Dynamic Structure of Mo-O Species in Ag-Mo-P-O Catalyst for Oxidative Dehydrogenation of Propane

Xin ZHANG¹*, Hui Lin WAN², Wei Zheng WENG², Xiao Dong YI²

¹State Key Laboratory of C1 Chemistry and Technology, Department of Chemistry, Tsinghua University, Beijing 100084.
²State Key Laboratory of Physical Chemistry for Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen 361005

Abstract: The dynamic structure of Mo-O species in Ag-Mo-P-O catalyst was studied by in situ confocal microprobe laser Raman spectroscopy (LRS) and catalytic test. The results indicate Mo-O species of MoO₃ transformed to Mo-O species of AgMoO₂PO₄ in C₃H₈/O₂/N₂ (3/1/4) flow at 773 K. This behavior is closely relative to oxidative dehydrogenation of propane and intrinsic properties of Mo-O species. The Mo-O species of AgMoO₂PO₄ may be active species for oxidative dehydrogenation of propane.

Keywords: Propane, oxidative dehydrogenation, Mo-O species, dynamic structure.

Oxidative dehydrogenation of propane still suffers from the low selectivity with increasing conversion, so it needs innovative concepts in the development of the catalysts to improve their catalytic performance. A better understanding the catalyst structure under the reaction conditions will be very helpful in search for a better catalyst. Unfortunately, few in situ studies in this area have been carried out so far 1-3. In this paper, the dynamic structure of Mo-O species in Ag-Mo-P-O catalyst was studied during oxidative dehydrogenation of propane by in situ confocal microprobe laser Raman spectroscopy (LRS) and evaluated the catalytic performance. The dynamic structure of Mo-O species in the catalyst, and its influence on catalytic performance are discussed.

Ag-Mo-P-O catalyst was prepared by the method of grinding (NH₄)₂H₂PO₄, MoO₃ and Ag₂O powder (Ag/Mo/P = 0.3/1/0.6, mole ratio) with certain amount of deionized water. The sample was dried in air at 383 K. After drying, the sample was calcinated at 623 K for 5 h and then at 823 K for 12 h.

The catalytic test was carried out at atmospheric pressure in a continuous flow system with a fixed bed quartz tube reactor (i.d.=6 mm). The feedstock and products were analyzed with two on-line gas chromatograph operating three columns, carbon molecular sieve column and Al₂O₃ column impregnating squalane (102-GC, TCD) for the separation of C₃H₈, C₂H₆, C₃H₆, C₂H₄, CO, CO₂, and GDX-103 (103-GC FID) for the separation of acrolein, acetone and propional, etc.

*E-mail: zhangxinzhanzen@yahoo.com.cn
XRD measurement was carried out by Rigaka Rotflex X-rays powder diffractometer with Cu Kα (λ=0.15064 nm). The in situ LR spectra were recorded by confocal microprobe laser Raman system (LabRaman I, Dilor) equipped with CCD detector, confocal microprobe and holographic notch filter. The Raman spectra were excited by an Ar+ laser (632.8 nm) with a power 5 mW. Before each experiment, the sample was heated at 773 K for 30 min in O2 flow and cooled to room temperature in the same flow.

No significant catalytic activity was found over Ag-Mo-P-O catalyst in the flow of C3H8/O2/N2 (3/1/4) below 673 K. When reaction temperature rising to 773 K, 67.9% selectivity in propene with 10.9% conversion of propane was obtained.

Figure 1 XRD pattern of Ag-Mo-P-O catalyst

Figure 2 in situ confocal microprobe laser Raman spectra of Ag-Mo-P-O catalyst in C3H8/O2/N2 (3/1/4) flow at specified temperatures.

