Effect of sulfation treatment to transition metal oxide on propane dehydrogenation property

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Propylene is one of the most important monomer in petro-chemistry. The propane dehydrogenation (PDH, $C_3H_8 \leftrightarrows C_3H_6 + H_2$) have gained extensive attention due to a direct production from economic feed stock of propane to valuable propylene. Recently, the iron-based catalyst supported on sulfated alumina was reported to be highly active and selective for PDH [1]. Although the sulfation treatment was effective for an improvement of catalytic performances, the reason has not been clarified so far. Hence, in this study, the effect of the sulfation treatment was investigated to improve the catalytic performance of transition metal oxide, and to clarify the reason for a high dehydrogenation performance.

The catalyst support of γ-Al_2O_3 was prepared by a sol-gel method. Then, ammonium sulfate was added to γ-Al_2O_3 sol. After calcination processes, a sulfated γ-Al_2O_3 support (SO_4^{2-}/Al_2O_3) was obtained. The transition metal oxide (Cr, Mn, Fe, Co, Ni, Cu) was supported by an evaporation to dryness. After a calcination of the catalyst, the sulfated metal oxide catalyst (M/SO_4^{2-}/Al_2O_3, M: Cr, Mn, Fe, Co, Ni, Cu) was obtained. The activity test was performed using a fixed bed reactor. The feed gas and temperature were C_3H_8/He=5/45 ml/min and 600°C.

Figs.1 (a) and 1(b) show C_3H_8 conversion and propylene selectivity over the M/Al_2O_3 and M/SO_4^{2-}/Al_2O_3 catalysts (M: Fe, Co). The Fe/Al_2O_3 and Co/Al_2O_3 catalysts showed a high propane conversion, however severe coke deposition occurred on these catalyst, which caused a reaction stopping at about 1 h. On the other hands, the sulfation treatment improved a stability, although the conversion was slightly decreased. The activity was gradually increased with time on stream over the Co/SO_4^{2-}/Al_2O_3

catalyst. From Fig.1(b), the propylene was almost not produced over the M/Al_2O_3 (M: Fe, Co) catalyst, and the main products were the methane and ethylene (not shown here). These products might be produced via propane decomposition and propylene hydrogenolysis. While, the sulfated catalysts showed a high propylene selectivity. The side reaction was largely suppressed by the sulfation.

Figs. 2(a) and 2(b) show S_{2p} XPS spectra of the Co/SO_4^{2-}/Al_2O_3 catalyst before and after dehydrogenation. From Fig. 2(a), the S^{6+} species was observed at 169.7 eV, which was attributed to the SO_4^{2-} added in the as-made catalyst [2]. Over the used catalyst, the S^{6+} species as well as $S^{\delta-}$ species were observed over the catalyst after dehydrogenation reaction. The result indicated that the S^{6+} species was reduced to $S^{\delta-}$ due to a reductive atmosphere. The produced $S^{\delta-}$ might be an important role as active-site for PDH because of the increasing activity with time on stream, as shown in Fig.1(a).
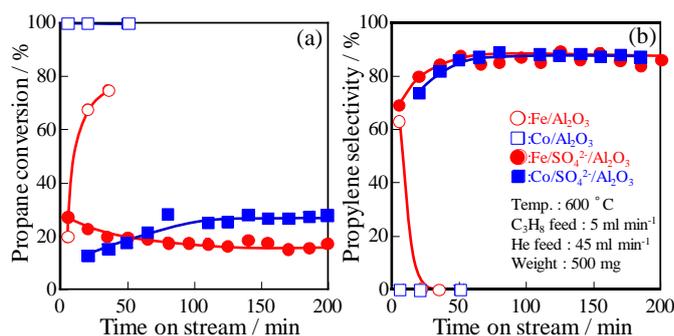

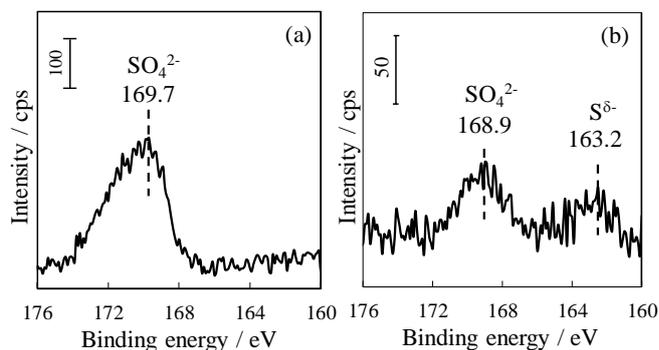Fig.1 Effect of sulfation treatment on dehydrogenation performance of Fe- and Co-based catalyst.

Fig. 2 XPS spectra of S_{2p} for Co/SO_4^{2-}/Al_2O_3 catalyst (a) before and (b) after PDH reaction.

REFERENCES

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[2] V.L. Tauson, *Dokl. Earth Sci.*, 425(3) (2009) 471-475.