TUNING CATALYTIC PERFORMANCE OF GALLIUM OXIDE FOR PROPANE DEHYDROGENATION BY INTRODUCING SINGLE PLATINIUM ATOMS

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Abstract

Density functional theory (DFT) calculations combined with microkinetic analysis have been performed to examine the reaction mechanism for propane dehydrogenation (PDH) on Ga_2O_3 and Pt_1-Ga_2O_3 catalysts. On Ga_2O_3(100), it is found that the dissociation of propane is the rate-limiting step for the overall reaction and the Lewis acid-base interaction has a significant effect on the elementary reactions involving paired amphoteric species, which promotes dramatically H diffusion and H desorption in form of H_2. When single Pt atoms are introduced onto the oxide surface, the surrounding O ions become less negatively charged than their counterparts coordinated to Ga. As a result, the Pt-O pair is more active for C-H bond activation than the Ga-O pair, and the energy barrier for the rate-limiting dehydrogenation step is lowered by 0.24 eV, resulting in the turnover frequency (TOF) four times that of Ga_2O_3(100). The introduction of single Pt atoms would raise the energy barrier for the recombination of atomic H by 0.75 eV, implying that the Pt-O pair plays a minor role in determining the rate for H_2 desorption.

Keywords

Propane dehydrogenation, Single-atom catalysts, Ga_2O_3, DFT, Microkinetic modeling.

Introduction

With the increase in exploration of shale gas, new cracker projects for ethylene production are based primarily on ethane feedstock, which yield almost no propylene. For this reason, propane dehydrogenation (PDH) has become an economically competitive propylene production technology. Al_2O_3-supported PtSn and CrO_x catalysts have been commercially used in this process. The search for new catalysts has been driven by the high cost of Pt and environmentally unfriendly Cr. Among the candidates, gallium oxide has been widely studied, but the catalytic performance remains to be improved. Although (Liu et al., 2008) had studied PDH on Ga_2O_3(100) from a theoretical perspective, the reaction mechanism is still under debate. Recently, (Sattler et al., 2014) reported a 1000 ppm Pt promoted Ga/Al_2O_3 catalyst, which showed high activity and stability. However, Pt occurs as nanoparticles or subnanometer-sized clusters in the reported catalysts. Further dispersing it to single atoms would not only approach 100 % utilization of precious Pt, but also bring about significantly increased catalytic performance.

Computational Details

Spin-polarized DFT calculations were performed using the Vienna ab initial Simulation Package (VASP). The generalized gradient approximation (GGA) with the BEEF-vdW exchange-correlation functional was employed to treat

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the exchange and correlation in the Kohn-Sham theory. The transition states are located by the dimer method.

Microkinetic analysis was based on a mean-field model and was solved using CatMAP python code. The calculations were performed at 895K and 1 bar of C_3H_8, in accord with experimental reaction conditions.

Results and Discussion

Lewis Acid-Base Interaction on Ga_2O_3(100)

The co-adsorption energy of amphoteric species on Ga(o)-O pair is much more negative than the sum of their respective adsorption energies when they are infinitely widely separated. Calculated Bader charge shows that the two fragments were oppositely charged when co-adsorbed on the Ga(o)-O pair. Thus, the charge transfer between the two fragments through the oxide surface might be responsible for the extraordinarily stable adsorption, which is known as the Lewis acid-base interaction.

PDH on Ga_2O_3(100) and Pt_1-Ga_2O_3(100)

The elementary reactions involved in PDH were examined on Ga_2O_3(100) and Pt_1-Ga_2O_3(100). Because H diffusion and H desorption in form of H_2 may readily take place, only dehydrogenation steps are shown in Figure 2. The energy barrier for the dissociation of propane is lower on the Pt-O pair than that on the Ga-O pair. However, the C-H bond cleavage is thermodynamically hindered on the Ga-O pair adjacent to Pt.

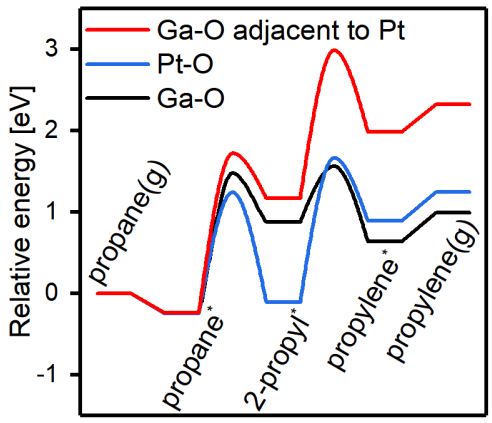

Figure 1. Energy profiles for PDH on different active sites.

Microkinetic Modeling Analysis

As shown in Figure 2, the reaction may proceed 33 times faster on the Pt-O pair than on the Ga-O pair. The recombination of atomic H is hindered by the introduction of single Pt atoms, and the Ga-O pair would dominate the kinetics of H_2 desorption.

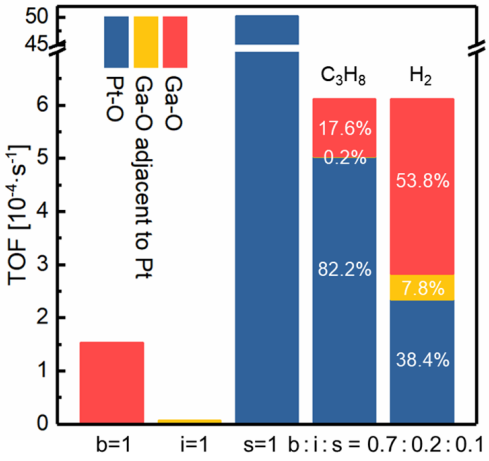

Figure 2. TOF on different active sites.

Conclusions

On Ga_2O_3(100), it is found that the dissociation of propane is the rate-limiting step for PDH and the Lewis acid-base interaction has a major effect on the elementary steps involving paired amphoteric species. Single Pt atoms donate less electrons to the surrounding O ions than Ga atoms do. As a result, the Pt-O pair is more active for C-H bond activation than the Ga-O pair. The TOF on Pt_1-Ga_2O_3(100) is four times that on Ga_2O_3(100). The recombination of atomic H is hindered by the introduction of single Pt atoms, and the Ga-O pair would dominate the kinetics of H_2 desorption.

Acknowledgments

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References

Liu, Y., Li, Z. H., Lu, J., Fan, K. N. (2008). Periodic Density Functional Theory Study of Propane Dehydrogenation over Perfect Ga_2O_3(100) Surface. *J. Phys. Chem. C.*, *112*, 20382.

Metiu, H., Chretien, S., Hu, Z. P., Li, B., Sun, X. Y. (2012). Chemistry of Lewis Acid-Base Pairs on Oxide Surfaces. *J. Phys. Chem. C.*, *116*, 10439.

Sattler, J. J., Gonzalez-Jimenez, I. D., Luo, L., Stears, B. A., Malek, A., Barton, D. G., Kilos, B. A., Kaminsky, M. P., Verhoeven, T. W., Koers, E. J., Baldus, M., Weckhuysen, B. M. (2014). Platinum-promoted Ga/Al_2O_3 as highly active, selective, and stable catalyst for the dehydrogenation of propane. *Angew. Chem. Int. Ed.*, *53*, 9251.