18B/2003G079

In-situ XAFS studies on structural change in mesoporous silica anchored Mo catalysts during 1-butene photo-metathesis reaction

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Introduction

Molecularly dispersed Mo catalysts supported on silica show a photo-activity toward an olefin photo-metathesis reaction. The active center of the photo-catalysis is the metal-carbene species [1], and hence, the control of the selectivity is difficult.

MCM-41 or SBA-3 possesses the highly ordered hexagonal mesoporous structures. These mesoporous space can be modified by introducing metal oxides to exhibit the steric effect around the active site. Thus, we prepared Mo/MCM-41 or Mo-SBA-3 catalysts and examined the 1-butene photo-metathesis activity.

We have already prepared an *in-situ* XAFS cell that could be used under irradiation and reaction gas passage [2]. The structural change around Mo atoms under the 1-butene photo-metathesis reaction was observed by using the *in-situ* XAFS technique. The effect of Mo atom distribution on the deactivation process is also discussed.

Experimental

Mo/MCM-41 catalysts were prepared by immersing MCM-41 in $MoCl_5$/cyclohexane under N_2. Mo-SBA-3 catalysts were synthesized using the $(NH_4)_6Mo_7O_{24}$ as Mo precursor. Mo loading was regulated to 10 wt%.

XAFS measurements were performed at BL-10B by using *in-situ* XAFS cell for photocatalysis. Mo K-edge *in-situ* XAFS spectra were collected in a transmission mode under an 1-C_4H_8 flow with 75 W high-pressure Hg lamp irradiation.

Results and discussion

Mo species in the Mo-SBA-3 and the Mo/MCM-41 catalysts were so highly dispersed that no crystalline MoO_3 diffraction peaks were observed (not shown). However, *ex-situ* XAFS analysis revealed that the small Mo clusters were formed in Mo/MCM-41.

The XAFS data were analyzed by curve-fitting (CF) method using empirically extracted parameters from K_2MoO_4. Coordination numbers (CN) of a Mo-oxygen coordination for each catalyst were evaluated and were normalized as shown in Figs. 1(A) and 1(B). The CN of Mo=O for both catalysts greatly diminished as introducing 1-butene under UV irradiation and kept constant after 60 min (Fig. 1(A)).

On the other hand, the behavior of CN(Mo-O) change during the reaction was very different between the Mo/MCM-41 and the Mo-SBA-3 catalysts (Fig. 1(B)). The CN(Mo-O) change for Mo/MCM-41 showed almost the same profile as CN(Mo=O) did. It is suggested that the Mo-O-Mo structure was deformed as photo-metathesis reaction proceeded. The CN(Mo-O) for Mo-SBA-3 increased in the first step and gradually decreased.

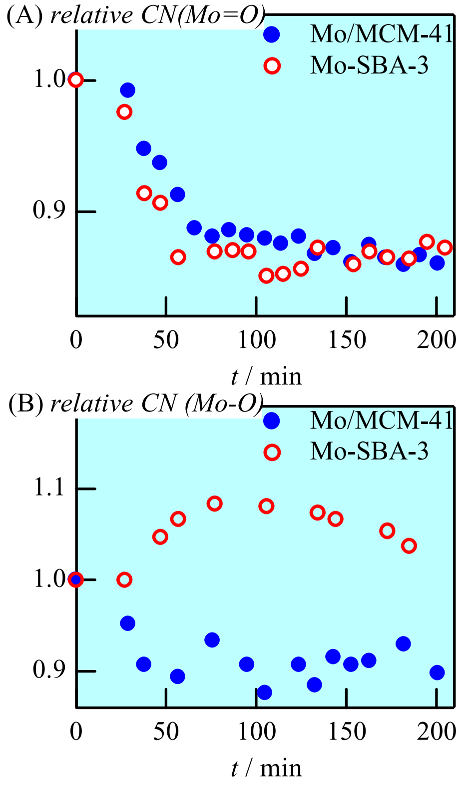

Fig. 1. Relative CN of (A) Mo=O and (B) Mo-O for Mo/MCM-41 and Mo-SBA-3 during 1-butene photo-metathesis reaction.

The deactivation processes for both catalysts were different. It seems that the recombination between Mo and support Si-O group is the main deactivation process for Mo-SBA-3.

References

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