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Short communication

Influence of the metal/metal oxide redox cycle on the catalytic activity of methane oxidation over Pd and Ni doped hydroxyapatite

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ABSTRACT

The methane oxidation reaction was investigated over Pd and Ni doped hydroxyapatite (HAP) catalysts. All catalysts were evaluated in both their reduced and oxidised forms, and the behaviour of the metals in the reaction was investigated. The obtained results demonstrated that the reaction proceeds through a redox cycle between metal oxide and reduced metal, however more stable catalysts with higher conversions were observed when the catalysts were pre-treated in oxygen. After CH_4 oxidation, all the samples were tested towards coke formation using TGA analysis; results showed that all the catalysts were resistant to the coking process under the conditions studied.

1. Introduction

Chemical reactions that take place during the oxidation of methane are governed by the thermodynamics of their reaction equilibria [1]. However, in the system where there is more than one equilibrium, there may be several possible different routes to obtain the desired products and/or by-products through side reactions (Fig. 1). Nevertheless, the major limitations of the oxidation of methane are safety issues regarding pure oxygen, which is considered as highly dangerous in industrial applications. Moreover, the high temperatures required to activate methane and oxygen make the reaction very difficult to control, where hot spots are formed on the surface of the catalyst, leading to local overheating and reduced stability, thus there is a constant need to develop stable catalysts that will be highly active in lower temperatures (< 500 °C) [2].

Noble metals, mostly Pt, Pd, Rh, Ru and Ir have been extensively studied on numerous supports, and have reported high catalytic activity towards methane, as summarised in an excellent recent review [3]. Nevertheless, due to the high cost and limited accessibility of noble metals, various transition metals, like Ni, Fe, Zr and Co have also been investigated. From a comparison of different noble and transition metals, however, Pd and Ni have been found to be the most active for this reaction [4]. Regarding different supports, numerous mesoporous materials have been studied due to their unpredictable intrinsic structural features, such as tunable pore diameter and good flexibility to accommodate metals onto the surface [5].

During methane oxidation, the conversion of PdO to Pd has a profound effect on the catalytic activity [6–8]. At low temperatures, PdO is thought to be the phase that is more catalytically active for methane oxidation and the transformation from PdO to Pd generally leads to a decrease in catalyst performance as the temperature increases [9]. Such a reaction is observed due to a redox cycle between the metal oxide and the reduced metal. However, Zhang et al. claimed that the highest catalytic activity is observed when the catalyst contains both Pd and PdO, and the presence of Pd/PdO interfaces generate oxygen mobility that is beneficial for CH_4 oxidation [10]. Nevertheless, understanding and controlling the phase transformations of metal based catalysts during methane oxidation is crucial and, thus, remains a subject of scrutiny.

Calcium hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) is a bifunctional material with both acidic and basic properties that is employed as a catalyst and a support for metallic catalysts [11–13]. Sugiyama et al. have extensively reported various stoichiometric forms of apatites and their excellent selectivity in partial methane oxidation in the presence and absence of tetrachloromethane (TCM) [14]. In addition, stoichiometric mesoporous HAP has been recently reported stable after pH, thermal and mechanical disturbances [15]. In fact, activation of methane has been attributed to basic sites present on the surface of the catalyst, therefore stoichiometric mesoporous HAP (Ca/P 1.67) has become extremely attractive support as it is extensively reported to possess hydroxyl groups that are available for the reaction [11,12].

The present work reports on methane oxidation under stoichiometric conditions over Pd and Ni doped HAP, and the behaviour of these metals during the reaction. Special attention is devoted to the influence of the conditions on the transition between metal oxide and reduced metal *via* reduction and oxidation of the metal species prior to

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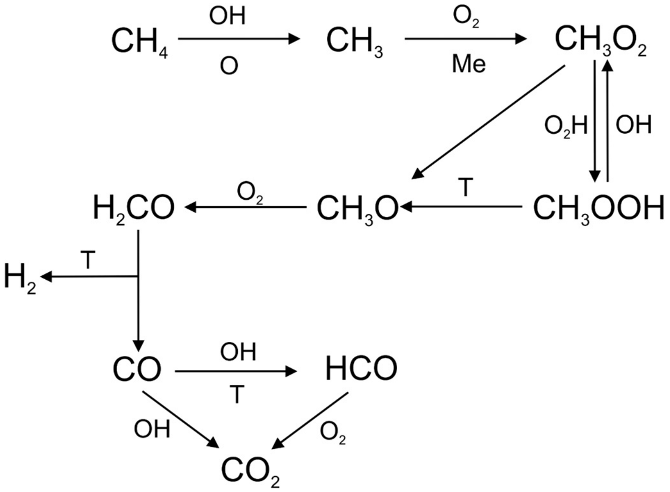

Fig. 1. Proposed reaction mechanism of methane over the catalyst in presence of oxygen.

catalysis. After the catalytic performance tests, all catalysts were investigated for coke formation resistance.

