

ODH of Propane over V_2O_5/TiO_2-SiO_2 Catalysts: Understanding the Structure-reactivity relationship

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Abstract

Supported vanadium oxides are extensively used as an effective catalyst for various selective catalytic oxidation processes. Among various oxide supports TiO_2 has drawn special attention since it imparts higher intrinsic activity for the vanadium oxide phase. However, commercially available TiO_2 (Degussa, P25, 50 m^2/g) undergoes anatase to rutile phase transition and a loss of surface area at higher temperature. Furthermore, anatase to rutile phase transition occurs at much lower temperature in the presence of vanadium oxide. The vanadium oxide content also plays a role. Therefore, synthesis of high surface area thermally stable TiO_2 is an interesting area of research. To increase the surface area and thermal stability, TiO_2 can be intimately mixed by various techniques with another high surface area thermally stable oxide support such as SiO_2 , Al_2O_3 etc.

The present study deals with the synthesis of high surface area TiO_2-SiO_2 (Ti-Si) mixed oxide supported vanadium oxide catalyst and applying it for the propane oxidative dehydrogenation (ODH) reaction. The results obtained for mixed oxide supported catalysts were compared with a vanadia-titania catalyst prepared from commercially available TiO_2 (Degussa, P25). For this purpose a series of well-characterized V_2O_5/TiO_2 (xVTi) and V_2O_5/TiO_2-SiO_2 (xVyTi-Si) catalysts are considered. The kinetic parameters for the ODH reaction, the pre-exponential factors and activation energies, are estimated by optimizing an objective function using Genetic Algorithm (GA). To understand the structure-reactivity relationship in more detail the catalysts will be characterized under *in-situ* condition with simultaneous collection of reaction data.

A series of vanadium oxide catalysts supported on Ti-Si mixed oxide support were synthesized by incipient wetness impregnation method to understand the effect of vanadium oxide loading on the structure-reactivity relationship and kinetic parameters for propane ODH reaction. A series of vanadium oxide catalysts supported on pure TiO_2 (P25 Degussa) were also synthesized for comparative purposes. The Ti-Si mixed oxide support was synthesized by incipient wetness impregnation (IWP) and sol-gel (SG) techniques. The precursor used for TiO_2 was titanium ethoxide (TE, Aldrich) and for SiO_2 was tetra ethyl orthosilicate (TEOS). For mixed oxide supports, the IWP of pretreated SiO_2 (aerosil) was carried out with an incipient volume of TE-ethanol solution. The paste formed was kept in desiccators for drying for 8h at

room temperature. In the SG route TEOS was added to the ethanol solution of TE and surfactant (Ti: Surfactant: EtOH =1:0.1:20). The entire mixture was refluxed for 2h at 358 K. Stoichiometric amounts of HCl-double distilled water solution were then continuously added drop-wise and stirred. The gel formed was aged for 24hr and dried in a vacuum desiccator for 48hr. Finally the supports were calcined at 723 K. The details for the synthesis of vanadium oxide supported catalysts can be found elsewhere [1, 2]. The vanadia supported catalysts were tested for the oxidative dehydrogenation of propane reaction, which was carried out in a down flow tubular quartz reactor. The reaction temperature was varied from 613 to 673 K and the $C_3H_8:O_2$ ratio was varied from 1:1 to 3:1. For kinetic parameter estimation a Mars-van Krevelen reaction model was used. Additional experimental details can be found elsewhere [1].

The BET surface area of various supported vanadium oxide catalysts and Ti-Si mixed oxide support reveal no significant changes for the VTi samples, whereas a decrease in surface area was observed for the VTi-Si mixed oxide support. This result suggests that the BET surface area of pure TiO_2 (P25) is not affected after synthesis. However, the corresponding surface area of the TiO_2 phase in the mixed oxide support is not known. H_2 -TPR profiles for various supported vanadia catalysts showed only single reduction peak. Raman spectroscopic studies reveal that for the Ti-Si mixed oxide support prepared by IWP possesses bulk titania above 30 wt % TiO_2 . Furthermore, Raman spectra of V50Ti-Si samples reveals the presence of surface vanadia species up to 7.5 wt. % V_2O_5 (7.5V50Ti-Si) and bulk V_2O_5 is observed for the 10V50Ti-Si sample.

