

Local structure of In-hydride species in zeolite and its reactivity for C₂H₆ dehydrogenation

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1. Introduction

Hydrides in/on solid materials have attracted significant attention in many research fields, including energy engineering, electrochemistry, and catalysis. Research on the synthesis, characterization, and catalytic function of the isolated surface hydrides is an attractive but formidable task.¹ In this study, in-situ IR and DFT calculation were carried out to find the formation of isolated In-hydride species in indium-exchanged CHA zeolite (In-CHA).² The catalytic ability of In-CHA on C₂H₆ non-oxidative dehydrogenation was examined, resulting in superior selectivity (96 %) and low coke formation during a long-term reaction (90h). By the combination of kinetic analysis and transition state (TS) calculation, it was elucidated that its catalytic performance was originated from the formation of not mono-hydride ([InH]²⁺) but di-hydride species ([InH₂]⁺) as active sites.

2. Experimental

In₂O₃ supported on the proton-type CHA (In₂O₃/CHA) was synthesized through impregnation of In(NO₃)₃·nH₂O (Kanto Chemical Co., Inc.) in the NH₄⁺-type CHA zeolite (Tosoh, SiO₂/Al₂O₃ = 22.3), followed by drying in an oven and calcination under air for 1 h at 773 K. Afterward, the reductive solid-state ion-exchange reaction of In₂O₃/CHA was conducted in the presence of H₂ at 773 K. For IR spectroscopic experiments, the In-CHA disk was prepared in-situ in a quartz reactor from a self-supported disk of In₂O₃/CHA. DFT calculations were performed using the Vienna ab initio simulation package (VASP) with a periodic boundary condition under the Kohn–Sham formulation.

3. Result and Discussion

The in-situ IR measurement of In-CHA treated with H₂ at 773 K (In-CHA(H₂)) was performed. The IR spectrum of In-CHA(H₂) exhibited a band with a maximum at 1720 cm⁻¹ (Figure 1a) arising from In–H stretching vibrations (ν(In–H)). This band remained unchanged even at 473 K. After H–D exchange reaction with D₂ at 373 K, ν(In–H) decreased and disappeared at 473 K. ν(In–H) appeared again by the following exposure to H₂ at 473 K. The gas-phase products were also analyzed by mass spectrometry during the H–D exchange reaction with an increase in the temperature from 313 to 473 K. The reaction of In-CHA(H₂) with D₂ afforded a positive peak for m/z = 3 with a negative peak for m/z = 4 around 373–473 K (Figure 1b), while a peak for m/z = 2 was hardly observed. A control experiment using proton-type CHA (H-CHA) instead of In-CHA (H₂-treated H-CHA with D₂) was conducted where no peak was observed for all signals,

supporting the occurrence of an H–D exchange reaction between In-hydrides and D₂.

In-CHA exhibited high selectivity (96 %) and durability for the nonoxidative ethane dehydrogenation without cofeeding of H₂. The activity and selectivity of In-CHA were maintained for at least 90 h, and the catalyst was reusable without loss of its efficiency. Based on the results of kinetic analysis and TS calculations, the formation of [InH₂]⁺ as active sites is responsible for the durable reaction due to the less formation of Bronsted acid sites and carbenium cations. More detailed reaction mechanisms and the relationship with the local structure of In-hydride species will be discussed

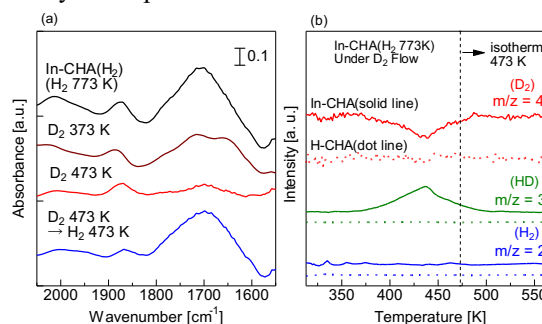


Figure 1 (a) FTIR spectra of In-CHA after H₂ treatment at 773 K (In-CHA(H₂)) and H–D exchange reactions. (b) Mass profiles for m/z = 2, 3, and 4 during H–D exchange reaction of In-CHA(H₂) (solid line) or H-CHA(H₂) (dot line) with D₂.

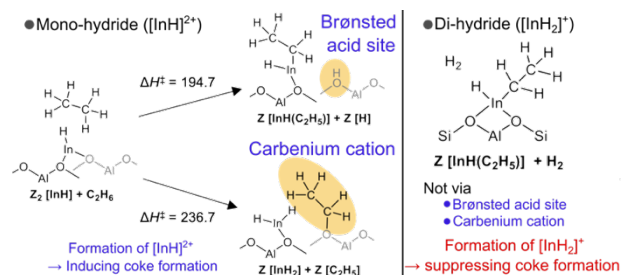


Figure 2 Reaction scheme of non-oxidative dehydrogenation of C₂H₆ on indium mono-hydride ([InH]²⁺) and di-hydride ([InH₂]⁺) species in zeolite.

References

- 1 C. Copéret, D. P. Estes, K. Larmier and K. Searles, *Chem. Rev.*, 2016, **116**, 8463.
- 2 Z. Maeno, S. Yasumura, X. Wu, M. Huang, C. Liu, T. Toyao and K. Shimizu, *J. Am. Chem. Soc.*, 2020, **142**, 4820.