Copper-based Intermetallic Electride Catalyst for Chemoselective Hydrogenation Reactions

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Abstract: Here we report that a new copper-based intermetallic electride catalyst, $LaCu_{0.67}Si_{1.33}$, in which Cu sites activated by anionic electrons with low work function are atomically dispersed in the lattice framework and affords selective hydrogenation of nitroarenes with high TOFs of 5084 h^{-1}. Kinetic analysis utilizing isotope effect reveals that the cleavage of H–H bond is the rate-determining step. The high carrier density and low work function (LWF) properties of $LaCu_{0.67}Si_{1.33}$ enable the activation of hydrogen molecules with extreme low activation energy (E_a = 14.8 kJ·mol^{-1}). Furthermore, preferential adsorption of nitroarenes via a nitro group is achieved by high oxygen affinity of $LaCu_{0.67}Si_{1.33}$ surface, resulting in high chemoselectivity.

Keywords: intermetallic electride, chemoselective hydrogenation, hydrogen activation.

1. Introduction

Single-atom catalysts with maximum atom efficiency are desirable for better utilization of the noble metal, which is now regarded as a new research frontier. However, such a highly dispersed system as single-atom sites tends to leach or aggregate during reaction process due to very high surface free energy.[1] We think isolation of active metal sites by combination with other metal to form intermetallic structures is an effective way to avoid aggregation and/or leaching. Furthermore, the electronic properties of the active sites can be controlled by proper choice of the component and structure of intermetallic compounds. Therefore, we tried to synthesize ternary intermetallic catalysts containing earth-abundant metal as active sites, in which the active metal sites are stabilized and dispersed in the lattice framework. Besides, it should be non-toxic and chemically stable under the reaction conditions.

2. Experimental

$LaCu_{0.67}Si_{1.33}$ powder was directly synthesized by arc-melting lanthanum, copper and silicon ingots with a stoichiometric ratio under an argon atmosphere. The ingot obtained was ground using an agate motor. $LaCu_{0.67}Si_{1.33}H_{0.3}$ powder was obtained from the $LaCu_{0.67}Si_{1.33}$ catalyst annealed at 400 °C under H_2 gas flow for 24 h.

3. Results and discussion

LaCuSi crystallizes in a hexagonal structure and Cu and Si atoms constitute a two-dimensional honeycomb network, whereas the La layers are located between each Cu/Si honeycomb layer with a distance of ca. 2.13 Å (Figure 1a). This large interlayer distance leaves open interstitial spaces between the honeycomb layers, denoted as X, with fractional coordinates of (2/3, 1/3, 0). Figures 1b show that LaCuSi has an interstitial band crossing the Fermi level, which coincides with the presence of the electron density peak at site X, implying that LaCuSi can be regarded as an intermetallic electride.[2] The work function of $LaCu_{0.67}Si_{1.33}$ was measured to be $\Phi_{WF} \approx 3.5$ eV. Given the LUMO of hydrogen molecules is located at 3.6 eV below the vacuum level, the free electrons would be efficiently donated from $LaCu_{0.67}Si_{1.33}$ to the LUMOs of the starting components, and expected to suppress the activation energy for H_2 dissociation (Figure 1c).