The TiO_2 (P-25) and prepared x%Ti-Si mixed oxide support were characterized by XRD for samples calcined at different temperatures. From the XRD pattern it was observed that TiO_2 (P-25) undergoes anatase to rutile phase transition starting from 873 K, whereas no anatase to rutile phase transition was observed for Ti-Si mixed oxide support even up to 1073 K. These studies appear to suggest that the SiO_2 substrate stabilizes the anatase phase and retards the anatase to rutile phase transition. XRD pattern of 2 and 4 VTi samples calcined at different temperatures reveal anatase to rutile phase transition starting at 873K and 723K respectively. No anatase to rutile phase transition was observed even up to 1073K for 2V50Ti-Si, whereas the rutile phase appeared at 973 K for the 4V50Ti-Si sample. The relative intensity of rutile phase increases rapidly with an increase in calcination temperatures for 2VTi and 4VTi. These results suggest that the Ti-Si support is thermally more stable than the TiO_2 (P-25) support even in the presence of surface vanadia species and ease of phase transition is related to vanadium oxide concentration. Similar results were also obtained from DTA analysis of the above samples.

To see the effect of calcination on reactivity, four catalyst samples 2VTi, 4VTi, 2V50Ti-Si and 4V50Ti-Si were pre-calcined at different temperature varying from 723 to 1073 K and were tested for propane ODH. It was observed that the propene yield and propane conversion decreases with an increase in calcination temperature for the 2VTi catalyst, whereas no significant change in propene yield and conversion was observed for 2V50Ti-Si catalysts. A drastic decrease in propene yield and propane conversion was observed with increase in calcination temperature for the 4VTi sample, whereas propene yield and propane conversion decreased gradually for the 4V50Ti-Si sample. This result reveals that deactivation of 2VTi, 4Ti and 4V50Ti-Si catalyst is associated with the loss of surface active vanadia sites, which is accompanied by the anatase to rutile phase transition.

Contact time studies were carried out with 2VTi, 2V_xTi-Si (x =30-70 wt %) and yV/50TiO₂-SiO₂ (y =2-7.5 wt %) catalysts at 653 K using propane to oxygen ratio of 2:1. From contact time studies it was observed that propane conversion increases with increase in titania content in the mixed oxide support. The increase in activity of 2V_xTi-Si with increase in titania content appears to suggest an increase in vanadia concentration on the TiO₂ phase supported on SiO₂. It was also observed that propane conversion is a function of vanadia loading for V50Ti-Si catalysts. At iso-contact time the 2V50Ti-Si revealed similar activity as the 2VTi sample. The propene selectivity decreases at iso-conversion with increase in titania content in the mixed oxide support and is different from the 2VTi catalyst. However, propene selectivity increases at iso-conversion with increase in vanadia loading for V50Ti-Si series of catalysts. At iso-contact time the propene yield was also observed to increase with increase in titania content of 30 to 50% and remained constant at higher titania content mixed oxide supported catalysts. An increase in propene yield at iso-contact time was also observed with increase in vanadia loading.

For kinetic parameter estimation for the above mentioned catalysts are shown in Table 1. Analysis of kinetic parameter reveals that the pre-exponential factor, k_{10} , for propene formation increases with increases in vanadia loading for samples below mono layer coverages. The pre-exponential factor for CO_x formation, k_{20} , also increases with increase in vanadia loading. The activation energy for the propene formation (69-72 kJ/mol) is relatively independent of vanadia loading, whereas the activation energy for CO_x formation increases slightly with loading from 46 to 54 kJ/mole. Kinetic parameters obtained for the 2V50Ti-Si sample are comparable to those for the 2VTi catalyst suggesting similar active surface vanadia sites present on both supports. It was reported that the increase in propene yield for a series reaction is achieved by increasing the rate constant ratio k_1/k_2 [1,2]. The increase of k_1/k_2 is possible by changing the catalyst or changing the reaction temperature. In the present study, the k_1/k_2 ratio

as shown in Fig increases with an increase in vanadia loading. This result suggests that propene yield increases with increase in vanadia loading. Similar

Table 1: Kinetic parameter for four catalysts for MVK model, $T_m=643.15$ K

Parameter	Unit	Catalysts			
		2V50Ti-Si	4V50Ti-Si	7.5V50Ti-Si	2VTi
k_{10}	ml STP min ⁻¹	44	67	113	40
k_{20}	(g cat) ⁻¹ atm ⁻¹	934	1204	1567	739
k_{30}		324	636	1269	345
E_1	kJ mole ⁻¹	71	72	69	70
E_2		46	47	54	43
E_3		155	134	133	144

trend in increase of propene yield are also observed from contact time study. The actual scenario behind the increase of k_1/k_2 ratio by modifying the catalysts is not well understood. For this it is necessary to study the reaction under *in-situ* condition which is currently underway.

References:

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