Effect of boron promotion on the yield and stability of Pt/SiO_2 catalysts during propane dehydrogenation

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1. Introduction.

Bimetallic Pt catalysts such as PtSn, PtGa, PtIn and PtGe, have received considerable attention to enhance the yield and stability of Pt catalysts in dehydrogenation reactions. The addition of a promotor enhances the catalyst lifetime by reducing carbon deposition (coking) and/or particle sintering. Boron promotion has been found to enhance the stability of Ni[1] and Co[2] catalysts without affecting their activity and selectivity, and improved selectivity over Pd-B[3] catalysts. Here we describe the synthesis of a series of boron promoted Pt/SiO_2 catalysts and evaluate the effect of boron on the activity, selectivity and stability during propane dehydrogenation.

2. Experimental Methods.

To prepare the boron promoted catalysts, the SiO_2 support was first impregnated with the appropriate amount of aqueous boric acid, stirred at 50˚C until total evaporation of the solvent, and calcined at 550˚C for 3 hour. The resulting solid was subsequently impregnated with a H_2PtCl_6 aqueous solution to introduce the appropriate Pt loading, again followed by stirring and calcination. By modifying the boric acid concentration, catalysts with different B loading were prepared, denoted as 0.2%B-3%Pt/SiO_2, 0.6%B-3%Pt/SiO_2, 1.0%B-3%Pt/SiO_2 and 3%Pt/SiO_2, all the element loadings are given in wt. %.

Propane dehydrogenation was performed with 20 vol.% C_3H_8, 20 vol.% H_2 balanced with He and 8 vol.% C_3H_8 balanced with He as reaction feeds, a reaction temperature of 600 or 625 ˚C, a total pressure of 1 atm and a C_3H_8 flow rate of 0.75 and 0.2 ml/s, respectively. Absence of heat and mass transfer limitation was confirmed. Two reaction cycles were performed with an intermediate oxidation and reduction step. A quadrupole mass spectrometer measured the yields online. Propylene, methane and hydrogen were the only detectable products.

3. Results and discussion.

The effect of boron promotion was first screened using a feed of 20% C_3H_8 and 20% H_2 for 15 minutes over 3%Pt/SiO_2 and B-3%Pt/SiO_2 with different boron loadings, the propylene site-time yield (STY, mol propylene · mol Pt^{-1} · s^{-1}) as function of time on steam (TOS) are shown in Figure 1a, to get more reliable catalyst performances, the catalytic propane dehydrogenation during the 2nd reaction cycle are used in this work. For all the catalysts, the propylene yield declines rapidly during the initial minutes. After about 10 minutes, the catalysts have adapted to the reaction conditions and the propylene yield becomes stable. The propylene STY of the B promoted 3%Pt/SiO_2 catalysts after 15 minutes is plotted as a function of the boron loading in Figure 1b. The addition of small amounts of boron is clearly beneficial and leads to a fourfold increase in the propylene STY.

The long-term stability was evaluated for the catalyst promoted by 0.4 %B without H_2 evaluate the catalyst deactivation and the role of H_2 in propane dehydrogenation, Figure 1c. Initial propylene yields are nearly identical for the promoted and unprompted catalyst, but the decrease in yield with time on stream is significantly reduced for the promoted catalyst. The initial rapid deactivation of Pt catalysts during alkane dehydrogenation is well-known[4], and attributed to coke formation. After this initial deactivation, the catalysts adapt to the reaction conditions and their performance becomes stable. Clearly, the presence of boron affects this final structure and more than doubles the STY by enhancing both the activity and the propylene selectivity (from 85% to 95%) of the Pt catalyst. Furthermore, compare to Figure 1a, the presence of H_2 improves the propylene STY over Pt catalyst for more than 20 times. To elucidate the effect of boron promotion on the catalyst activity, the catalyst were characterized using XRD, XPS, CO-DRIFTS, EXAFS, TEM and EDX.