The XRD pattern showed that the catalyst was mainly composed of MoO3 and AgMoO2PO4 (Figure 1). The Raman spectra of Ag-Mo-P-O catalyst in the flowing C3H8/O2/N2 (3/1/4) with flow rate 20 mL/min at specified temperature are shown in Figure 2. MoO3 could be detected by the bands at 996 (νMo=O), 818 (νas Mo-O-Mo), 666 (νs Mo-O-Mo) cm−1. The Raman spectra belonging to AgMoO2PO4 were found near 943, 910 (νMo=O), 882, 843 cm−1 (νas Mo-O-Mo). With increase of the reaction temperature, the intensity of Raman bands decreased gradually. At 773 K (the temperature of propane oxidation), only the Raman bands assignment to AgMoO2PO4 was found and the bands intensity hardly changed within 15 min. These phenomena suggested that the Mo-O species of MoO3 might transform to the Mo-O species of AgMoO2PO4 in the flowing C3H8/O2/N2 (3/1/4) at 773 K, and the Mo-O species of AgMoO2PO4 remained stable under such reaction conditions. 67.9% selectivity in propene with 10.9% conversion of propane was obtained on Ag-Mo-P-O catalyst in C3H8/O2/N2 (3/1/4) flow at 773 K, therefore, the Mo-O species of AgMoO2PO4 may be the active species for oxidative dehydrogenation of propane.
Figure 3 presents Raman spectra of O$_2$-pretreated Ag-Mo-P-O catalyst exposed to a flow of C$_3$H$_8$/N$_2$ (4/21). Both Raman bands of MoO$_3$ and AgMoO$_2$PO$_4$ could be detected on the catalyst at the temperature below 673 K. At 773 K, however, only the Raman bands of AgMoO$_2$PO$_4$ could be observed, and the bands intensity decreased continuously within 15 min. Subsequently, the sample was exposed to C$_3$H$_8$/N$_2$/O$_2$ (3/1/4) flow for 15 min. The Raman bands attributed to AgMoO$_2$PO$_4$ and MoO$_3$ were found to appear again. After that, it was switched to a flow of O$_2$ at 773 K, the bands intensities of both AgMoO$_2$PO$_4$ and MoO$_3$ were found to increase. These results indicated that the transformation of Mo-O species was closely related to propane oxidation over the catalyst.

MoO$_3$ is a complicate layer and zigzag raw structure, which is built by rather distorted [MoO$_6$]$^{6-}$ octahedron. In c axis direction (001), there are holes in MoO$_3$ layer structure. Such structure makes the transformation of Mo-O species in MoO$_3$ possible.$^{5-8}$ McCarron$^8$ observed that α-MoO$_3$ could transformed to β-MoO$_3$ by thermal treatment. Mestl et al.$^5$ considered that the reduction of MoO$_3$ or MoO$_3$-supported oxide led to different MoO$_x$ species such as surface complex, cluster, extended structure, etc.

In the framework of AgMoO$_2$PO$_4$, six [MoO$_6$]$^{6-}$ octahedron are connected with six [PO$_4$]$^{3-}$ tetrahedron to form heteropolyoxymolybdate. Six Mo atom coordinate with nineteen oxygen atom in this heteropolymolybdate, that is, Mo-O species of AgMoO$_2$PO$_4$ like [Mo$_{6}$O$_{19}$]$^{1-}$ species.$^9$ In addition, the characteristic Raman bands of [Mo$_{6}$O$_{19}$]$^{1-}$ species appear near 940 and 910 cm$^{-1}$ which are similar to the characteristic Raman bands of AgMoO$_2$PO$_4$. This result further confirmed that the structure of Mo-O species in AgMoO$_2$PO$_4$ is similar to [Mo$_{6}$O$_{19}$]$^{1-}$ species. [Mo$_{6}$O$_{19}$]$^{1-}$ species has Lindqrist- Aronsson structure which has very low reduction potential and can keep structure stable in oxidation-reduction process.$^{10}$ Hence, Mo-O species of AgMoO$_2$PO$_4$
can effectively carry through Mars van Krevelen redox cycle and keep the structure stable under the reaction condition of propane oxidation, leading to the higher selectivity in propene and activity of oxidative dehydrogenation of propane. Lee et al.\textsuperscript{11} considered a cluster type of molybdenum oxide MoO\textsubscript{x} on the MgMo\textsubscript{x}O\textsubscript{y} catalyst surface was necessary for the oxidative dehydrogenation of propane to propene while the crystalline surface MoO\textsubscript{3} had no effect on this reaction. These reports are in agreement with our observations.

Acknowledgment

Thanks the financial support of Ministry of Science and Technology (G1999022408).

References


Received 19 December, 2001