

Development of superior Cr₂O₃/Al₂O₃ catalysts for fixed bed dehydrogenation of light alkanes

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Introduction

The Houdry® process is an established technology in Industry [1-3], used to produce on-purpose olefins such propene, isobutene and butadiene. These olefins are used for production of various important commodity chemicals such as polypropylene, propylene oxide, and isooctene. The dehydrogenation of light alkanes is thermodynamically challenging (1) with commercially relevant production yields being achieved only at temperatures of 550-700°C.



The catalyst is cycled through dehydrogenation, coke burn-off and reduction cycles within approximately 20 minutes. This environment is extremely challenging for any catalyst and significant catalyst degradation is seen in the plant process within 2-3 years. The activity of the catalysts declines with time on stream, the surface area is reduced and Cr transforms in into the catalytically inactive α -Cr-alumina phase [4]. The aging process results in a catalyst with increased skeletal density, low surface area and low activity and selectivity in the dehydrogenation reaction. In order to develop a catalyst with improved lifetime over the state of the art, we combine accelerated aging tests, compositional variations in the catalyst and activity testing as well as characterization of aged catalyst samples.

Materials and Methods

Catalysts investigated are commercial Houdry® catalysts in addition to developmental formulations with small amounts metal oxide promoters as well as processing variations in catalyst preparation.

Catalysts (20g samples) were aged in a tubular plug flow reactor at 800-900°C, or alternatively, sample baskets were inserted into catalyst beds in commercial isobutene dehydrogenation reactors. The catalysts were removed from the reactors after 18-24 months on stream.

Characterization was done via XRD, BET surface area, N₂ and Hg porosimetry as well as activity testing in a tubular plug flow reactor.

Results and Discussion

Several Catalyst samples were prepared by modification of the existing formulation with metal oxide promoters. These catalysts were tested comparatively in isobutene and propane dehydrogenation. In addition, the catalysts underwent accelerated aging protocols and were also aged in a commercial isobutene dehydrogenation reactor. The results show that the current commercial catalyst outperforms older formulations with respect to alkene yield and lifetime in the reactor. Experimental catalysts containing metal oxide promoters have a significantly improved hydrothermal stability vs. the commercial catalysts as seen by higher surface areas of aged catalysts and significantly higher alkene yield in activity testing. Comparison with aged catalysts from production plants shows that the hydrothermal aging, combined with redox

cycling closely resembles the surface area, α -Cr-alumina formation and activity of the plant-aged catalysts.

Activity tests of two catalysts (fresh and aged) show that the higher surface area retention also provides higher activity retention (Fig. 1). Selectivity of both fresh and aged catalysts was very high (>95%), and no distinction was possible based on selectivity. However, the activities and therefore the yields of alkene were significantly improved with modified catalysts 2. This increased yield translates directly in longer lifetime and higher process profitability. The formation of α -Cr-alumina was significantly reduced in material 2 (data not shown).

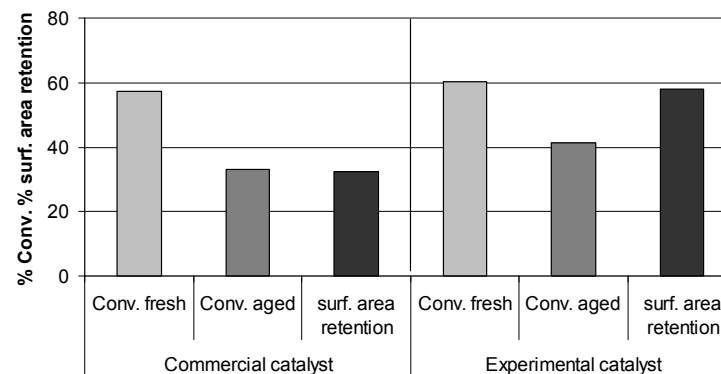


Fig. 1: Activity and surface areas of fresh aged catalysts

In conclusion, we were able to simulate plant aging using advanced aging protocols coupled with activity testing and characterization. New formulations containing metal oxide promoters show improved stability in the process with time-on-stream.

Significance

Development of improved economical fixed bed dehydrogenation catalysts is important for supporting new propene production facilities and to gain a better fundamental understanding of catalyst aging under severe hydrothermal and redox conditions.

References.

1. Bhasin, M.M., J.H. McCain, B.V. Vora, T. Imai, and P.R. Pujado, Appl. Catal. A: General, 221 (2001) 397-419.
2. Buyanov, R.A. and N.A. Pakhomov, Kinetics and Catalysis, 42 (2001) 64-75.
3. Weckhuysen, B.M. and R.A. Schoonheydt, Catal. Today, 51 (1999) 223-232.
4. Rokicki, A. Catalyst and Process Improvements for Increased Stability CATOFIN i-C4 and C4 Dehydrogenations. in USA Catalysts in Petroleum Refining and Petrochemicals; Proceedings of the Audi-Japanese Symposium. 2001.

