

Lean methane combustion over palladium loaded on alumina and HBETA zeolite – the role of the support on water vapour inhibition

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Abstract

Catalytic combustion of ventilation air methane is a potential solution for abatement of this greenhouse gas (GHG) source. A leading hypothesis for the observed catalyst deactivation of palladium-based catalysts when operating at low temperature is water poisoning. In this research, high silica BETA and alumina solids were used as supports for the Pd-based catalyst. The long term stability of methane conversion is significantly improved over HBETA compared to alumina supported Pd. TEM and chemisorption analyses confirms a greater level of dispersion of Pd in the HBETA compared to alumina support. TPD results shows that the Pd/Alumina catalyst adsorbs more water vapour at lower temperatures compared to Pd/HBETA resulting in an enhancement in the extent of 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 feature is also consistent with the supposition that Pd/HBETA has greater lattice oxygen mobility and a higher potential storage capacity compared to that of Pd/Al₂O₃. In addition, it was found that at lower temperatures, the effective surface coverage of oxygen was higher for Pd/HBETA compared to Pd/Alumina which was confirmed by TPD analysis.

1 Introduction

Catalytic combustion of VAM is a potential solution for reducing the net level of GHG fugitive emissions from mining [1]. Catalyst deactivation of palladium based catalysts during methane oxidation is a major challenge associated with this catalytic processes. 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 [2]. 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 [3]. For example, high Si/Al in a zeolite is equivalent to a reduction in the aluminum concentration and in turn a reduction in the concentration of bridging OH groups and a more neutral framework. This reduction in OH groups results in a decrease in the propensity of zeolites to interact with water molecules, i.e., a higher hydrophobicity and even greater thermal stability [4].

In this research, HBETA and alumina were used as supports for Pd. The activity and stability of these catalysts were evaluated under VAM oxidation conditions, and the role of support on catalytic combustion of methane in the absence and presence of water vapor in the feed and generated during reaction was studied. The physical and chemical properties of Pd/HBETA was investigated in order to have better understanding of the performance of high silica Beta zeolite in comparison with a conventional Pd/Alumina catalyst for VAM oxidation.

2 Experimental

2.1 Catalyst Preparation

HBETA (Si/Al₂=300) was purchased from Zeolyst International, Kansas, USA and alumina spheres (phase, purity) of diameter 1.5-2 mm were purchased from Sasol (South Africa) and ground via mortar and pestle to a powder form. Reagent grade palladium (II) nitrate was purchased from Sigma-Aldrich. 1.2 wt% palladium was loaded on calcined samples using incipient wetness impregnation, using Pd(II) nitrate solution (10 wt% in 10 wt% nitric acid). Catalysts were oven dried at 110°C for approximately 20 h. The dried catalyst was then crushed and sieved to 250 – 400 µm. The sieved catalyst particles were calcined in a tubular fixed-bed reactor at 500°C for 2 h under air.

2.2 Characterization Techniques

Surface area measurements were performed by using Micromeritics Tristar surface area analyser via nitrogen adsorption and desorption at 77 K. Micromeritics Vacprep 061 was used for degassing of the samples. A JEOL 2100 Transmission Electron Microscope (TEM) with EDS was used for imaging nano-sized Pd particles on the surface of the support. A purpose built Chemisorption apparatus, with volumetric glass apparatus, was used to measure metal dispersion and active particle size by hydrogen chemisorption at 35°C. 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 H₂O and O₂ desorption.

2.3 Catalytic Activity Measurements

Catalytic combustion of lean methane was performed in a tubular stainless steel fixed bed micro reactor. The inlet methane concentration was set at 0.7% in air with a total gas hourly space velocity (GHSV) of 100 000 h⁻¹. Methane

conversion was monitored using a gas chromatograph (Shimadzu GC-2014) with packed Hysep and Molecular Sieve dual column, and a thermal conductivity detector (TCD). The temperature of the bed was measured by a thermocouple placed into the catalyst bed. An average carbon mass balance of 97% was obtained for all experiments. For the saturated feed experiment, water vapour was introduced into the feed stream. The average water vapour concentration was determined by a humidity probe and determined to be constant, with approximately 85% relative humidity (RH) at ambient temperature ($25^{\circ}\text{C} \pm 3^{\circ}\text{C}$).

