REDUCTION OF THE Al-Cr DEHYDROGENATION CATALYST SELECTIVITY AS A RESULT OF ITS DEACIVATION

Vladimir. Fridman*, Elizabeth Romaine- Schmidt
Sud-Chemie Inc, Louisville, KY 40210, USA
Vladimir.Fridman@sud-chemie.com

Introduction

The Al-Cr catalyst has been a subject of detailed studies and investigations for more than 100 years. However, there are still some unknown phenomena that require additional understanding of the system. One of these unexplained observations was a reduction of the olefin selectivity on the old version of the Al-Cr catalyst as a result of its deactivation [1]. This phenomenon was usually observed in the end of the catalyst life. The goal of the current study is to understand the changes with Al-Cr catalyst as a result of the catalyst deactivation that led to the sharp reduction of the main olefin selectivity.

Results and Discussion

This study was conducted on Cr_2O_3/Al_2O_3 catalysts prepared similar to [2]. A series of Al-Cr catalysts with different ages was tested for activity and selectivity in isobutane dehydrogenation in the temperature range 540-620 ˚C at LHSV-$2h^{-1}$.

The catalysts were aged by two methods to the different aging levels: by artificial accelerating aging method and in the adiabatic reactor at similar to commercial conditions. The aging levels were quantified by number of days operated in the red-ox regime assuming commercial operation conditions. The fresh and aged samples were studied by XRD and TEM-EDX. Surface area of chromium and its dispersion were determined by O_2 chemisorption. Acidity of the catalyst was measured by ammonia adsorption.

According to the results of this study, deactivation of the Al-Cr catalyst during red-ox cyclic operation in process of paraffin dehydrogenation is accompanied by steady reduction of the total surface area, by agglomeration of the chromium oxide and increasing of its clusters size. As result of the aging, a large proportion of chromium atoms **was** migrated from α-Cr_2O_3 to the solid solution of Cr_2O_3 in newly-produced α-Al_2O_3. The study of the surface composition of the catalysts with different ages indicated that ratio of Cr to Al was approximately constant and independent of the age. This indicates that migration of chromium from oxide to solid solution with α-Al_2O_3 did not lead to the migration of chromium atoms from the surface to the bulk of the carrier. Although the Cr atoms in the solid solution with α-Al_2O_3 were still on the surface of the catalyst, these chromium atoms had very low surface area and no activity in the dehydrogenation reaction. Similar activity was observed on the solid solution of α-Cr_2O_3 in α-Al_2O_3 which was synthesized, characterized and tested. Unlike the chromium atoms, the alkali metal atoms reduced their presence on the surface by migration from the surface to the bulk. It resulted in reduction of chromium surface area and catalyst activity (Table I). The isobutylene selectivity was relatively stable until the concentration of the solid solution of α-Cr_2O_3 phase in α-Al_2O_3 (Table I) was less than 50%. However, when concentration of the-(Cr, Al) phase became higher than 50% and dispersion of chromium was reduced at least three times, the catalyst selectivity started to deteriorate. The total catalyst acidity decreased with aging level of the sample. At the same time, the relative catalyst acidity per chromium surface area was almost stable for catalysts with age less than 300 DOS, but it grew sharply in the end of the catalyst life (Table I). It changed ratio between rates of main and side reactions and reduced isobutylene selectivity.

Table I: Properties of the fresh and aged Al-Cr catalysts

Catalyst Properties	Samples aged by artificially accelerated aging method				Samples aged at similar to commercial conditions		
Catalyst Age DOS*	0	30	270	380	180	350	645
Reduction of SA %	0	7	63	78	27	69	81
XRD α -Cr_2O_3 in Al_2O_3 % [wt]	0	ND	28.2	54.7	12.3	58.4	73
Chromium surface $m^2/m^2 *10^3$	9.8	5	3.4	3.3	3.1	3.4	2.9
Chromium Particle Diameter Å	180	375	1400	1800	790	1680	3200
Acidity mmol NH_3 /g	2.76	2.6	1.26	0.83	1.73	1.45	1.17
Relative acidity µmol NH_3 $/m^2$	23	24.5	29.1	32.2	24.9	29.5	5.2.1
Surface ratio Cr/Al at/at	0.2	0.19	0.19	0.19	0.19	0.22	0.21
Surface ratio alkali Me/Cr at/at$*10^2$	7.1	7.9	8.3	5.6	7.3	7.9	4.4
Reduction of isobutane conversion %	0	11	46.8	81.8	27.1	54.7	79.9
Isobutylene selectivity at 45% conversion	93.4	93.5	88.6	72.4	89.9	80.3	68.5
* Days On Stream (DOS) estimated for artificially aged catalysts							

Conclusion:

1) Deactivation of Al-Cr catalyst leads to the restructuring of the surface that results in the faster reduction of the amount of the dehydrogenation active sites than acid sites that reduces the catalyst selectivity.

2) The possible reason for increasing of the relative catalyst acidity is a migration of alkali metals from the catalyst surface to the bulk.

References

1) Information obtained from the customers.
2) US Patent No 2,956,030