Formation of Acrolein in the Propane Oxidation over VTeO/SiO_2 Catalysts

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VTeO/SiO_2 catalyzed the oxidation of propane into acrolein with a maximal yield of 6.6% obtained at 520 °C. The catalytically active sites of the catalysts were investigated using propene and allyl bromide as molecular probes. The V^{5+} sites were responsible for oxidative dehydrogenation of propane, whereas the Te^{4+} sites for α-H abstraction of propene and O-insertion of allyl species.

Direct oxidation of propane into oxygenates has been attracting interest for the utilization of hydrocarbon resources. The catalysts employed are mainly multi-component oxides. Among them, Mo–V–Te–O[1,2] and Mo–V–Te–Nb–O[3] catalysts showed high catalytic activity for the selective oxidation/ammoxidation of propane to acrylic acid and/or acrylonitrile. For the Mo-containing catalysts, it has been generally recognized that Te^{4+} is the active site for α-H abstraction of propene formed during (amm)oxidation of propane, while Mo^{6+} site for O or NH insertion.[4–6] Although V–Te–O[7] and Te–V–P–O[8] catalysts have been studied for methanol oxidation to formaldehyde and propane oxidation to acrylic acid, respectively, no further studies were made on supported V–Te–O catalysts for propane oxidation. Especially, no any studies were made on the role of Te^{4+} site over this binary oxide system. This communication reports for the first time the results of propane oxidation to acrolein over VTeO/SiO_2 catalysts, with emphasis on exploring how their catalytically active sites function in the reaction.

A series of VTeO/SiO_2 catalysts were prepared by wet impregnation of SiO_2 with an aqueous solution of ammonium metavanadate and tellurium acid. After being dried overnight at 110 °C, the samples were then calcined at 600 °C in air for 5 h and denoted as V_xTe_y/SiO_2, where x and y indicate atomic percents of V and Te, respectively. The catalytic activity for propane oxidation was measured in a fixed bed flow reactor (quartz tube, 5-mm i.d.) under the following conditions: $P_R = 1$ atm; $W_{cat} = 0.27$ g; feed (molar ratio) $C_3H_8/O_2/He = 1.2/1/1.2$; $F_{feed} = 17.6$ mL/min. The oxidation of propene and allyl bromide was performed with the pulse method at 420 and 300 °C, respectively. Pulse of 0.4 mL propene–oxygen mixture ($C_3H_6/O_2 = 1.2$), 0.4 mL propene or 0.3 µL allyl bromide was introduced into a stream of N_2 carrier gas passing through the catalyst bed (0.31 g) at a flow rate of 20 mL/min. The products were analyzed by gas chromatography. X-ray diffraction measurements were performed on a Rigaku Rotaflex D/max-C X-ray power diffractometer with Cu Kα radiation. XPS spectra were taken by a VG ESCLAB MK-II system with Al Kα (1486.6 eV) as the X-ray source. The C 1s as a reference signal was adjusted to 284.6 eV.

In the XRD studies, the peaks due to TeO_2 were clearly observed on 3Te/SiO_2 at $2\theta = 26.1$, 29.8, 37.3, and 48.6°, but no peaks of the phases containing V or Te could be detected on 3V/SiO_2 and $3V_xTe/SiO_2$ ($x = 0.1$–3.0) catalysts. It reveals that over the VTeO/SiO_2 catalysts, TeO_x and/or V–Te–O_x species are highly dispersed due to the interaction between V and Te species. XPS spectra of the catalysts above showed that the BE values of V $2p_{3/2}$ and Te $3d_{5/2}$ are 517.1 ± 0.1 and 576.4 ± 0.1 eV, assignable to V^{5+} and Te^{4+}, respectively.[9,11]