3 Results and discussion

3.1 Catalyst Stability

The stability of Pd/HBETA and Pd/Al₂O₃ under VAM conditions, for 24 h continuous reaction on stream, was assessed. As plotted in Fig. 1, the stability of both catalysts was assessed under dry conditions during the early period of each experiment. Following this period, 30 000 ppm water vapour, balanced in air, was introduced into the feed stream. This resulted in a sudden drop in catalyst activity for both catalysts. During time on stream analysis, the Pd/HBETA catalyst was shown to rapidly return to its initial activity while the Pd/Al₂O₃ catalyst continued to deactivate over the 24 h period of reaction. This highlights a start difference in the influence water vapour has on the stability of the catalyst in terms of the use of different supports. Pd/HBETA displayed a resistance to water poisoning in comparison to Pd/Al₂O₃, which deactivated even under dry feed conditions.

It has been reported that 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 [5]. The reason for continued deactivation of Pd/Al₂O₃ 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/Al₂O₃ by formation of Pd(OH)₂ species and these species in turn block access to the PdO sites for methane dissociation. This interpretation is consistent with that proposed by others in the literature [5].

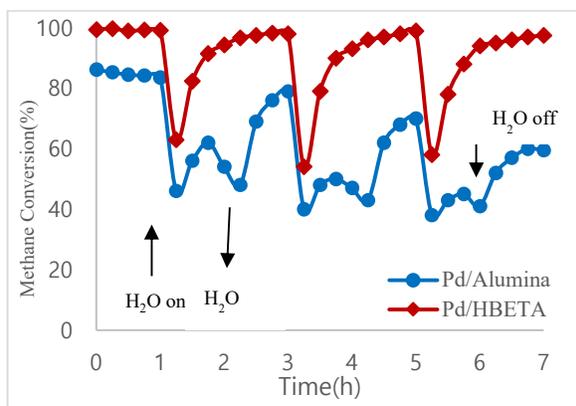


Figure 1: Methane conversion as function of time on stream at a constant bed temperature 400°C , GHSV $100\,000\text{ h}^{-1}$.

Stability tests were performed at 400°C , a temperature at which

water inhibition was found to be significant over Pd/Al₂O₃. Fig. 2 shows the experimental results for methane conversion over Pd/Al₂O₃ to achieve 90% conversion and how this temperatures is needed to be altered in order to maintain this conversion level. In order to maintain a methane conversion level of 90%, the temperature was increased to over 500°C progressively during the 50 h period of time on stream. It is evident that the catalyst stability after 50 h of reaction at the temperature over 500°C , presumably at a temperature which is sufficient to eliminate the inhibiting effect of water causing deactivation of the catalyst. It can be concluded that the water inhibition effect is most notable at temperatures less than 500°C . Note that there is still slow deactivation occurring at temperatures higher than 500°C .

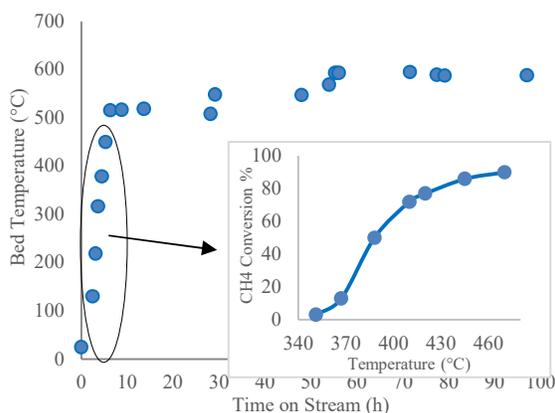


Figure 2: Methane conversion over Pd/Al₂O₃ to achieve approximately 90% conversion as a function of time on stream, GHSV $100\,000\text{ h}^{-1}$

