

# Suppressing Pt Sintering by Physical and Chemical Stabilization: Highly Regenerable PtGa/Al<sub>2</sub>O<sub>3</sub> Catalyst [1]

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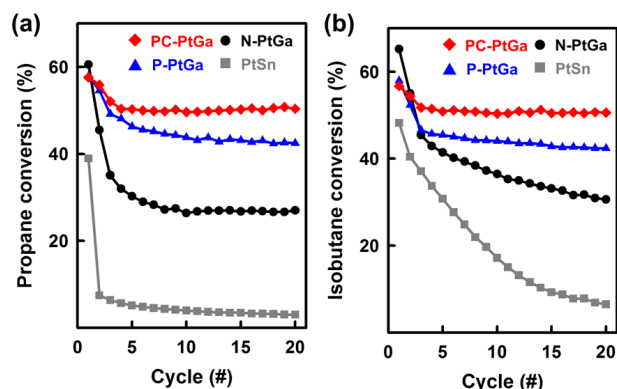
Due to the increasing demand of light olefin, light alkane dehydrogenation has gained increasing scientific attentions in these days. The dehydrogenation of light alkanes, however, requires very high reaction and regeneration temperature which can result in irreversible catalyst deactivation [2].

Recently, Sattler et al. reported a Pt-promoted Ga/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for highly active, selective, and regenerable propane dehydrogenation catalyst [3]. The catalyst showed superior catalytic activities even compared with a commercial CrO<sub>x</sub> catalyst. The catalyst showed conversion drop from 45% to 30% at the early cycles of catalytic reaction and regeneration, but afterward the catalyst showed stable catalytic performances. The initial conversion drop could be attributed to Pt sintering during catalyst regeneration because the authors reported significant Pt sintering after oxidation treatment at high temperature. In this respect, it is reasonably expected that stabilization of Pt under such a harsh reaction/regeneration condition can even further improve the catalytic performance of PtGa/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

In the present work, we investigated physical and chemical method for stabilizing Pt against thermal sintering. For the former, Pt was introduced during the synthesis of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> via sol-gel chemistry, which can increase the interfacial contact between Pt and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> due to the partial entrapment of Pt inside  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. For the latter, atomically dispersed Ce was doped on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which can stabilize Pt via strong Pt-O-Ce interaction. The physically stabilized Pt catalyst is denoted as 'P-PtGa', whereas the catalyst that is simultaneously stabilized physically and chemically is denoted as 'PC-PtGa'. For comparison, an ordinary, non-stabilized PtGa/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ('N-PtGa')

catalyst was also prepared using a commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support by the incipient wetness method reported by Sattler et al. [3]

Initial catalytic conversions of three catalysts during 20 reaction-regeneration cycles in propane and isobutane dehydrogenations are shown in Figure 1. Compared with N-PtGa, PC-PtGa catalyst showed remarkably improved catalyst stability in both reactions. P-PtGa catalyst showed intermediate behaviors between those of N-PtGa and PC-PtGa.



**Figure 1.** (a) Propane and (b) isobutane conversions over twenty repeated propane and isobutane dehydrogenation cycles.

ICP-AES and Ga K-edge XANES showed that all the samples retained their bulk Ga compositions and coordination states after 20 cycles of reactions indicating that Ga contents and states cannot explain the significant differences in the catalytic regenerability among the catalysts. On the other hand, HAADF-STEM investigation revealed that sintering degree of Pt increased in the order of PC-PtGa ( $d_{\text{TEM}}=4.4$  nm) < P-PtGa ( $d_{\text{TEM}}=8.2$  nm) < N-PtGa ( $d_{\text{TEM}}=18$  nm) after 20 cycles of propane dehydrogenation. Consistent with HAADF-STEM analysis, CO chemisorption value decreased in the order of PC-PtGa > P-PtGa > N-PtGa. The present results clearly revealed that the physical and chemical stabilization of Pt can significantly increase the catalytic stability under high temperature reaction/regeneration cycles.

## REFERENCES

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- [2] J.J.H.B. Sattler et al., Chem. Rev., 114 (2014) 10613.
- [3] J.J.H.B. Sattler et al., Angew. Chem. Int. Ed., 126 (2014) 9405.