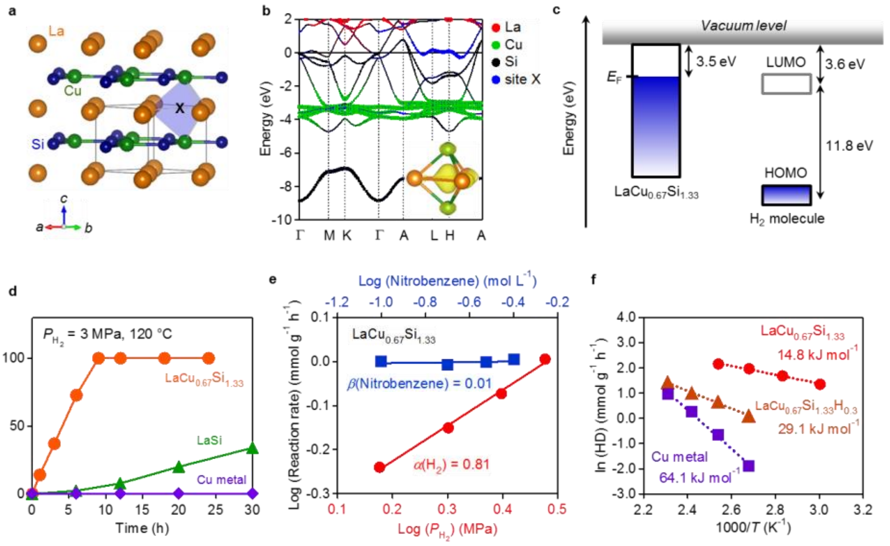

Figure 1. a, Crystal structure of stoichiometric LaCuSi. b, Calculated band structure of stoichiometric LaCuSi. c, Comparison of the Fermi level of $LaCu_{0.67}Si_{1.33}$ and the unoccupied (LUMO) state of H_2. d, Time-dependent catalysis over $LaCu_{0.67}Si_{1.33}$, LaSi, and elemental Cu catalysts. e, Dependence of reaction rate on nitrobenzene concentration and hydrogen pressure over the $LaCu_{0.67}Si_{1.33}$ catalyst. f, Arrhenius plots for $LaCu_{0.67}Si_{1.33}$ and $LaCu_{0.67}Si_{1.33}H_{0.3}$ catalysts. Apparent activation energy calculated from Arrhenius plots for the reaction rate in the temperature range of 60–160 °C.

In Figure 1d, $LaCu_{0.67}Si_{1.33}$ hydrogenates nitrobenzene without producing any intermediates or byproducts during the entire reaction process and the yield of aniline reaches 99% in 9 h. The reaction rates are sensitive to the hydrogen pressure but independent of the nitrobenzene concentration, which results in kinetic reaction orders of $\alpha(H_2) = 0.81$ and β(nitrobenzene) = 0.01, respectively (Figure 1e). These contrastive kinetic parameters imply that $LaCu_{0.67}Si_{1.33}$ breaks through the limitation of nitrobenzene activation, and hydrogen activation is the rate-controlling step. The H_2–D_2 exchange reaction was also investigated and in Figure 1f, the activation energy on $LaCu_{0.67}Si_{1.33}$ (14.8 kJ·mol^{-1}) is much lower than previously studied noble metal catalyst and Cu metal (64.1 kJ·mol^{-1}) (Figure 1f). The activation energy of the corresponding H^- incorporated sample ($LaCu_{0.67}Si_{1.33}H_{0.3}$), in which anionic electron is captured by hydrogen to form H^-, also exhibits a larger activation energy (29.1 kJ·mol^{-1}). Therefore, the presence of anionic electrons in $LaCu_{0.67}Si_{1.33}$ plays a crucial role in the activation of H_2 molecules and the catalytic activity for the selective hydrogenation of nitroarenes.[3]

4. Conclusions

In summary, the Cu-based intermetallic electride $LaCu_{0.67}Si_{1.33}$ was found to exhibit excellent catalytic activity for various selective hydrogenation reactions. It possesses both a high carrier density and a LWF, and exhibits much higher activity than conventional transition metal nanoparticles on oxide or carbon supports. Mechanistic studies demonstrated that electron transfer from anionic electrons in $LaCu_{0.67}Si_{1.33}$ bulk promotes H_2 dissociation on the highly charged anti-bonding orbital of molecular hydrogen, which is the rate-determining step of the investigated hydrogenation reactions. The preferential adsorption of the reactant on the catalyst surface through the oxygen-containing group leads to excellent selectivity. $LaCu_{0.67}Si_{1.33}$ itself serves as a hydrogenation catalyst without the need for metal loading on the surface; therefore, this study establishes transition metal based LWF materials as new catalysts for such reactions, which should simplify the entire preparation and reaction processes for hydrogenation.

References

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