

In-situ XAFS measurement of mesoporous silica supported Mo catalysts during 1-butene photo-metathesis reaction

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Introduction

The specific surface area of the highly ordered hexagonal mesoporous silica (MCM-41, SBA-3) is typically more than 1000 m²·g⁻¹, and it could be a good catalyst support. We prepared Mo/MCM-41 catalysts with high molybdenum loading (5-40 wt%) by using an ultrasonically controlled homogeneous deposition-precipitation method [1]. These catalysts showed an photoactivity toward an 1-butene photo-metathesis reaction.

The photo-catalysis depends on the local structure around a Mo atom and the support. In this study, structural change around Mo atoms under the 1-butene photo-metathesis reaction was observed by using the *in-situ* XAFS technique. The effects of the Mo loading and the preparation method on the catalysis are investigated.

Experimental

The ultrasonically controlled homogeneous deposition-precipitation method [1] was applied for the preparation of Mo/MCM-41 catalysts. The adequate amount of MCM-41 was added to a Mo(CO)₆ decalin solution, and the mixed solution was ultrasonicated under an ambient condition for 5 h. The filtrate was washed with pentane and was dried under vacuum [uls Mo/MCM, in short]. An impregnation catalyst was also prepared by using MoCl₅ and SBA-3 [imp Mo/SBA].

XAFS measurements were performed at BL-10B by using *in-situ* XAFS cell for photocatalysis [2]. Mo K-edge *in-situ* XAFS spectra were collected in a transmission mode under an 1-C₄H₈ flow with 75 W high-pressure Hg lamp irradiation.

Results and discussion

Fig. 1 showed the *in-situ* XANES spectra for 40 wt% uls Mo/MCM during the 1-butene photo-metathesis reaction. Each spectrum was collected every 10 min. The small pre-edge peak appeared at about 20000 eV is attributed to an 1s-4d transition peak, and its intensity depends on the symmetry around the Mo atom.

The relative pre-edge peak height of each catalyst was shown in Fig. 2. The intensity was slightly diminished with irradiation in the absence of 1-butene, which means that the pre-edge peak reflects the photo-excitation of Mo=O site (Fig. 2(A)). By introducing 1-butene under irradiation, an additional decrease of the pre-edge peak intensity was observed as shown in Fig. 2(B). It indicates

that the Mo=O site was consumed as the photo-metathesis reaction proceeded. It is clearly observed that the peak intensity reduction for the impregnation catalyst is faster compared with that for the ultrasonicated catalyst. The propene photo-metathesis reaction proceeded at the carbene species produced by the photo-excited Mo=O site from propene [2]. It seems that the rate of the carbene production and the deactivation rate are faster on the impregnation catalyst than on the ultrasonicated catalyst.

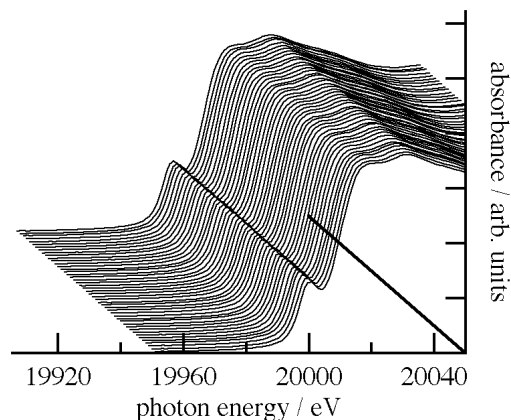


Fig. 1. *In-situ* XANES spectra for 40wt% uls Mo/MCM during the 1-butene photo-metathesis reaction.

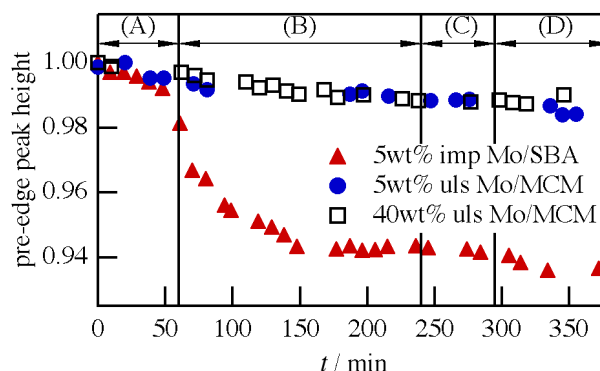


Fig. 2. Change in 1s-4d pre-edge peak height of Mo K-edge XANES spectra; (A) irradiated, (B) irradiated with 1-C₄H₈, (C) dark condition with 1-C₄H₈, (D) same as (B).

References

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