Effects of additives on the activity and selectivity of supported vanadia catalysts for the oxidative dehydrogenation of propane

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ABSTRACT

The activity and selectivity of alumina- and magnesia-supported vanadia for propane oxidative dehydrogenation can be enhanced by can be enhanced by interactions of vanadia with molydena for the alumina-supported catalyst and by phosphorous doping for the magnesia-supported catalyst.

1. INTRODUCTION

Oxidative dehydrogenation (ODH) of propane to propene is an attractive alternative to non-oxidative dehydrogenation, because ODH is favored by thermodynamics even at low temperatures and does not lead to the formation of coke and lower molecular weight products. Vanadia supported on Al_2O_3 and MgO have emerged as the most active and selective catalysts among those that have been investigated [1-8]. Investigations of propane ODH on VO_x/Al_2O_3 have shown that the highest specific activity is achieved at near-monolayer coverages of polyvanadate species, 7.5 V/nm^2 [2-8]. When vanadia is supported on MgO, neither polyvanadate nor V_2O_5 domains are formed and, instead, small domains of $Mg_3(VO_4)_2$ are formed [1, 2 (and references therein), 9]. The specific rate for ODH increases with increasing apparent surface density of V_2O_5, reaching a plateau at a surface density of about 4 V/nm^2, which corresponds closely to the surface density of VO_x in $Mg_3(VO_4)_2$. The objective of the present studies was to investigate whether even higher ODH activities and propene selectivities could be achieved by modification of alumina and magnesia supported vanadia. The influence of using a molybdena monolayer between the vanadia and the alumina was examined in the case of VO_x/Al_2O_3 [10], whereas doping the magnesia with phosphorous was examined in the case of VO_x/MgO [11].

2. Experimental

$VO_x/MoO_x/Al_2O_3$ was prepared as follows. Alumina was first impregnated with an aqueous solution of ammonium heptamolybdate in order to deposit an equivalent monolayer of MO_x on to the support. The deposited material was dried and then calcined in air at 773 K. Vanadia was then deposited on to this support via impregnation from a isopropanol solution of vanadyl isopropoxide. The dried material was then calcined a second time at 773 K. The BET surface area of the $VO_x/MoO_x/Al_2O_3$ materials was 190 m^2/g. Raman spectroscopy revealed that the molybdena layer decreased the tendency of vanadia to form V_2O_5 domains and enhanced the formation of polyvandate species. TPR experiments showed that the molybdena layer increased the reducibility of the dispersed vanadia relative to that observed for vanadia dispersed on pure alumina.

High surface area MgO (~200 m^2/g) was doped with P by adding an appropriate quantity of $(O)P(O^tBu)_3$ and then calcining this material in air at 823 K. Vanadia was then dispersed on the P-doped MgO by contacting the support with $(O)V(O^tBu)_3$ and then calcining the solid mixture in air at 823 K. The resulting material has a BET surface area of ~ 190 m^2/g. The only species observed by Raman spectroscopy is magnesium orthovanadate, irrespective of the degree of P-doping.

Propane ODH rates were measured in a quartz microreactor. The partial pressure of propane was 13.5 kPa and that of oxygen, 1.7 kPa. The reaction products were analyzed by gas chromatograph. The propane and oxygen conversions were kept below 2% and 20%, respectively, in all experiments.

3. RESULTS AND DISCUSSION

3.1 Effects of MoO_x on alumina-supported VO_x

Figure 1a shows initial propene formation rates normalized per V-atom as a function of V surface density. The specific rate of ODH reached a maximum at a surface density of ~7-8 VO_x/nm^2. At a given V surface density, propene formation rates are 1.5-2.0 times higher when VO_x is dispersed on MoO_3/Al_2O_3 than on pure Al_2O_3. The trend shown for high surface densities in Fig. 1 is consistent with the expected loss of accessibility of V centers as three dimensional V_2O_5 structures form at apparent VO_x surface densities above 7.5 V/nm^2.

The increase in the specific rate of propane ODH with V surface density below 7.5 V/nm^2 seen in Fig. 1a for vanadia dispersed in alumina and alumina

