

Platinum-Tin Encapsulated Zeolite Catalysts with High Sn Loading: Boosted Performance in Methylcyclohexane Dehydrogenation

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Significance and Relevance

In this study, Pt-Sn bimetallic catalysts were designed for the first time with a high Sn content (2.8 wt.%-3.9 wt.%, Sn/Pt ratio = 6-8) in zeolite mother gel for methylcyclohexane (MCH) dehydrogenation. A well-defined Pt₁Sn₆@S-1 catalyst with a unique Pt core-Sn shell structure was prepared via a facile one-pot hydrothermal synthesis method. This encapsulated catalyst exhibited excellent catalytic performance and overwhelming superiority over supported catalysts, showing high activity (1343 mmol_{H₂}/g_{Pt}/min), toluene (TOL) selectivity (~100%), and durability (>80% for 33 h).

Introduction and Motivations

MCH dehydrogenation to TOL is one of the desired reaction systems for hydrogen storage and production due to its low toxicity, high reusability, and high hydrogen density.¹. Pt-based catalysts are currently the mainstream materials for this reaction, but these catalysts still suffer from insufficient activity, low selectivity, and short-term stability. The further improvement of catalytic performance is of great significance for the application of MCH catalysts. Alloying with Sn could effectively modify the local structure of Pt,² thus promoting the performance; encapsulating Pt-Sn species in zeolite matrix could prevent sintering,³ achieving high activity and stability. Herein, PtSn@S-1 catalysts were prepared, and the structure-property relationship was systematically studied.

Materials and Methods

The catalysts were prepared by a one-pot hydrothermal synthesis method.⁴ The Pt and Sn precursor solution with different Sn/Pt ratios, tetrapropylammonium hydroxide, tetraethyl orthosilicate and deionized water were mixed and stirred for 6 h to prepare the zeolite mother gel. After hydrothermal treatment (170 °C for 3 d), followed by centrifugation, drying (80 °C for overnight) and H₂ reduction (400 °C for 2 h), the encapsulated Pt₁Sn_x@S-1 (x = 1, 4, 6, 8) catalysts were obtained. The activity test was performed at 300 °C using 50 mg of catalysts, and the feeding gas was 1.6% MCH/Ar (20 ml/min). The durability test was measured at 350 °C and co-fed with 1.6% MCH, 5% H₂ and Ar balance.

Results and Discussion

The Pt₁Sn₆@S-1 catalyst with high Sn loading (2.8 wt.%) was successfully prepared for MCH dehydrogenation with a H₂ revolution rate of 1343 mmol_{H₂}/g_{Pt}/min (Fig. 1a), which was nearly twice the activity of the reported best catalyst.⁵ The well formation of zeolite particles in MFI-type for these PtSn@S-1 catalysts with high Sn loading was confirmed by HAADF-STEM and XRD. Despite the high Sn/Pt ratio, the Pt nanoparticles in Pt₁Sn₆@S-1 was well dispersed with average size of only 1.4 ± 0.5 nm (Fig. 1b). On the contrary, Pt₁Sn₆/S-1 presented terrible Pt dispersion with a much higher Pt nanoparticle size of 3.1 ± 1.8 nm (Fig. 1c). Compared with supported Pt₁Sn₆/S-1, no XPS signals of Pt could be observed for Pt₁Sn₆@S-1 catalysts (Fig. 1d), confirming the encapsulation of Pt in S-1 zeolite matrix. Although Sn primarily exists in an oxidized form in both Pt₁Sn₆/S-1 were extra-framework Sn species on the surface of zeolite proved by UV-Vis. Combined with the characterization of CO-FTIR and WT-EXAFS, a unique Pt core-Sn shell structure was confirmed for Pt₁Sn₆@S-1 catalyst.

As shown in Fig. 1e, the initial activity (at 10 min) could be significantly improved along with the Sn/Pt ratio, and $Pt_1Sn_6@S-1$ showed the highest MCH conversion rate without H_2 . The PtSn@S-1 catalysts with high Sn/Pt ratio of 6-8 presented minimal differences between initial activity and final activity (at 60 min), showing good stability. The selectivity of $Pt_1Sn_6@S-1$ have been checked by IR



spectra, and no peak assigned to by-product CH₄ could be detected, confirming the high TOL selectivity. The long-term stability of PtSn@S-1 catalysts were further measured and excellent durability (>80% for 33 h) was demonstrated for Pt₁Sn₆@S-1 even under a harsher condition (WHSV= 120,000 ml/g/h). Though a slight deactivation could be observed for Pt₁Sn₆@S-1 catalyst, this catalyst could be effectively regenerated by H₂, further confirming its excellent performance. The origin of this excellent performance has been further studied by MCH breakthrough curve, TOL-TPD, and the state of active sites after reaction.

In summary, Pt-Sn nanoparticles were successfully encapsulated within the S-1 zeolite matrix even with such high Sn loadings (2.8 wt.%-3.9 wt.%). These PtSn@S-1 catalysts demonstrated excellent activity, selectivity and durability for MCH dehydrogenation. A unique Pt core-Sn shell structure was generated over Pt₁Sn₆@S-1 catalyst. Owing to it, the electronic environment of Pt was altered and the TOL desorption properties were enhanced, thereby leading to excellent performance.



Figure 1 (a) Scheme of MCH dehydrogenation over $Pt_1Sn_6@S-1$; (b-c) HAADF-STEM images and (d) Pt 4f and Sn 3d XPS spectra of $Pt_1Sn_6@S-1$ and $Pt_1Sn_6/S-1$; and (e) activity test of PtSn@S-1 catalysts.

References

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