3.2 Physical and Chemical Properties of Catalyst

The ICP result showed the concentrations of palladium on the surface of Pd/HBETA and Pd/Al₂O₃ were 1.18 wt% and 1.06 wt%, respectively. Surface area of Pd/HBETA and Pd/Al₂O₃ were determined by N₂ physisorption. Not surprisingly, Pd/HBETA has much higher surface area compared to Pd/Alumina because of the nature of pore micropores in zeolite HBETA. The BETA zeolite framework provides approximately 20.5 % accessible volume [6]. The gas adsorption analysis was used to estimate the Langmuir surface area of $694\text{ m}^2\text{g}^{-1}$ and $247\text{ m}^2\text{g}^{-1}$ for Pd/HBETA and Pd/Al₂O₃, respectively. Since the surface area of Pd/HBETA is more than double that for Pd/Al₂O₃, it may provide a more accessible surface for Pd particles dispersion. Therefore, it is suggested that the nature of BETA support appears to engender relatively high level of Pd particle dispersion in comparison to an alumina support, consistent with the TEM images shown in Fig. 3.

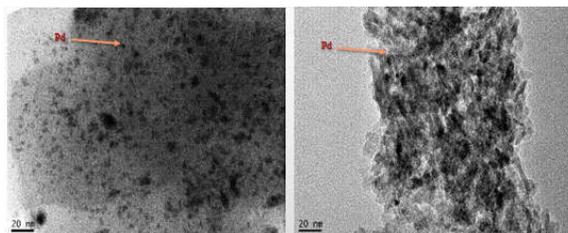


Figure 3: TEM images for Pd/HBETA (left) and Pd/Al₂O₃

(right).

Scanning Transmission Electron Microscopy (STEM) was used to study Pd dispersion on the surface of Pd/HBETA and Pd/Al₂O₃ catalysts. Fig. 3 shows a typical TEM image and on the surface of these catalysts, respectively. STEM images disclose a smaller average Pd particle size, with a higher level of dispersion on the surface of HBETA compared to that of Al₂O₃. Statistical analysis shows the distribution of Pd particles in the range of 1 nm to 10 nm on both catalyst supports. Based on TEM analysis, most of the PdO particles on the Pd/ HBETA support are in the average range of 2-3 nm compared to 4-5 nm for Pd/Al₂O₃. It can be concluded that the nature of support influences the distribution and morphology of Pd nanoparticles, and this finding has been reported by others in literature [7, 8]. The trend in the differences in Pd dispersion has also been confirmed by H₂-chemisorption, with Pd dispersion from H₂-chemisorption at 35°C suggests a Pd dispersion of 24.6 % for Pd/HBETA and 17.4% for Pd/ Al₂O₃.