A series of VO_x/SiO_2 catalysts with various V contents (1–12%) were tested for propane oxidation at 500 °C. It was found that the main products were propene, CO and CO_2, while acrolein selectivity was less than 12%. With an increase in V loading, CO_x selectivity increased at the expenses of the selectivities to propene and acrolein, while propane conversion increased and attained a maximum value at 3% loading. The effect of Te added to 3V/SiO_2 on the catalytic action was studied and the results are shown in Figure 1. Under the reaction conditions, no activity was found for 3Te/SiO_2, but the addition of Te to 3V/SiO_2 led to a great change in the catalytic performance. At 500 °C (Figure 1a), the selectivity of acrolein increased with Te content, as opposite to the activity and the selectivity to propene. Meanwhile, the selectivity to CO_x sharply decreased at first and then remained almost unchanged as Te content exceeded 0.5%. In Figure 1b, the product selectivities of the catalysts are compared at 10% propane conversion. The results were obtained by changing reaction temperature from 450 to 500 °C. At the fixed conversion, CO_x selectivity increased with increasing Te content beyond 0.5%. It probably resulted from the elevated reaction temperature. Higher Te content led to lower activity, which required higher temperature for a fixed conversion, and thus resulted in a deep oxidation. Except for CO_x, the variation of product distribution with Te content was similar to that observed at 500 °C. The results indicate that in the propane oxidation on VTeO/SiO_2 catalysts, V^{5+} is mainly responsible for the activation of propane to produce propene, while Te^{4+} is beneficial to the transformation of propene to acrolein.

For 3V0.5Te/SiO_2 catalyst, the effect of reaction temperature on the catalytic performance for propane oxidation is shown

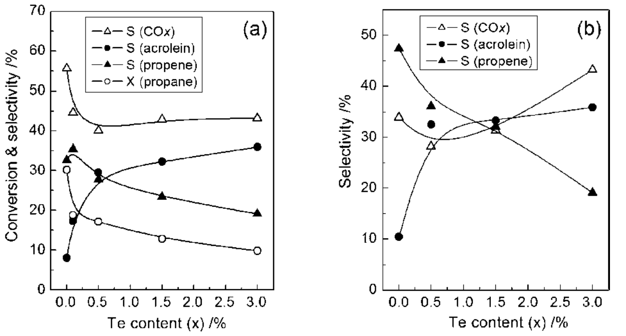

Figure 1. Catalytic performance of $3V_xTe/SiO_2$ catalysts for propane oxidation to acrolein at (a) 500 °C and (b) 10% propane conversion.

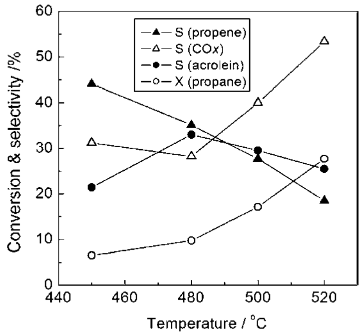

Figure 2. Effect of reaction temperature on the catalytic performance of 3V0.5Te/SiO_2 catalyst for propane oxidation to acrolein.

in Figure 2. Propane conversion increased monotonously with the temperature, as opposite to propene selectivity. The maximal yield of acrolein of 6.6% was obtained at 520 °C. Coinciding with propene selectivity decreasing from 44.1% at 450 °C to 35.1% at 480 °C, acrolein selectivity increased from 21.4 to 33.0%, whereas CO_x selectivity remained almost unchanged. This implies that the higher temperature promotes the conversion of propene to acrolein. With the further increase of temperature beyond 480 °C, CO_x selectivity sharply increased and acrolein formation declined due to deep oxidation.

The results above reveal that in the selective oxidation of propane to acrolein, propene is a dominant primary product. For propene oxidation to acrolein, it is generally believed that the reaction proceeds mainly through two steps, i.e, α-H abstraction of propene and O-insertion into allyl species.[10] To investigate the role of the catalytically active sites over the VTeO/SiO_2 catalysts, propene and allyl bromide were used as molecular probes and the reaction results were obtained by pulse method. The results of pulse experiments with C_3H_6 and C_3H_6/O_2 are shown in Figures 3a and 3b, respectively. In both that cases, 3V/SiO_2 showed the lowest activity among the catalysts studied and the activity increased with Te addition, as opposite to the case of propane oxidation. These could be attributed to that the α-H abstraction of propene is facilitated by Te^{4+} sites, since the α-H abstraction is generally believed as a rate-determining step in propene oxidation.[10] By comparing Figures 3a with 3b, it is also found that due to the presence of gas-phase oxygen, propene conversion and CO_x selectivity increased at the expense of acrolein formation. It indicates that the gas-phase oxygen and/or the surface oxygen species over the catalysts, which resulted from the adsorption and activation of the gas-phase oxygen, are active but less selective than the lattice oxygen in the reaction.