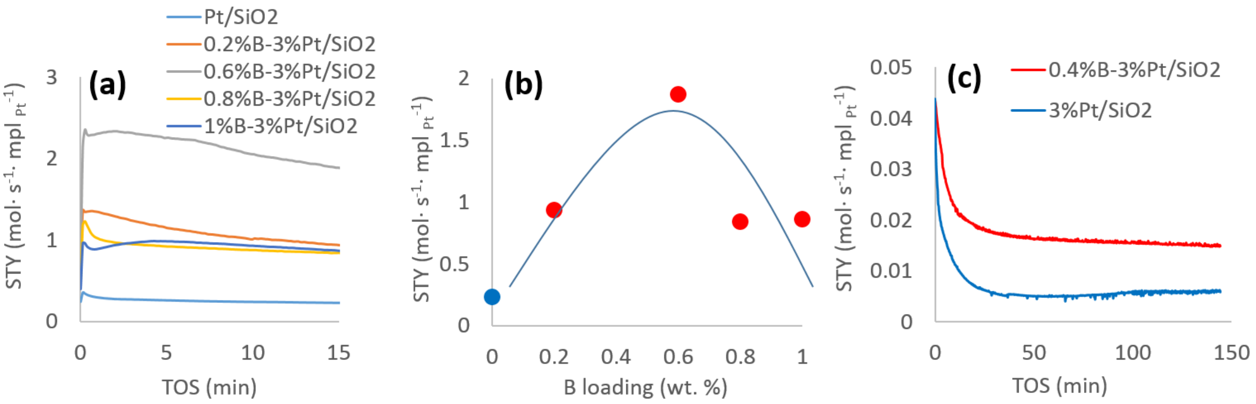

Figure 1. Catalytic propane dehydrogenation over boron-pomoted Pt/SiO_2 and Pt/SiO_2 catalysts (a) STY for propylene production at 600˚C over $3\%Pt/SiO_2$ and $B\text{-}3\%Pt/SiO_2$ with different boron loading ($20\%C_3H_8$, $20\%H_2$ balance in He), the conversion of propane for all the catalysts are between 8% to 11%; (b) the catalytic trend between B loading and STY for propylene production after 15 minute reaction as shown in (a); (c) STY for propylene production at 625˚C for 150 minutes reaction over $3\%Pt/SiO_2$ and $0.4\%B\text{-}3\%Pt/SiO_2$ ($8\%C_3H_8$ balance in He).

The location and the thermodynamic stability of boron introduced to the Pt catalysts were evaluated using Density Functional Theory. The calculations show that boron binds strongly at subsurface octahedral sites, and removal by hydrogenation or by carbon are highly unfavorable under dehydrogenation conditions (600˚C and 1 atm) with ΔG_{rxn} of 157 and 178 kJ/mol, respectively.

4. Conclusions

The effect of boron promotion of the activity, stability, and selectivity of Pt/SiO_2 catalysts was evaluated for the first time. The addition of 0.4% boron was found to enhance the stability and the propylene STY of 3%Pt catalysts three-fold. This work demonstrate that boron is a versatile promotor for hydrocarbon conversion reactions, and its role can be extended[5] from Co, Ni, and Pd to Pt-based catalysts.

References

(1) Xu, J.; Chen, L.; Tan, K. F.; Borgna, A.; Saeys, M. *J. Catal.* **2009**, *261*, 158-165.
(2) Tan, K. F.; Chang, J.; Borgna, A.; Saeys, M. *J. Catal.* **2011**, *280*, 50-59.
(3) Chan, C. W. A.; Mahadi, A. H.; Li, M. M.-J.; Corbos, E. C.; Tang, C.; Jones, G.; Kuo, W. C. H.; Cookson, J.; Brown, C. M.; Bishop, P. T.; Tsang, S. C. E. *Nat Commun* **2014**, *5*.
(4) Redekop, E. A.; Galvita, V. V.; Poelman, H.; Bliznuk, V.; Detavernier, C.; Marin, G. B. *ACS Catalysis* **2014**, *4*, 1812-1824.
(5) Nandula, A.; Trinh, Q. T.; Saeys, M.; Alexandrova, A. N. *Angew. Chem.* **2015**, *127*, 5402-5406.