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A combined XANES/Raman in situ study on oxidation of propene over
 V_2O_5 /ZSM-5 and V_2O_5 /Y

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It has been previously reported that nanoparticles of V_2O_5 on different micro and mesoporous supports exhibit activity for oxidation of propene.^{1,2} Oxidation of propene and propane are of interest as they yield different oxygenates, known as fuel additives, where acrolein and acrylic acid are the main desired products. Previous studies have revealed that different VO_x species are formed depending on both the method of deposition, parent material and vanadia loading.^{3,4} The key to understanding these materials is to correlate the activity with the species present.⁵ We have developed a method for depositing vanadium species into various supports by ion-exchange with VO_2^+ and VO^{2+} solutions at different pH which affects both the vanadia loading and the vanadium species formed.

The samples were placed in an in situ cell and heated in O_2/He to 250°C. The samples were then cooled to 150°C followed by heating to 400°C in C_3H_6/O_2 , while collecting XANES, Raman and mass. spec data.

The results from the mass spec. showed that acrolein was formed during the reaction which is shown in figure 1. Prior to the in situ experiment EXAFS was collected at room temperature. From the EXAFS refinements, the nanoparticles of V_2O_5 were not detected. By Raman it was found that V_2O_5 /ZSM-5 have the same Raman spectra as bulk V_2O_5 as shown in figure 2 below. This means that Raman is sensitive concerning the detection of small particles. It has been reported that Raman is good to detect crystalline V_2O_5 .¹ It is concluded that nanoparticles of V_2O_5 exists on the inner surfaces of the zeolites.

XANES was collected simultaneously with the Raman, and the XANES for bulk V_2O_5 and the ion exchanged H-ZSM-5 (V_2O_5 /ZSM-5). Figure 3 show the in situ results for V_2O_5 /ZSM-5. As the figure illustrates the redox cycle is observed in the presence of propene and oxygen. That is that vanadium is reduced by propene and then reoxidised by oxygen.

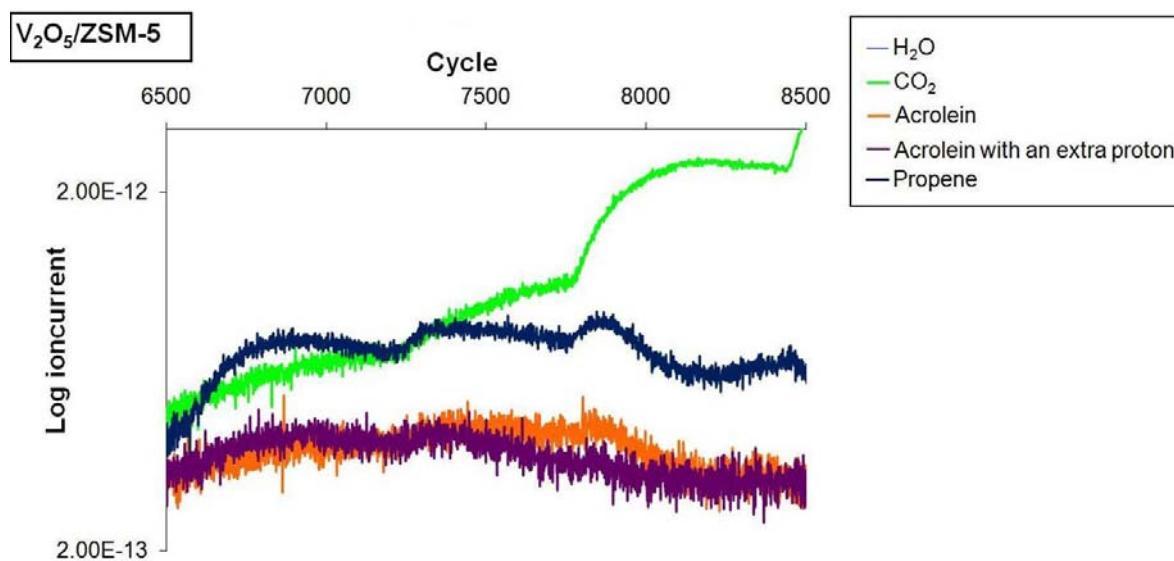


Figure 1: The mass spectra of the *in situ* measurement over $V_2O_5/ZSM-5$, which showed the formation of acrolein