Intrinsic catalyst activity achieved by conducting experiments at varying temperatures under the condition of methane conversion below 12% (GHSV) of 100 000 h⁻¹. The performance of the catalysts was evaluated in the terms of activation energy and turn over frequency (TOF). Arrhenius plots are shown in Fig. 4 for both catalysts evaluated under dry and saturated conditions, and the TOF values and reaction rates for methane conversion under dry and saturated feed are summarized in Table 1. The Arrhenius plots indicates that a higher rate of methane oxidation per active sites is evident for Pd/HBETA when compared to the reaction rate over Pd/Al₂O₃. It should be noted that the Alumina and HBETA (without Pd loading) catalysts were evaluated under the same reaction conditions, and no evidence of methane conversion was detected at temperatures below 500 °C. This result clearly indicates that the Pd particles on these supports is responsible for methane conversion. Under dry feed conditions, the TOF of the fresh Pd/HBETA and Pd/Al₂O₃ catalysts at 345°C were 0.029 s⁻¹ and 0.017 s⁻¹ respectively. In addition, an apparent activation energy of 81.1 kJ/mol was estimated over Pd/HBETA, compared to 87.4 kJ/mol over Pd/Al₂O₃. Under saturated feed conditions, the TOF estimated for the fresh Pd/HBETA was 0.023 s⁻¹ at 345 °C showing a slight decreasing in comparison with TOF calculated at the same temperature under dry feed condition. In contrast, a TOF of 0.008 s⁻¹ was measured under saturated conditions at 345 °C over Pd/Al₂O₃. The results over Pd/Al₂O₃ disclose a notable reduction in reaction rate following the addition of water to the feed, while inhibition for Pd/HBETA under the same conditions was negligible. The apparent activation energy increased for both catalysts, reaching 110.9 kJ/mol for HBETA and 162 kJ/mol for Pd/Al₂O₃. The activation energy obtained for fresh Pd/Al₂O₃ is comparable to that reported in literature [8, 9] where under dry and saturated feed condition the activation energies were quoted in the range of 70 to 90 kJ/mol and 150 to 166 kJ/mol, respectively. Change in the activation energy has been attributed to the PdO stability under variable conditions, conditions which change with alteration in the water reaction order [9].

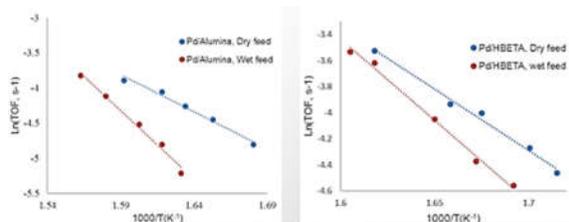


Figure 4: Arrhenius plot of Pd/Al₂O₃ and Pd/HBETA catalyst under dry and saturated feed condition, 7000 ppm methane, saturated feed included 30 000 ppm water vapour, balanced in methane and air, GHSV = 100 000 h⁻¹.

Table.1 Kinetic data for Pd/HBETA and Pd/Al₂O₃ catalysts

samples	condition	Reaction rate (mol / (g _{cat} · s) × 10 ⁻⁷)	TOF (s ⁻¹)	E _a (kJ/mol)
Pd/Al ₂ O ₃	Dry	4.66	0.017	87.5
Pd/Al ₂ O ₃	Saturated	2.20	0.008	162.2
Pd/HBETA	Dry	14.2	0.029	82.1
Pd/HBETA	Saturated	12.1	0.023	110.9

Reaction rate and TOF was calculated at temperature of $T = 345^{\circ}\text{C}$

The surface properties of Pd/HBETA in comparison with Pd/Al₂O₃ were also investigated by Temperature Program Desorption (TPD) analysis. The effect of water vapour on catalyst activity was examined using this technique in order to understand the interactions between water, support and active sites of catalyst.

In order to understand the role of support oxygen capacity and mobility involved in catalytic activity in presence of water vapour, O₂ and H₂O were co-adsorbed over Pd/HBETA and Pd/Al₂O₃ catalysts. In order to prepare catalysts for this aspect of the study, catalyst samples were heated under vacuum at 500°C for 1 h to remove any pre-adsorbed compounds. Following exposure of the catalyst to oxygen and H₂O(v) at 110°C, the samples were heated under vacuum to 800°C. Fig. 5 shows that the maximum rate of oxygen desorption was observed below 400°C for Pd/HBETA and above 600°C for Pd/Alumina, the trend be the opposite to that observed for H₂O desorption (see Fig. 5). These observations would suggest that the oxygen adsorption capacity of Pd/HBETA is higher than Pd/Alumina. It is reported in literature that high Pd dispersion on the support can lead to higher oxygen adsorption capacity [10], and this is consistent with the results of TEM analysis where Pd/HBETA has a higher level of Pd dispersion compared to Pd/Alumina. Additionally, the support can play an important role in influencing Pd oxygen adsorption. It is generally accepted that there is a strong correlation between the oxygen adsorption capacity of noble metals and their catalytic activity, and the influence of support on the Pd adsorption of oxygen [10, 11]. This role can be attributed to the creation of oxygen vacancies in the support and increased lattice oxygen mobility, which would suggest that the desorption peak at around 400°C in Pd/HBETA (attributed to surface oxygen adsorbed on PdO species) leads to a higher catalytic activity at this temperature, which was consistent with the data acquired in the present study. In addition, the peak that appears above 600°C could be assigned to the decomposition of a PdOx species at high temperatures [12, 13] and this occurred along with a change in color of the recovered catalyst from TPD apparatus caused by Pd reduction at high temperatures.

