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

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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 MoO_3 transformed to Mo-O species of $AgMoO_2PO_4$ in $C_3H_8/O_2/N_2$ (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 $AgMoO_2PO_4$ 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 $(NH_4)H_2PO_4$, MoO_3 and Ag_2O 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 tubular 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 Al_2O_3 column impregnating squalane (102-GC, TCD) for the separation of C_3H_8, C_3H_6, C_2H_4, C_2H_6, CO, CO_2, and GDX-103 (103-GC FID) for the separation of acrolein, acetone and propanal, *etc*.

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XRD measurement was carried out by Rigaka Rotflex X-rays powder diffractometer with Cu $K\alpha$ (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 O_2 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 $C_3H_8/O_2/N_2$ (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.

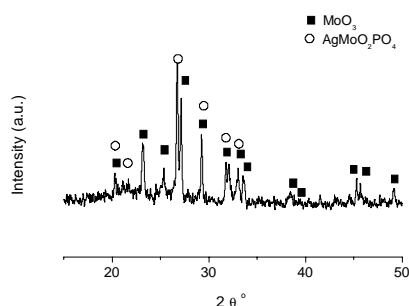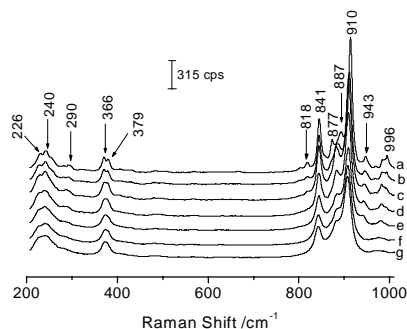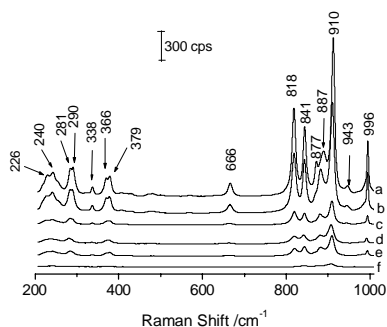**Figure 1**   XRD pattern of Ag-Mo-P-O catalyst

Figure 2   *in situ* confocal microprobe laser Raman spectra of Ag-Mo-P-O catalyst in $C_3H_8/O_2/N_2$ (3/1/4) flow at specified temperatures.

a: r.t., b: 373 K, c: 473 K, d: 573 K e: 673 K, f: 773 K-5 min, g: 773 K-15 min.

The XRD pattern showed that the catalyst was mainly composed of MoO_3 and $AgMoO_2PO_4$ (**Figure 1**).   The Raman spectra of Ag-Mo-P-O catalyst in the flowing $C_3H_8/O_2/N_2$ (3/1/4) with flow rate 20 mL/min at specified temperature are shown in **Figure 2**. MoO_3 could be detected by the bands at 996 ($\nu_{Mo=O}$), 818 ($\nu_{as\ Mo-O-Mo}$), 666 ($\nu_{s\ Mo-O-Mo}$) cm^{-1}[5,6].   The Raman spectra belonging to $AgMoO_2PO_4$ were found near 943, 910 ($\nu_{Mo=O}$), 882, 843 cm^{-1} ($\nu_{as\ Mo-O-Mo}$)[7].   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 $AgMoO_2PO_4$ was found and the bands intensity hardly changed within 15 min.   These phenomena suggested that the Mo-O species of MoO_3 might transform to the Mo-O species of $AgMoO_2PO_4$ in the flowing $C_3H_8/O_2/N_2$ (3/1/4) at 773 K, and the Mo-O species of $AgMoO_2PO_4$ 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 $C_3H_8/O_2/N_2$ (3/1/4) flow at 773 K, therefore, the Mo-O species of $AgMoO_2PO_4$ may be the active species for oxidative dehydrogenation of propane.

Figure 3(a) *in situ* confocal microprobe laser Raman spectra of Ag-Mo-P-O catalyst in C_3H_8/N_2 (4/21) flow at specified temperatures.

Figure 3(b) *in situ* confocal microprobe laser Raman spectra of Ag-Mo-P-O catalyst in different gas flows at 773 K.

a: r.t., b: 373 K, c:473 K, d:573 K, e: 673 K, f: 773 K-15min.
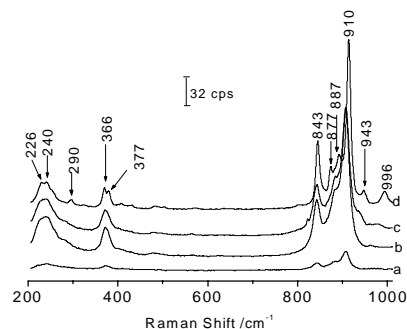
a: in C_3H_8 for 15min, b: in $C_3H_8/O_2/N_2$ flow for 5min after a, c: in $C_3H_8/O_2/N_2$ flow for 15min after a, d: in O_2 flow for 5min after c.

Figure 3 presents Raman spectra of O_2-pretreated Ag-Mo-P-O catalyst exposed to a flow of C_3H_8/N_2 (4/21). Both Raman bands of MoO_3 and $AgMoO_2PO_4$ could be detected on the catalyst at the temperature below 673 K. At 773 K, however, only the Raman bands of $AgMoO_2PO_4$ could be observed, and the bands intensity decreased continuously within 15 min. Subsequently, the sample was exposed to $C_3H_8/N_2/O_2$ (3/1/4) flow for 15 min. The Raman bands attributed to $AgMoO_2PO_4$ 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 $AgMoO_2PO_4$ 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[6-8]. 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 $AgMoO_2PO_4$, six $[MoO_6]^{6-}$ octahedron are connected with six $[PO_4]^{3-}$ tetrahedron to form heteropolymolybdate. Six Mo atom coordinate with nineteen oxygen atom in this heteropolymolybdate, that is, Mo-O species of $AgMoO_2PO_4$ like $[Mo_6O_{19}]^{2-}$ species[9]. In addition, the characteristic Raman bands of $[Mo_6O_{19}]^{2-}$ species appear near 940 and 910 cm^{-1} which are similar to the characteristic Raman bands of $AgMoO_2PO_4$[5, 6]. This result further confirmed that the structure of Mo-O species in $AgMoO_2PO_4$ is similar to $[Mo_6O_{19}]^{2-}$ species. $[Mo_6O_{19}]^{2-}$ 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 $AgMoO_2PO_4$

can effectively carry though 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.*[11] considered a cluster type of molybdenum oxide MoO_x on the $MgMo_xO_y$ catalyst surface was necessary for the oxidative dehydrogenation of propane to propene while the crystalline surface MoO_3 had no effect on this reaction. These reports are in agreement with our observations.

Acknowledgment

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