

## Characteristics of Coke Formation over Pt/Al<sub>2</sub>O<sub>3</sub> Catalysts in Propane Dehydrogenation

Jinsoo Choi\*, Won-Il Kim, Hyong Lim Koh, Young Kyo Choi  
Petrochemical Team, Hyosung R&DB Labs., 183, Hoge, Dongan, Anyang, Gyeonggi  
431-080 (Korea)  
\*choijinsoo@hyosung.com

### Introduction

The increase in propylene demands during the last 20 years requires an alternative technology because of the poor selectivity to propylene in traditional processes such as steam cracking and fluid catalytic cracking. Direct propane dehydrogenation (PDH) resolves the stringent problem producing highly selective propylene (selectivity > 80%), and it recently becomes a commercially promising technology, especially in the Middle East area [1].

Studies are still conducted to overcome the intrinsic constraints like thermodynamic equilibrium and endothermic energy via oxidative dehydrogenation and isothermal reactions. A variety of efforts in minimizing the coke formation has also been devoted to prolonging the catalytic activity and the life time [2]. Coke formation is strongly dependent upon catalytic active sites, reaction conditions, and other structural defects of metal oxides. The formation usually occurs in two step procedures as the activation energy for the monolayer formation is smaller than that for the multilayer [3-4].

In this study, efficient retardation of the coke formation has been achieved using Pt-based catalysts by doping attenuates, restructuring alumina supports, and adjusting reaction conditions. The unique characteristics of the resulting cokes can provide an optimized operational condition including catalyst regeneration and a new strategy for catalyst synthesis.

### Materials and Methods

The reaction was carried out in a plug flow reactor at isothermal and isobaric conditions. The cokes formed within 20 hrs reaction were analyzed by temperature programmed oxidation (TPO) with 5% O<sub>2</sub>/He with detecting CO/H<sub>2</sub>O/CO<sub>2</sub> effluents via Quadrupole Mass Spectroscopy. Platinum-alumina catalysts were synthesized by a conventional impregnation method. Comparisons were also made with many of catalysts from an actual PDH plant.

### Results and Discussion

Coke formation rate gradually increases as a function of reaction time resulting in a gradual decrease in catalytic activity. The selectivity, however, does not decrease as fast as the conversion does. The resulting cokes are analyzed by TPO, simply showing a bimodal pattern of species. Monolayer appears dominantly at the beginning of reaction, and then multilayer cokes abruptly increase to the amount as shown in Fig. 1. After accumulated at 0.1 wt.%, the cokes become rigid and entangled on the catalyst surface.

Characteristics of active sites are not much affected by the coke formation. The selectivity usually maintains initial values even with a gradual decrease in conversion. The active sites, however, is highly susceptible to metal contaminants, and this contamination eventually causes high coke levels and catalytic deactivation. The result implies that the cokes

are readily formed at defects of catalysts created mostly during the commercial process. The activity decrease from gradual encroachment by cokes is rather negligible.

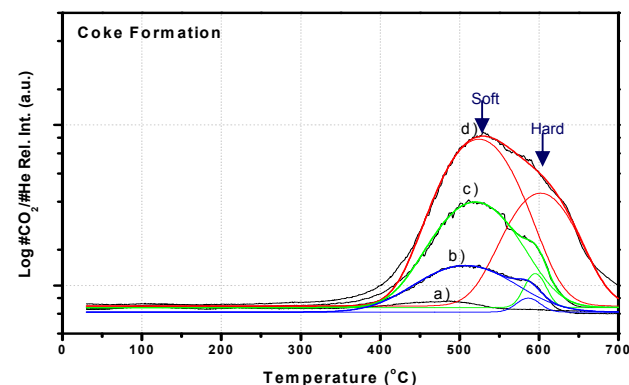
**Table 1. Changes in catalytic activity with various metal contaminants after 20 hrs reaction at the condition of 620°C, 0.5 atm, C<sub>3</sub>H<sub>8</sub>/H<sub>2</sub>=1.0, and total flow rate=480 ml/min**

Catalyst	Conv	Selec	Coke formation
Catalyst A	33.9	96.7	3.96 %
Catalyst A + Metal 1	29.9	95.8	6.95 %
Catalyst A + Metal 2	11.1	91.4	7.28 %
Catalyst A + Metal 3	6.5	86.0	7.09 %

Initial activities over catalysts shown in Table 1 exhibited similar values of 38% in conversion and 95% in selectivity. Very small amounts of metal contaminants less than 0.01 wt.% became the major cause in an abrupt increase of coke formation as well as catalytic deactivation.

### Significance

Diminishing coke level on catalysts is a crucial factor for determining regeneration rates that directly correlates with the catalytic selectivity and the unit consumption. Energy and cost savings are largely dependent on the operational variations such as the level of coke formation.



**Figure 1.** Temperature programmed oxidation of dehydrogenation catalysts with coke levels of a) 0.037 wt.%, b) 0.150 wt.%, c) 0.598 wt.%, and d) 1.245 wt.%.

### References

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