The TPD data indicates that varying the type of support, the oxygen adsorption capacity and potentially lattice oxygen mobility of the catalyst can lead to a change in the inhibiting effect of water over the catalyst. Pd/HBETA has enhanced

oxygen storage capacity compared to Pd/Al₂O₃, and these attributes are supported by TPD data analysis. Oxygen storage and lattice oxygen mobility of a catalyst is involved in limiting water inhibition [14, 15]. Evidence for the presence of stored and mobile oxygen was observed in oxygen desorption TPD results displayed in Fig.5, where oxygen and water were co-adsorbed over the samples. It was found that at lower temperatures, the effective surface coverage of oxygen was higher for Pd/HBETA compared to Pd/Alumina. Moreover, competitive adsorption between H₂O and O₂ led to lower oxygen surface coverage over the Pd/Al₂O₃ catalyst which resulted in a lower stability. This suggests that the high silica zeolite, with their particular adsorption characteristics, would be a more suitable support compared to alumina for Pd metal catalyzed methane combustion at low temperatures.

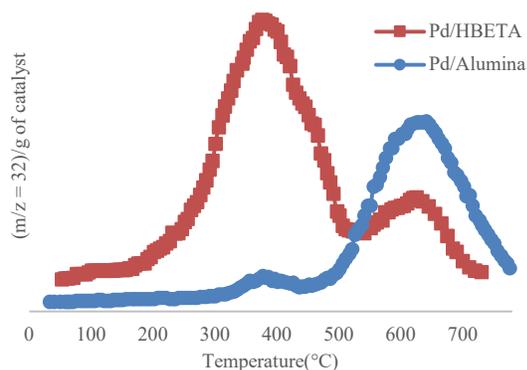


Figure 5: TPD spectra of O₂ ($m/z = 32$) desorbed from catalysts. Oxygen was co-adsorbed with H₂O at 110°C.

4 Conclusions

Lean methane conversion over Pd loading on HBETA and alumina was investigated. Methane conversion, as a function of time on stream under humid conditions, results in an improvement in the stability of HBETA compared to alumina support. TEM and chemisorption analyses confirm a greater level of dispersion of Pd in the HBEA compared to alumina support. The significant increase in apparent activation energy for Pd/Al₂O₃ comparison with Pd/HBETA under saturated feed conditions indicates that the Pd dispersed on the surface is not the only factor responsible for methane conversion and that the interaction of Pd and support with water vapour can cause significant effect on methane conversion. The high Si/Al ratio in Pd/HBETA (and corresponding reduced aluminium concentration) leads to a more neutral framework which results in greater hydrophobicity and higher thermal stability. This, in turn, resulted in decreasing catalyst potential for oxygen adsorption due to competition of active sites with water vapour, confirmed by TPD results. This feature is also consistent with the supposition that Pd/HBETA has greater oxygen storage capacity compared to that of Pd/Al₂O₃, which has again been confirmed by TPD analysis.

5 Acknowledgment

We would like to acknowledge ACARP for their generous financial support of the project. We thank Hongwei Liu for assistance with TEM analysis. We are grateful to acknowledge financial support provided by University of Newcastle. Also,

we would appreciate Jenny Zobec and Huiming Zhang from the X-ray Unit at UON for their help in TEM analysis.

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