Understanding Catalyst (de)activation in methane oxidation.

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Abstract:

We report some recent results on oxidative methane conversion over porous transition metal catalysts. We discuss combustion as well as selective oxidation of methane and the importance of the structure and chemical properties of the transition metal site and the properties of the catalyst support. *In situ* spectroscopic techniques and reactor studies were employed to develop an understanding of the important parameters influencing methane activation. We observed structural changes in catalysts during time on stream and the activity was influenced by the catalyst properties. This knowledge was demonstrably leading to the development of highly active and stable catalytic systems.

Keywords: *In situ* spectroscopy, methane oxidation, catalyst structure.

1. Introduction

While a significant body of literature on methane oxidation exists in the literature, the long term stability of catalyst under realistic conditions is still not fully understood. At low temperature deactivation can be due to water poisoning, sintering and change of the active phase. For example at temperatures below 450°C, a leading hypothesis for catalytic deactivation is poisoning of the catalyst by water vapour, which results in the formation of surface $Pd(OH)_2$ species. This catalyst inhibition due to water vapour is dependent on the type of support especially when oxygen mobility on the support has been found to influence water inhibition effect on the catalytic reaction [1]. The presence of strong polar groups such as hydroxyl groups or metal-oxygen vacancies on the surface of the catalyst are the primary source of hydrophilicity of the conventional heterogeneous materials such as alumina and zeolites [2]. In this research, zeolite and alumina supported transition metal catalysts (Pd, Co, Fe) with varying aluminium content were used to untie the various parameters important for the activity of the catalyst. We also demonstrate using X–ray absorption and infrared spectroscopy to discuss the role that acidity plays for the activity, stability and selectivity of the catalytic system which is not well established.

2. Experimental

Transition metal nitrates were used to exchange zeolite catalysts of different structure (MOR, MFI, BEA, FAU). The dried catalysts were crushed and sieved to 250 – 400 µm. A JEOL 2100 Transmission Electron Microscope (TEM) with EDS was used for imaging nano-sized particles on the surface of the support. In situ IR spectroscopy was carried out in transmission mode using 13 mm wafer. Spectra under in situ conditions were recorded with an BRUKER TENSOR 27 Fourier Transform Infrared spectrometer. The quantity of Pd loaded on catalysts was measured using a Varian 715-ES inductively coupled plasma optical emission spectrometer (ICP-OES). A purpose built Temperature-programmed desorption (TPD) apparatus with a Pfeiffer Prisma quadrupole mass analyser was used for detection the H_2O and O_2 desorption.

3. Results and discussion

In Fig .1, the stability of two different Pd supported catalysts was assessed under dry conditions during the early period of each experiment. Following this period, 30 000 ppm water vapour, with balance air, was introduced into the feed stream.

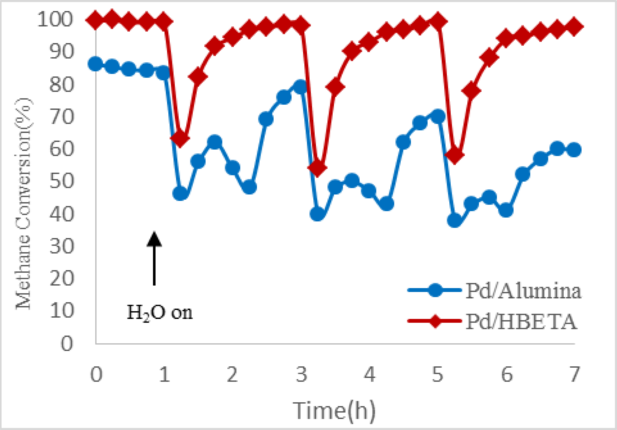

Figure 1: Methane conversion as function of time on stream at a constant bed temperature 400°C, GHSV 100 000 h^{-1}.

The presence of water vapour in the inlet feed stream is the primary factor for Pd based catalyst deactivation, greater than catalyst deactivation through the production of water vapour during the reaction [3]. The reason for continued deactivation of Pd/Al_2O_3 catalyst by water inhibition may be related to the presence and role of hydroxyl groups on the surface of the alumina. Hydroxyl groups originating from water vapour accumulate on the active sites of Pd/Al_2O_3 by formation of $Pd(OH)_2$ species and these species in turn block access to the PdO sites for methane dissociation [4].While the catalyst can recover from the deactivation quickly when water vapour is removed, it is evident there is a significant longer term decline of the activity of the catalyst. Over 1500 h, significant reduction of the activity was observed. Information about distribution of Pd, C and O on the surface used catalyst shows the presence of carbon clusters on the surface of the used catalyst.EDS analysis for carbon shows the agglomeration of carbon on the used catalyst is in the same spots as the Pd and O cluster.

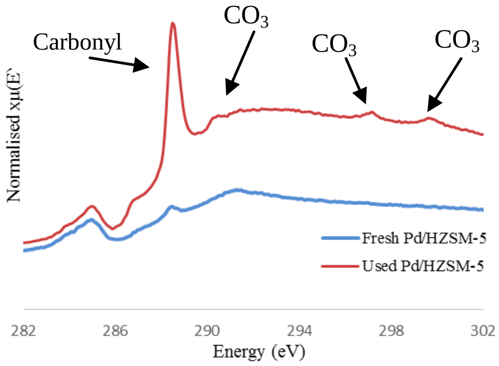

Fig.2. Carbon XANES spectra for fresh and used Pd/HZSM-5

This evidence gives us an indication of formation of a complex compound between Pd, C and O. To identify the nature of these carbon species, carbon XANES and in situ IR spectroscopy was used. Fig 2 shows carbon Xanes of the used catalyst. The analysis results that there is a remarkable difference in intensity of peak position at 288.6 eV, which is exhibit a strong resonance, consistent with the position of a carbonyl resonance reported in literature. In addition, three small peaks emerged in used catalyst at around 290.3 eV, 297.3 eV and 299.7 eV. It is suggested that these peaks are primary and secondary absorption peaks of palladium carbonate like species. In situ IR spectroscopy and TGA confirms these results.

4. Conclusions

In situ IR, XAS and high resolution TEM and chemisorption analyses confirms the structural and chemical changes associated with deactivation of methane combustion catalysts. TPD results show that the Pd/Alumina catalyst adsorbs more water vapour than High Si/Al zeolites resulting in an increased water inhibition. Evidence for the presence of stored oxygen was observed in oxygen desorption results, where oxygen and water were co-adsorbed over the samples. This is consistent with the supposition that Pd/zeolite has greater lattice oxygen mobility and a higher potential storage capacity compared to that of Pd/Al_2O_3. At lower temperatures, the effective surface coverage of oxygen was higher in Pd/zeolites compared to Pd/Alumina which was confirmed by TPD analysis. Surprisingly, we also observed significant amounts of carbon species and identified them as Pd[O][C] species with low index planes similar to PdO (101) and PdO (100)which are suggested to be inactive palladium species.

References

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