



A bimetallic catalyst on a dual component support for low temperature total methane oxidation



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ARTICLE INFO

Article history:

Received 30 October 2015

Received in revised form

23 December 2015

Accepted 9 January 2016

Available online 14 January 2016

Keywords:

Palladium

Platinum

Titania

Zeolite

Methane oxidation

ABSTRACT

Palladium, platinum bimetallic catalysts supported on η -Al₂O₃, ZSM-5(23) and ZSM-5(80), with and without the addition of TiO₂, were prepared and used for low temperature total methane oxidation (TMO). The catalysts were tested under reaction temperatures of 200–500 °C with a GHSV of 100,000 mL g⁻¹ h⁻¹. It was found that all four components, palladium, platinum, an acidic support and oxygen carrier were needed to achieve a highly active and stable catalyst. The optimum support being 17.5% TiO₂ on ZSM-5(80) where the T_{10%} was observed at only 200 °C. On addition of platinum, longer time on stream experiments showed no decrease in the catalyst activity over 50 h at 250 °C.

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1. Introduction

Methane is an abundant resource which can be found in large quantities in natural gas reserves and can be produced from bioderived sources through, for example, anaerobic digestion [1,2]. However, its high symmetry and resulting stability makes direct conversion to liquid fuels or chemical feed stocks inherently challenging and direct conversion to higher value chemicals to date is uneconomical [3,4] when compared with syngas routes [5–7].

As a fuel, natural gas is very attractive as it generally contains low levels of pollutants such as nitrogen or sulfur and produces low levels of CO₂ per energy produced [8]. However, complete combustion can be difficult to achieve with traces often released in the exhaust gas streams and given its global warming potential this is problematic [9].

Furthermore CO and, depending on the source of the gas, SO_x species from impurities in the feed [10] can be produced. Also at high combustion temperatures NO_x can be formed thereby

necessitating the development of catalytic systems to facilitate complete combustion at low temperatures [11–14].

Many metals have been studied as methane combustion catalysts including platinum [11,15], palladium [16–18], and copper [19] with palladium being recognised as the most active [12,20,21]. Carstens et al. [22] reported that the mechanism of reaction occurs through dissociative adsorption of CH₄, preferentially on metallic palladium and subsequent oxidation by PdO species. Their studies on a Pd/ZrO₂ catalyst showed that activity increased, up to a maximum, with an increasing proportion of surface PdO. This activity was enhanced by the presence of small amounts of reduced Pd on the catalyst surface allowing dissociative adsorption. This is in agreement with Burch et al. [20] who showed that the activity increased until an optimum oxide coverage of approximately 3–4 monolayers was obtained. Lin et al. using ¹⁸O₂ species over a pre-oxidised Pd/TiO₂/Al₂O₃ catalyst [12] also agreed with this mechanism. Therefore, Pd(0) is required to adsorb methane while PdO species are needed for oxidation. It is known that the PdO/Pd(0) redox cycle can be controlled by addition of an oxygen carrier such as TiO₂ to the support. For example Lin et al. [12] reported a decrease in T_{10%} of 30 °C on addition of 20 wt% TiO₂ but the best catalyst still showed a T_{10%} greater than 250 °C at a space velocity of 33,000 mL h⁻¹ g⁻¹, one third of that used herein.

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Palladium complex species are reported to be more electron deficient on more acidic supports compared to neutral supports [23–25]. This increased electrophilicity alters the Pd(0)/PdO redox cycle and therefore catalyst activity. Stakheev et al. [25] used XPS while Wang et al. [26] used DFT calculations to assess the effect of support acidity on PdO bond strength which was found to increase with the number of protons present on a ZSM-5 surface. M'Ramadji et al. [18] recognised the role of support acidity in methane combustion over Pd/ZSM-5 and reported a $T_{10\%}$ of most catalysts ranging from 220 to 400 °C at a space velocity of 36,000 h⁻¹.

This equilibrium between PdO and Pd(0) is also affected by a number of parameters such as temperature, oxygen partial pressure, metal particle size and interaction with the support [27]. However poor stability of the PdO at temperatures between 650 and 850 °C due to Pd(0) formation and irreversible sintering presents major obstacles. Addition of CeO₂ can inhibit this deactivation and recently Cargnello [28] described the preparation of a Pd@CeO₂ core shell catalyst on functionalised Al₂O₃ which remained stable over 5 runs. However even with such specifically designed materials, analysis by Zhang [29] shows formation of clouds of palladium resulting in an intimately mixed Pd/Ce/SiO₂ mixed species at elevated temperatures.

Comparison of Pd, Pt and their combination has shown that the addition of a second metal limits deactivation [30] and a $T_{10\%}$ as low as 228 °C was observed with a 0.2 wt% Pt and 0.3 wt% Pd bimetallic catalyst supported on TiO₂ at a space velocity of 21,000 h⁻¹. Improved stability of Pd/Pt bimetallic catalysts was also reported by Persson et al. with a $T_{10\%}$ between 450 and 750 °C at a space velocity of 250,000 h⁻¹ [14]. This has been attributed to either the Pt preventing the particle growth of the PdO [31], a change in the morphology or metal loss from the monometallic palladium catalyst [32]. Although there is some debate in the literature about increased activity with bimetallic catalysts [14], it is generally accepted that the bimetallic is more stable.

It should be noted that under realistic operating conditions water, sulfur, nitrogen and phosphorous containing compounds also affect performance. The effect of such additives is dependent on the combination present and also the support [33]. Addition of 15% water to a hierarchical Pd@CeO₂/Si-Al₂O₃ catalyst resulted in deactivation [34], however no deactivation was observed over a similar Pd@ZrO₂ catalyst with 10% water in the feed [35]. Gremminger et al. [36] carried out an extensive study on catalyst poisoning of PdPt/Al₂O₃, identifying SO₂ as the most detrimental.

