Controllable Synthesis of Pt-Sn Bimetallic Catalyst from Surface Chemistry Approach for Propane Dehydrogenation to Propylene

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Abstract: A surface organometallic chemistry strategy was applied for the preparation of supported Pt-Sn bimetallic catalysts on different supports. This controllable synthesis approach enables to in-situ generate Pt-Sn clusters below 1 nm at the surface of various supports with precious tuning structure of Pt-Sn clusters at a molecular level. The prepared Pt-Sn bimetallic catalysts exhibit high performances in propane dehydrogenation to propylene, and the activity-structure relationship has been elucidated.

Keywords: Propane dehydrogenation, Bimetallic catalyst, Surface chemistry.

1. Introduction
The global propylene production technique is currently undergoing a significant change, since it gradually shifts away from co-production towards more on-purpose production process. Propane dehydrogenation to propylene has shown great benefits for the production of propylene, and therefore this economical process becomes a potential solution for filling the gap between propylene supply and demand in the future. Pt-Sn bimetallic catalysts exhibit high performances in propane dehydrogenation to propylene reaction; however, the rational design and synthesis of Pt-Sn bimetallic catalyst still remains a big challenging. A surface organometallic chemistry strategy has been utilized for precisely tailoring the structure of Pt-Sn catalyst from an atomic level to nano-scale. The synthesized Pt-Sn catalysts exhibit high efficiency in the production of propylene from propane dehydrogenation reaction.

2. Experimental
A grafting synthesis approach based on surface organometallic chemistry concept was used for the preparation of Pt-Sn bimetallic catalysts. This synthesis was carried out by a sequential grafting of Pt and Sn organometallic complex at the surface of dehydrated SiO$_2$, Al$_2$O$_3$ and TiO$_2$ at room temperature. A condensation between hydroxyl group at the surface of support and alkyl group in Pt and Sn organometallic complex resulted in a formation of anchored surface compounds. Then, a hydrogenysis of the formed surface compounds in a flow of hydrogen at 100 °C for 1 hours led to an in-situ formation of Pt-Sn cluster at the surface of different supports. Pt-Sn catalysts on various supports with different Sn/Pt ratios were fully characterized by N$_2$ adsorption, XRD, Solid NMR, STEM, in-situ IR, and XPS techniques.

3. Results and discussion
Figure 1 shows STEM images of a typical sample of Pt-Sn bimetallic particles supported on Al$_2$O$_3$, which reveals that these ultra-fine Pt-Sn particles are homogeneously distributed at the surface of Al$_2$O$_3$, and no obvious agglomerate is observable at the surface of Al$_2$O$_3$. The formation of Pt-Sn cluster with a uniform distribution at the support surface is attributed to the application of unique surface organometallic chemistry strategy in the synthesis. Pt-Sn bimetallic particles synthesis precursors (organometallic complex) is chemically bonded to the support surface, which significantly prevents the growth and aggregation of Pt-Sn particles during the synthesis. Moreover, the mild synthesis condition is beneficial for the formation of small Pt-Sn clusters.
Figure 1. STEM of Pt-Sn bimetallic particles supported on Al₂O₃.

The prepared Pt-Sn catalysts exhibit high performance in propane dehydrogenation reaction (Figure 2). High propane conversion and propylene selectivity (close to 100%) were achieved at a low temperature of 550 °C, which corresponds to 38% propylene yield. Most importantly, these catalysts exhibited an excellent stability during the reaction, and no evident loss of activity was observed for time-on-stream of 24 hours.

Figure 2. Propane dehydrogenation to propylene over different Pt–Sn/Al₂O₃ catalysts at 550 °C.

4. Conclusion

Supported Pt-Sn catalysts were prepared by a unique surface organometallic chemistry strategy. This synthesis approach affords a promising opportunity for the precious control of structures of supported bimetallic catalysts. The synthesized Pt-Sn catalysts showed high performances for the production of propylene from propane dehydrogenation process. The enhanced catalytic efficiency of Pt-Sn catalysts is mainly ascribed to the homogeneous distribution of Pt-Sn cluster at the surface of support.

References