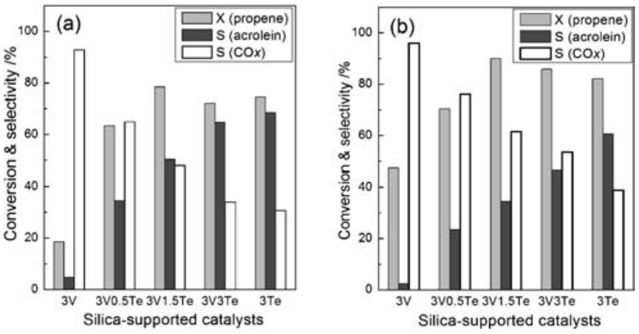

Figure 3. Results of pulse reactions of C_3H_6 (a) and C_3H_6/O_2 (b) over SiO_2-supported VTeO catalysts at 420 °C.

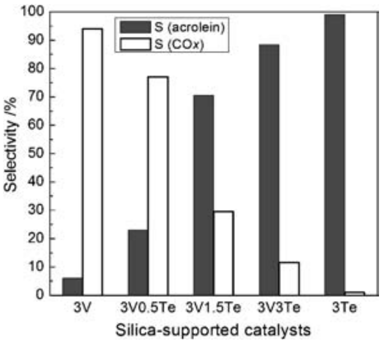

Figure 4. Results of pulse reaction of allyl bromide over SiO_2-supported VTeO catalysts at 300 °C.

The results of pulse experiments with allyl bromide are shown in Figure 4. Under the reaction conditions, allyl species is expected to be generated by decomposition of allyl bromide in situ in the catalytic reactor. Total conversion of allyl bromide was obtained on all the catalysts, but their products were quite different. On 3V/SiO_2 little acrolein was formed, while CO_x selectivity amounted to 94%. With the increase of Te content, the fraction of acrolein was notably increased and, especially, an acrolein selectivity of ca. 100% was attained on 3Te/SiO_2. It implies that Te^{4+} (actually oxygens associated) is effective in O-insertion of allyl species to form acrolein. Thus, it is more likely that during propane oxidation to acrolein over the VTeO/SiO_2 catalysts, the Te^{4+} sites are responsible not only for the α-H abstraction of propene, but also for the O-insertion into the allyl species. As for the V^{5+} sites, they are mainly active for oxidative dehydrogenation of propane, whereas less active for the subsequent step, i.e, propene oxidation to acrolein. The XRD results indicated an interaction between V and Te species on VTeO/SiO_2 catalysts. The interaction may also play a role in the catalytic reaction. Therefore, detailed characterizations and further studies are needed.

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References and Notes

1 W. Ueda, K. Oshihara, *Appl. Catal., A* **2000**, *200*, 135.
2 K. Oshihara, T. Hisano, W. Ueda, *Top. Catal.* **2001**, *15*, 153.
3 H. Watanabe, Y. Koyasu, *Appl. Catal., A* **2000**, *194–195*, 479.
4 J. C. J. Bart, N. Giordano, *J. Catal.* **1980**, *64*, 356.
5 R. K. Grasselli, *Appl. Catal.* **1990**, *57*, 149.
6 R. K. Grasselli, J. D. Burrington, D. J. Buttrey, P. DeSanto, Jr., C. G. Lugmair, A. F. Volpe, Jr., T. Weingand, *Top. Catal.* **2003**, *23*, 5.
7 G. Bliznikov, Y. Pesheva, D. Klissurski, M. Marinov, V. Kozhukharov, *Appl. Catal.* **1987**, *29*, 211.
8 M. Ai, *J. Catal.* **1986**, *101*, 389.
9 K. Asakura, K. Nakatani, T. Kubota, Y. Iwasawa, *J. Catal.* **2000**, *194*, 309.
10 M. M. Bettahar, G. Costentin, L. Savary, J. C. Lavalley, *Appl. Catal., A* **1996**, *145*, 1.
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