Chromium oxide supported on Zr modified alumina for stable and selective propane dehydrogenation in oxygen free moving bed process

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Abstract: Propane dehydrogenation in oxygen free environment over alumina-supported chromium oxide catalysts with different chromium loading was studied within short time-on-stream range for the fluidized moving bed applications. For this purpose, a series of $CrO_x/Al_2O_3$and $CrO_x/Zr\text{-}Al_2O_3$ catalysts were prepared and examined. The activity loss was mainly due to agglomeration of the chromium species, reduction of the surface area, and transformation of Cr^{6+} species into stable Cr_2O_3 species. Contrarily, Zr modified alumina support successfully suppressed the formation of chromia/alumina solid solution phase and substantially improved the catalytic activity after the aging treatment by increasing the dispersion of chromium oxide.

Keywords: Chromia, Alumina, Zr modification, Propane, Dehydrogenation

1. Introduction

Propylene can be produced through a propane dehydrogenation in order to meet the regional demand and market supply-demand balance. Yet the demand for a new dehydrogenation technology, which can efficiently supply the sufficient heat needed for endothermic reaction and can continuously regenerate the catalyst in order to maximize the propylene production rate, has remained unsatisfied. For this reason, our group has investigated an Zr modified alumina oxide catalyst for a circulating fluidized moving process with oxygen looping system in which the catalyst is continuously circulated from reactor to regenerator.

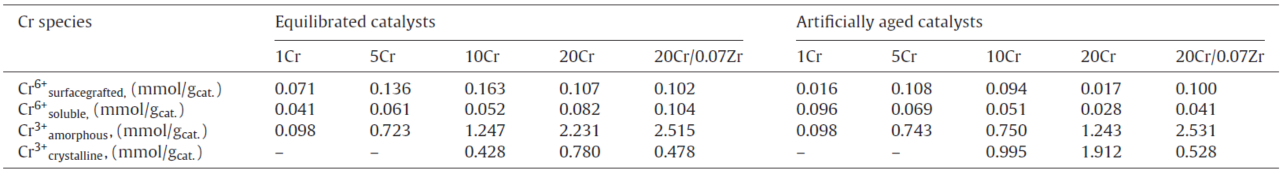
2. Experimental

Equilibrated and artificially-aged catalysts, CrO_x/γ-Al2O3 and CrO_x/Zr modified γ-Al_2O_3 catalysts, were characterized in order to investigate the factors affecting propylene selectivity and catalyst durability by pore analysis, temperature-programmed reduction (H2-TPR), temperature-programmed desorption (NH3-TPD), X-ray diffraction patterns (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS).

Dehydrogenation of propane was conducted in a continuous flow fixed-bed quartz reactor equipped with multi-position valves in the absence of external oxygen source. The reactant was pulse-injected at 600℃ for 16 s and the products were simultaneously sampled in 16-position valve at a 1 s interval.

3. Results and discussion

In order to quantitatively analyze different Cr species, H_2-TPRresults and XRD results are presented and investigated(**Table 1**). These quantitative analyses were carried out, based on the hypothesis that the reduction of Cr^{6+} with H_2 is theoretically proceeded by the reaction $\mathbf{2CrO_3 + H_2 \rightarrow Cr_2O_3 + 3H_2O}$.



Cr species	Equilibrated catalysts					Artificially aged catalysts				
	1Cr	5Cr	10Cr	20Cr	20Cr/0.07Zr	1Cr	5Cr	10Cr	20Cr	20Cr/0.07Zr
$Cr^{6+}_{surfacegrafted,}$ $(mmol/g_{cat.})$	0.071	0.136	0.163	0.107	0.102	0.016	0.108	0.094	0.017	0.100
$Cr^{6+}_{soluble,}$ $(mmol/g_{cat.})$	0.041	0.061	0.052	0.082	0.104	0.096	0.069	0.051	0.028	0.041
$Cr^{3+}_{amorphous}$, $(mmol/g_{cat.})$	0.098	0.723	1.247	2.231	2.515	0.098	0.743	0.750	1.243	2.531
$Cr^{3+}_{crystalline}$, $(mmol/g_{cat.})$	–	–	0.428	0.780	0.478	–	–	0.995	1.912	0.528

Table 1. Quantitative analysis of Cr species of the catalysts.

