that a combination of the electride concept with TM can be realized in RTX compounds for catalysis as exemplified in LaCoSi for N_2 activation. The negatively charged Co and the specific crystal structure of LaCoSi were suggested as the key factors, and a "hot-atom" mechanism was proposed. We expect a large enhancement of the activity by increasing the surface area of LaCoSi (only <2 m^2/g at present) and the application of RTX intermetallic catalysts for other catalytic reactions.

References

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