Study of the local structure of the molybdenum catalyst after high-temperature reduction in hydrocarbons atmosphere.

Mariya Myradova[1], Piotr Michorczyk[1], Anna Rokicińska[2], Piotr Kuśtrowski[2], Alexey Maximenko[3]

[1]Department of Organic Chemistry and Technology, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland
[2]Department of Chemical Technology, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland
[3]National Synchrotron Radiation Centre SOLARIS, Jagiellonian University, Czerwone Maki 98, 30-392 Krakow, Poland

Molybdenum-based catalysts are promising catalysts for olefin metathesis due to their high activity and selectivity at low temperatures (20-200°C). Typically, the active phase is deposited on a silica or alumina support. The commonly accepted catalytic mechanism of olefin metathesis is the carbene mechanism, in which metal alkylidene centres (active sites) are formed in-situ as a result of contact of the metal oxide with the olefin. Still, the formation mechanism of these sites is unknown as well as the structure of the surface oxide forms is not well defined. The number of active sites can be increased by pre-activating the catalyst. High-temperature activation in hydrocarbon flow (CH_4, C_2H_4, C_3H_6) is one of several examples. During the TPRS tests in the CH_4 and C_3H_6 atmosphere, it was noticed that around 600°C, hydrocarbon decomposition products - CO, CO_2, H_2, and in the case of C_3H_6, additionally CH_4, begin to form. A further increase in temperature led to a decrease in H_2 and CO formation and benzene and ethylene began to emerge.[1,2] The behaviour of the catalyst below 600°C is similar to the initial stage of methane dehydroaromatization. This type of reaction usually utilizes zeolite-supported MoO_3. During the induction period, CH_4 is consumed without the formation of benzene, indicating that $Mo^{(VI)}$ become carbided, and above 600°C benzene and hydrogen are observed as main products.

MoO_3 with different content (n=3,5,10,20 wt.%) deposited on silica were subjected to a high-temperature reduction in short-chain alkanes. According to the literature,[3] during high-temperature exposure in carbohydrates atmosphere MoO_3 should change it's local structure depending on it loading on the surface of the support into oxycarbides and/or carbides, which may contribute to the formation of active sites in the low-temperature olefin metathesis reaction. To explain the bulk structure of MoO_3, structural changes caused by reduction with alkanes and the generation of active sites for metathesis, except basic physicochemical studies, XANES studies for $n MoO_3/SiO_2$ in oxidized and reduced states were performed.

In this communication, the effect of high-temperature reduction in alkane atmosphere on local structure of MoO_3 and catalytic activity of MoO_3/SiO_2 in low-temperature olefin metathesis is investigated.

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3. Schwach, P., Pan, X. & Bao, X. Direct Conversion of Methane to Value-Added Chemicals over Heterogeneous Catalysts: Challenges and Prospects. *Chem. Rev.* **117**, 8497–8520 (2017).