Increase of chromium content results in the formation of Cr/Al solid solution(**Fig. 1**). High dispersion of chromium oxide at high catalyst loading is very important for improving catalyst durability.

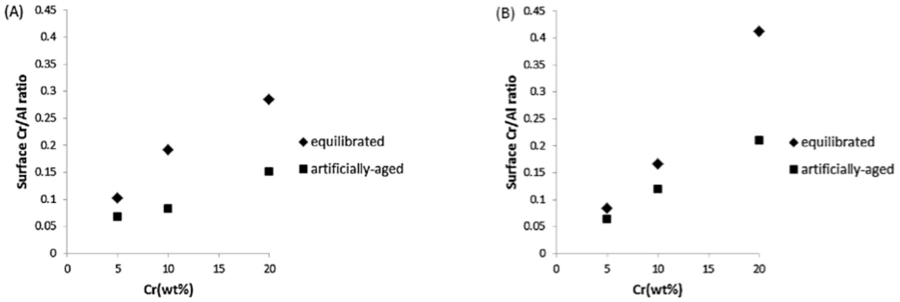


Figure 1. Surface Cr/Al atomic ratio as a function of Cr loading amount in equilibrated and artificially-aged (A) CrO_x/γ-Al_2O_3 catalysts and (B) CrO_x/Zr-Al_2O_3 catalysts (Zr/Al molar ratio, 0.07).

For equilibrated (**Fig. 2(A)**) catalysts, Zr-Al_2O_3 supported catalyst showed superior propylene selectivity for all conversion level. This result could be ascribed to the low propylene reactivity of Zr-Al_2O_3 support. After the artificial aging (**Fig. 2(B)**), while the conversion of Zr-Al_2O_3 supported catalyst decreased slightly, the conversion of Al_2O_3 supported catalyst decreased significantly. Thus, Zr-Al_2O_3 support enhanced not only the propylene selectivity but also the long-term catalyst stability.

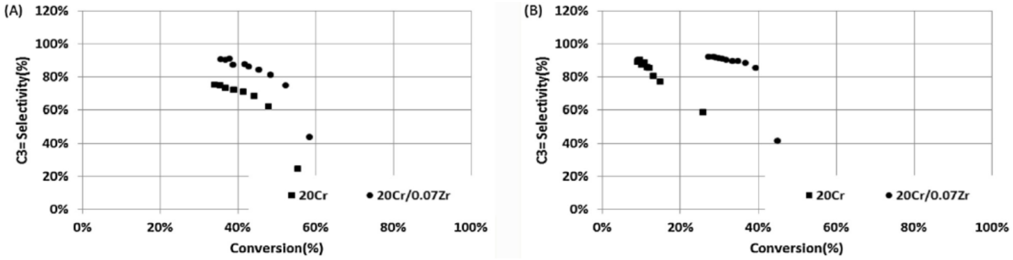


Figure 2. Propane dehydrogenation results performed over the (A) equilibrated and the (B) artificially-aged 20Cr catalysts and 20Cr/0.07Zr catalysts.

4. Conclusions

Propane dehydrogenation, using a number of equilibrated and artificially-aged CrO_x/γ-Al2O3 and CrO_x /Zr modified γ-Al_2O_3 catalysts, was carried out within short time-on-stream in the gas phase oxygen free condition. The catalyst samples were characterized for gaining insights into long-term catalyst stability and high propylene yield. The results obtained by pore and surface analyses revealed that the chromium species of the higher Cr loaded catalyst was more easily sintered and the sintering was more pronounced during the artificial aging treatment due to the mobility of the Cr species on alumina surface. The catalyst sintering in samples with high chromium loading was closely correlated with the reduced catalytic activity(propane conversion). When the chromia/alumina solid solution was formed during the artificial aging step, the propane conversion was decreased drastically. In order to solve this low catalyst stability, Zr-Al_2O_3 support was adopted. The enhanced catalyst stability and high propylene selectivity of Zr-Al_2O_3 supported catalyst were observed. These results were due to high dispersion of chromium oxide at high loading. With the successful suppression of α-Cr_2O_3 formation by zirconium modification, an optimal PDH catalyst applicable for a long-term operation in fluidized moving bed could be designed.

References

1. S. Sim, S. Gong, W. C. Choi *et al.*, J. Mol. Catal. 436 (2017) 164-173.