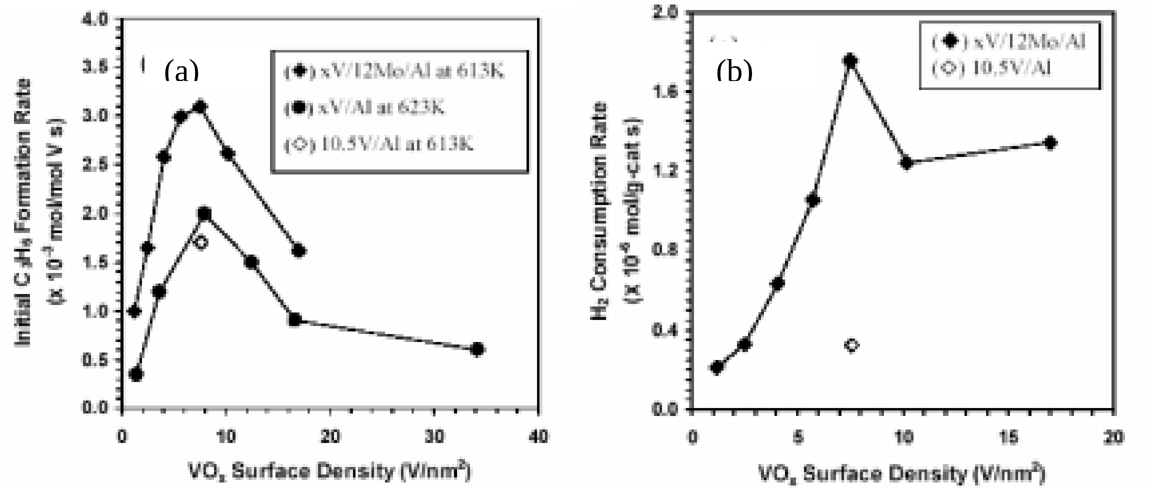
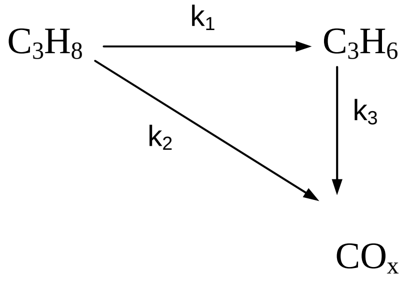


Fig. 1. Effect of VO_x surface density on (a) the specific activity of VO_x/Al_2O_3 and $VO_x/MoO_x/Al_2O_3$ and (b) the rate of H_2 reduction at 613 K.

covered by a monolayer of molybdena is closely associated with an increase in the reducibility of VO_x domains [8]. This relationship is clearly observed in Fig. 1b. The higher propane ODH activity and reducibility of vanadia dispersed on alumina containing a monolayer of molybdena is believed due to the formation of V-O-Mo bonds between the two dispersed oxide layers, and may reflect the formation of polymolybdovanadate structures [10].

Previous kinetic and mechanistic studies of propane ODH on VO_x and MoO_x catalysts have shown that primary and secondary reactions can be accurately described by the scheme [2, 3, 5-7, 8]:



Each reaction is accurately described using pseudo-first-order dependencies on propane and propene reactants and zero-order in O_2 [3, 6, 7]. The k_2/k_1 and k_3/k_1 ratios reflect relative rates of C_3H_8 combustion and dehydrogenation, and of C_3H_6 combustion and dehydrogenation, respectively. Figure 2a show k_2/k_1 ratios as a function of VO_x surface density. These ratios decrease with increasing VO_x surface density up to ~2 V/nm^2 and then increase monotonically for higher surface densities. The k_2/k_1 ratios increased with increasing V surface density on both supports, but they were significantly lower on MoO_x/Al_2O_3 than on pure Al_2O_3 supports at all surface densities.

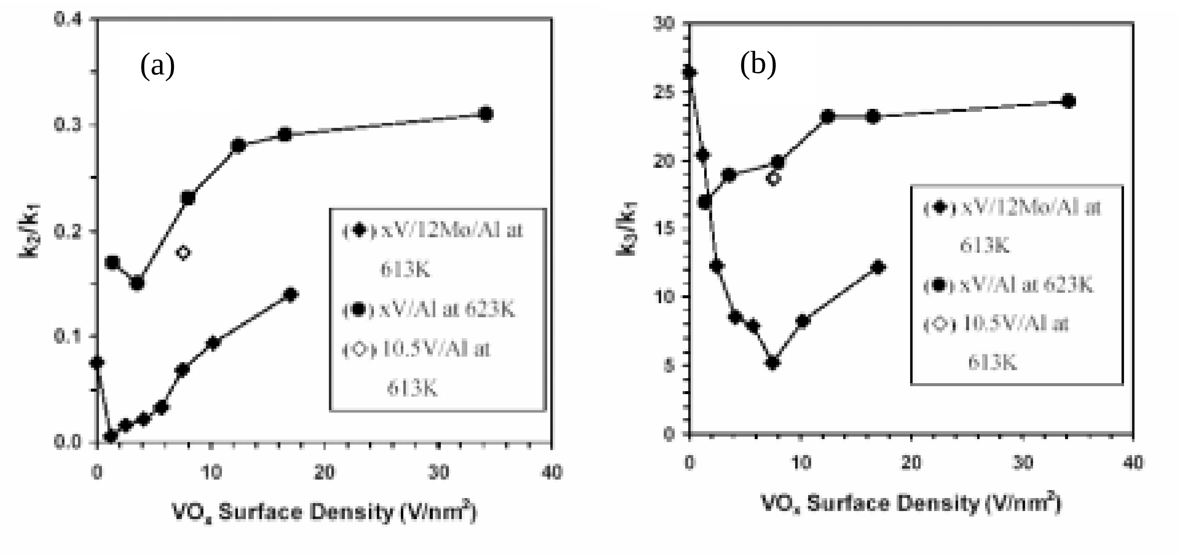


Fig. 2. Effect of VO_x surface density on (a) k_2/k_1 and (b) k_3/k_1.