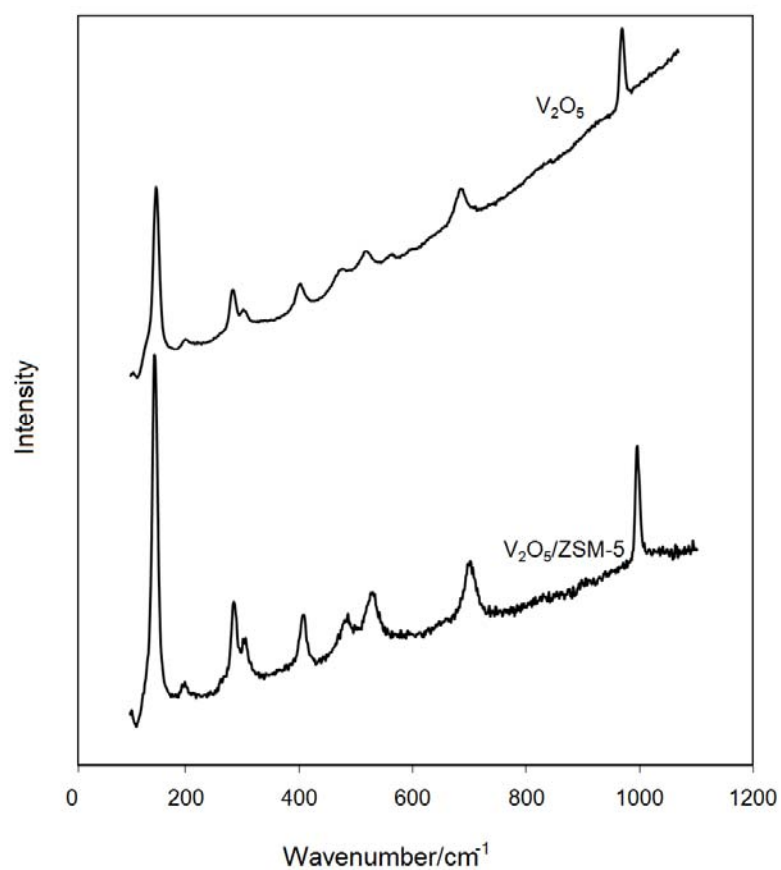


Figure 2: The Raman band of crystalline V_2O_5 and $V_2O_5/ZSM-5$

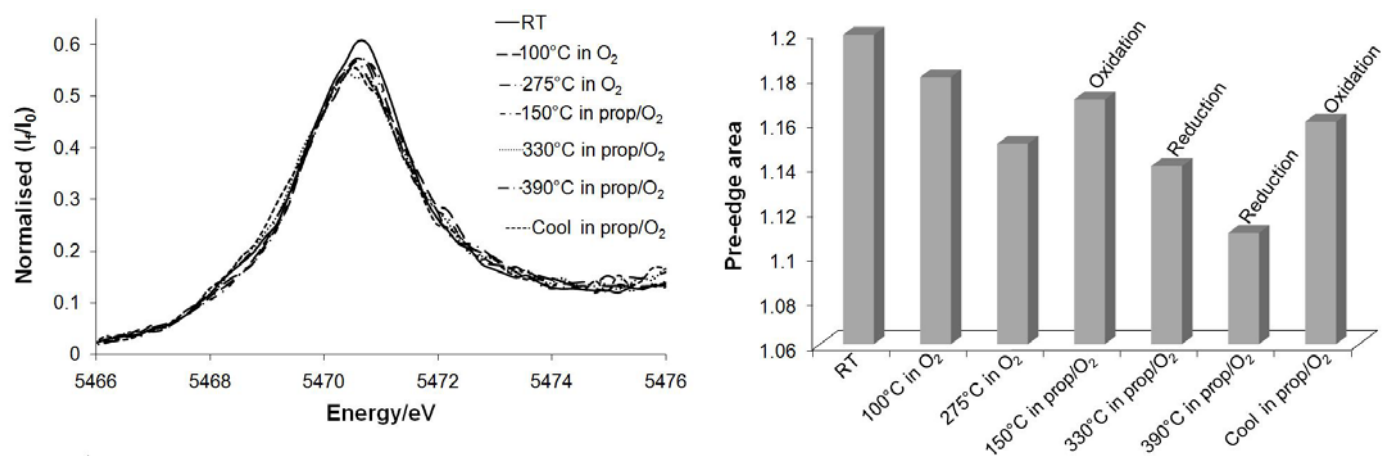


Figure 3: The *in situ* XANES measurement for V₂O₅/ZSM-5

References

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