The above discussion leads to the conclusion that a bimetallic catalyst should be used together with a support containing both oxygen transport and acidic components. Hence at least four components would be required for low temperature operation. Herein we demonstrate that such a four component catalyst, based on a bimetallic catalyst (Pd/Pt) for stability, TiO₂ for oxygen mobility and an acidic support (η -Al₂O₃ or H-ZSM-5) for the reoxidation of Pd(0), is superior to simpler catalysts. This four component catalyst has been optimised within the parameters used and facilitates methane combustion with a $T_{10\%}$ of 200 °C at realistic space velocities of 100,000 mL g⁻¹ h⁻¹.

2. Experimental

2.1. Materials

The chemicals used in the present study were all analytical grade, from Sigma-Aldrich, UK or Alfa Aesar and were used without further purification. Aluminium nitrate nonahydrate ($\geq 98\%$), ammonia solution (35%), palladium (II) nitrate dihydrate (Pd(NO₃)₂·2H₂O, $\sim 40\%$ Pd basis), potassium tetrachloropalladate (II) (K₂PdCl₄, $\geq 99.995\%$), ammonium tetrachloroplatinate (II)

((NH₄)₂PtCl₄, 99%), titanium (IV) oxide anatase nanopowder (TiO₂, 99.7%) were all obtained from Sigma-Aldrich. Zeolite H-ZSM-5(80) (SiO₂:Al₂O₃ 80:1 mol ratio), zeolite H-ZSM-5(23) (SiO₂:Al₂O₃ 23:1 mol ratio) and tetraammineplatinum (II) hydroxide in solution (Pt(NH₃)₄(OH)₂, assay 9.09%) were obtained from Alfa Aesar. All gases Ar, CH₄, O₂/Ar and Ne were obtained at 100% purity from BOC gases, UK.

2.2. Catalyst preparation

2.2.1. The supports

The preparation of the alumina support has been described in a previous work [37]. For the aluminium nitrate precursor, after the precipitation by ammonia solution, the resulting precipitate was calcined at 550 °C and designated as AN550. H-ZSM-5(80) and H-ZSM-5(23) were used as received.

2.2.2. Preparation of bimetallic Pd/Pt on η -Al₂O₃ or on H-ZSM-5 supports with the addition of TiO₂

Bimetallic catalysts were prepared by a wet impregnation method with the aid of sonication. Pure supports AN550, H-ZSM-5(80) or H-ZSM-5(23) were placed in a vial and the mass of metal precursor solution or slurry, required to give a 5 wt% palladium and 2 wt% platinum loading was added followed by TiO₂ to give 25 wt% in deionised water (5 mL). The mixture was sonicated at 80 °C (Crest ultrasonic bath model 200HT), under a 45 kHz frequency for 3 h. All mixtures were dried at 120 °C overnight in an oven before being calcined in air at 500 °C for 4 h with a heating ramp of 2 °C min⁻¹.

Six catalysts with the compositions given below, in wt%, were prepared to determine the effect of the precursor and support used. All catalysts contained 25%TiO₂.

Catalyst 1: 5% Pd (NO₃) + 2% Pt (Cl) + 68% AN550

Catalyst 2: 5% Pd (Cl) + 2% Pt (NH₃) + 68% AN550

Catalyst 3: 5% Pd (Cl) + 2% Pt (Cl) + 68% AN550

Catalyst 4: 5% Pd (Cl) + 2% Pt (Cl) + 68% H-ZSM-5(80)

Catalyst 5: 5% Pd (NO₃) + 2% Pt (NH₃) + 68% H-ZSM-5(80)

Catalyst 6: 5% Pd (NO₃) + 2% Pt (NH₃) + 68% H-ZSM-5(23)

The chlorinated catalysts (1 to 4) were further washed with deionised water until no halide was detected using AgNO₃. The washed catalysts were calcined in air at 250 °C for 3 h with a heating rate of 2 °C min⁻¹.

2.2.3. Different TiO₂ loadings on PdPt/H-ZSM-5(80)

The catalysts used to study the effect of TiO₂ loading were based on the metal (Pd and Pt) precursors and loadings used in Cat 5. The metal loading was 7 wt% with the overall support being 93 wt% of the catalyst. A range of titania loadings of (0, 5, 10, 17.5, 25, 35, 46.5, 68 and 83 wt% TiO₂) on H-ZSM-5(80) were prepared by altering the mass of H-ZSM-5(80) and TiO₂ used. After drying, the catalysts were calcined in air at 500 °C for 4 h with a heating ramp of 2 °C min⁻¹. Catalysts are denoted as: 0%TiO₂, 5%TiO₂, 10%TiO₂, 17.5%TiO₂, 25%TiO₂ (Cat 5), 35%TiO₂, 46.5%TiO₂, 68%TiO₂ and 83%TiO₂.

2.2.4. Effect of preparation method, metal dispersion and sonication

The effects of the preparation method on the observed rate of reaction were tested by preparing a 5% Pd (NO₃), 2% Pt (NH₃), 17.5 wt% TiO₂ and 75.5 wt% H-ZSM-5 (80) catalyst in three different ways to that described in Section 2.2.3, Cats 7–9.

For Cat 7, TiO₂ was placed in the vial first, followed by the solutions of the metal precursors and finally the H-ZSM-5. The mixture was sonicated, dried and calcined according to Section 2.2.2. Cats 8 and 9 were prepared as per Cat 7 but with TiO₂ either ground together thoroughly with the bimetallic zeolite catalyst (Cat 8) or added in water and sonicated before drying and calcination (Cat 9).

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