The influence of vanadia surface density on k_3/k_1 ratios is shown in Fig. 2b. The k_3/k_1 ratio decreases with increasing surface density up to 7.5 VO_x/nm^2, and then increase gradually as V surface densities increases beyond this value. The values of k_3/k_1 are much lower for VO_x domains supported on MoO_x/Al_2O_3 than for domains supported at similar surface densities on Al_2O_3. These data indicate that the molybdenum interlayer suppresses propene combustion rates relative to propane ODH rates. On Al_2O_3, the k_3/k_1 ratio increases monotonically with increasing vanadia surface density. The high initial value of k_3/k_1 on MoO_x/Al_2O_3 reflects a significant catalytic contribution from MoO_x domains, which show much higher k_3/k_1 ratios than VO_x domains (13, 14). As vanadia covers an increasing fraction of the exposed MoO_x surface, it reduces the contributions from the latter to combustion rates, because the specific activity of vanadia is much higher than that of molbydena [12, 13]. A minimum k_3/k_1 value is achieved at a surface density of 7.5 VO_x/nm^2, which corresponds to a theoretical polyvanadate monolayer. Above a surface density of 7.5 V/nm^2, however, k_3/k_1 increases with increasing surface density as in the case of pure Al_2O_3 supports. In spite of some residual contributions from less selective MoO_x domains, VO_x domains dispersed on MoO_x/Al_2O_3 give much lower k_3/k_1 ratios than when dispersed on Al_2O_3 at all VO_x surface densities. This appears to reflect the higher dispersion of VO_x species on MoO_x/Al_2O_3 supports than on Al_2O_3, which minimizes unselective reactions prevalent in V_2O_5 crystallites. These unselective reactions lead to the observed increase in k_3/k_1 ratios with increasing VO_x surface densities on both MoO_x/Al_2O_3 and Al_2O_3 supports.

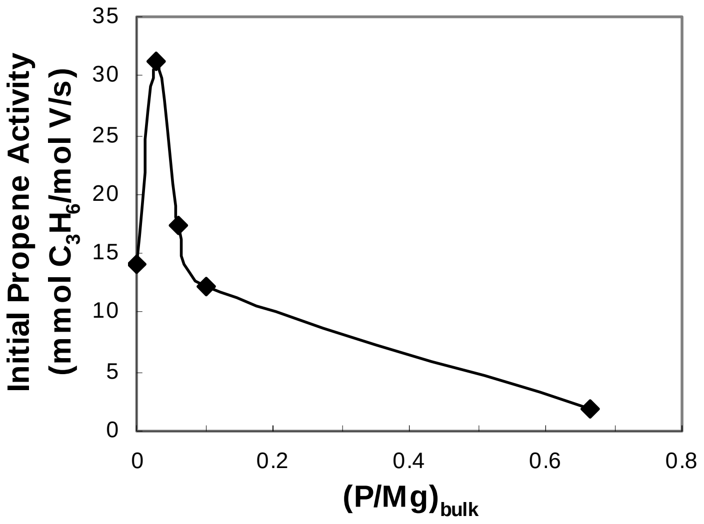


Fig. 3. Effect of P/Mg ratio on the specific activity of VO_x/P-MgO (VO_x surface density = 3.4 V/nm^2) at 773 K.

3.2 Effects of P on magnesia-supported VO_x

The rate of propane ODH on P-doped VO_x/MgO increased with increasing P doping as shown in Fig. 3, reaching a factor of two relative to the rate observed on pure MgO, and then decreased for P-doping levels above 5 wt% P_2O_5. This trend exactly parallels that observed for the effects of P-doping on the reducibility of the vanadia. However, P-doping had no effect on the either the selectivity of propane ODH to propene or the secondary combustion of propene. TPR shows that with increasing P-doping of MgO, the reducibility of vanadia passes through a maximum at doping level of 5 wt% P_2O_5.

4. CONCLUSIONS

In summary, the present studies have shown that the rate of propane ODH to propene over alumina- and magnesia-supported vanadia can be enhanced by increasing the reducibility of the supported vanadia. This effect is consistent with the finding that the first step in the ODH of propane involves the reductive addition of C_3H_8 to a surface VO_x species to form a surface propoxide species. While the selectivity of propane ODH to propene and the secondary combustion of propene to CO_x are unaffected by P-doping of VO_x/MgO, a significant enhancement in both properties is observed when a layer of molybdena is introduced between highly dispersed vanadia and alumina.

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