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Insight into the active site of MoO_x/SBA-15 in propene metathesis

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Introduction

Supported molybdenum oxide is an active catalyst for propene metathesis. The surface metal-carbene sites (Mo=CHR) generated from the reactant propene are believed as the active centers for the metathesis reaction. The carbene counting technique revealed that only less than 1% of total Mo atoms form carbene species [1], implying huge potential for catalyst improvement. Insight into the carbene formation process is necessary to understand the reason for this low participation and to strategize a gain of it.

We investigated propene adsorption onto MoO_x/SBA-15 by microcalorimetry and IR spectroscopy to get insight into the active site formation process. We have found that the amount of propene adsorption sites determined by microcalorimetry and the active site density measured by post-reaction carbene titration are consistent and correlate with the metathesis activity. Strong interaction of propene with MoO_x sites might be indicative for high specific activity of these sites in propene metathesis.

Experimental

Molybdenum was introduced onto mesoporous silica (SBA-15) through an amino-functionalization/anion exchange procedure [2], and the precursors were then calcined at 823K in air. In addition to physicochemical characterizations by N_2 physisorption, XRF, XRD, SEM-EDX, Raman and UV-Vis, adsorption of propene was studied by microcalorimetry and IR spectroscopy. Propene metathesis activity was measured using a conventional fixed bed gas flow reactor at 1bar and at 323K. Catalysts were activated at 823K for 0.5h and cooled to 323K in a dehydrated 20%O_2-Ar flow before testing. An improved version of the dynamic active site counting technique originally developed by Handzlik [1] was employed after the catalysis, wherein CD_2=CD_2 was used as the probe olefin to titrate Mo=CH-CH_3 centers which should liberate CD_2=CH-CH_3 via metathesis reaction. The amount of liberated CD_2=CH-CH_3 was quantified with a mass spectrometer. The twofold amount of CD_2=CH-CH_3 normalized by the weight of the catalyst was assumed as the active site density.

Results/Discussion

MoO_x/SBA-15 showed significant activity for the propene metathesis. The activity strongly depends on the molybdenum loading (Figure 1. a), the activities of 10 and 5%Mo catalysts after 15h TOS were 7.5 and 0.34 mmol g^{-1} h^{-1}, respectively. The active site titration procedure after the catalytic test estimated the carbene site density as 15 and 3.7μmol g^{-1} for 10% and 5%Mo, respectively. The higher value for 10%Mo is coherent with the activity result. However, the difference in activity is greater than that of active site density. This result implies that not only the active site density but also the intrinsic activity of the carbene site is higher for the 10%Mo.

The differential heat of adsorption of propene at reaction temperature (323K) onto MoO_x/SBA-15 pretreated at 823K in O_2 (0.2bar) was significantly higher than on bare SBA-15 (Figure 1. b). It should be noted that the metathesis reaction is essentially thermoneutral. The 10%Mo showed a plateau up to ~15μmol g^{-1} with a high differential heat of propene adsorption (~80kJ mol^{-1}). The concentration of these strong adsorption sites well coincides with the active site density measured by titration. The plateau-like adsorption energy profile evidences surface homogeneity. The 5%Mo showed less adsorption sites and weaker interaction at low coverage, which agrees with the lower activity as well as the lower intrinsic activity of the carbene site. The re-adsorption profiles of the two molybdenum containing samples after evacuation (not shown) were almost identical to the bare SBA-15, indicating strong and irreversible adsorption on MoO_x sites, which might be relevant to the genesis of the active carbene species.

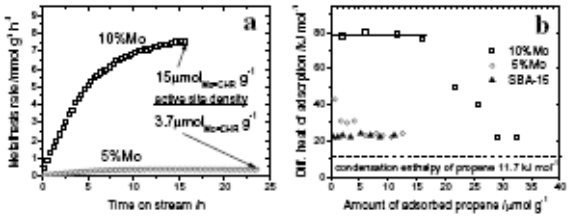

Figure 1. (a) Propene metathesis activity of MoO_x/SBA-15 at 323K. Results of post-reaction active site titration are inserted in the plot. (b) Differential heats of propene adsorption at 323 K on MoO_x/SBA-15 as a function of coverage.

References.

1. J. Handzlik , J. Ogonowski, *Catal. Lett.*, 88, 119(2003)
2. J. Thielemann, J. Kröhnert and C. Hess, *J. Phys. Chem. C*, 114, 17092(2010)