2. Experimental methods

2.1. Materials and chemicals

All chemicals were obtained from Sigma-Aldrich and solutions were made using deionised water with a resistivity not < 18.2 MΩ cm.

2.2. Synthesis of catalysts

To synthesise mesoporous HAP different soft-templates were employed, such as polyoxyethylene (20) sorbitan monostearate (Tween 60, 26 g), nonaoxyethylene dodecyl ether ($C_{12}EO_9$, 10.66 g), or a mixture of Tween 60 and $C_{12}EO_9$ and a hard-template (carbon nanorods), synthesised following the same procedure as reported in our previous study [16]. For soft templates, $Ca(NO_3)_2$ (7.88 g) was mixed with KH_2PO_4 (2.72 g), dissolved in water (26.60 mL) and acidified by concentrated HNO_3 (13.60 mL). This acidic solution was then added to a template and heated to 60 °C with stirring until a clear solution was formed. The solution was cooled and treated with NaOH (0.1 M) added dropwise to precipitate HAP at pH 9.5. The suspension was stirred overnight, filtered, washed with ethanol and water, dried and calcined in air for 5 h at 550 °C [17].

For the hard template route, carbon nanorods (0.6 g) were dispersed in water (6 mL) using an ultrasonic bath, then added to a solution of $(NH_4)_2HPO_4$ (0.4 M, 100 mL) that was stirred at room temperature (18–22 °C) in a beaker. $Ca(NO_3)_2$ (0.6 M, 100 mL) was then added dropwise over one hour. The pH was maintained through the addition of NaOH (0.1 M) within the range 9.4–9.5. This 'milky' suspension was then stirred overnight. The resulting precipitate was filtered, cleaned alternately with water and ethanol three times, dried and calcined in air for 48 h at 550 °C using a ramp rate 1 °C min^{-1}.

Ion exchange was used to apply metal to the surface of the HAP. HAP (1 g) was stirred with a Pd or Ni precursor (50 mg) dissolved in water at ambient conditions for 3 days. The precipitate was then filtered, dried at 60 °C and calcined at 550 °C for 6 h. The preparation methods of all catalysts are shown in Table 1.

Table 1
Summary of preparation methods of the catalysts.

Sample name	HAP	Metal precursor
Pd_O_1	Tween 60	$PdCl_2$
Pd_O_2	Tween60 + $C_{12}EO_9$	$PdCl_2$
Pd_O_3	$C_{12}EO_9$	$Pd(NO_3)_2$
Pd_O_4	Carbon nanorods	$Pd(NO_3)_2$
Pd_O_5	Carbon nanorods	$PdCl_2$
Ni_O_1	Tween60 + $C_{12}EO_9$	$NiNO_3$
Ni_O_2	Tween 60	NiO
Ni/Pd_O_1	Carbon nanorods	$Pd(NO_3)_2$, $NiNO_3$

2.3. Characterisation of materials

Microscopic images were recorded using a JEOL 3000F high resolution transmission electron microscope (HR-TEM) at 300 kV. X-ray diffraction (XRD) was conducted using a Panalytical X'Pert Powder diffractometer with Cu K_α radiation ($\lambda = 1.5406$ Å). Nitrogen adsorption/desorption measurements were obtained using a Micromeritics ASAP 2020 Surface Analyser at − 196 °C. First, samples were degassed under vacuum ($p < 10^{-3}$ Pa) for 3 h at 300 °C. Thermogravimetric analysis (TGA) measurements were recorded using a Perkin Elmer 4000 instrument. X-ray photoelectron spectroscopy (XPS) analysis was performed using Monochromated Al Kα X-ray source (1486.7 eV), Specs PHOIBOS 150 mm hemispherical analyser with 9-channeltron detection.

2.4. Oxidation of methane

The catalytic experiments were performed in a fixed-bed quartz reactor (Carbolite type 3216) operated at atmospheric pressure. A feed mixture of 100 mL min^{-1} comprising CH_4:O_2:He in the proportions 5:10:85 was used in all catalytic tests(GHSV of 20,000 mL h^{-1} g^{-1}). Prior to reaction, each catalyst (0.2 g) was reduced in a flow of 30 mL min^{-1} H_2 for 1 h at 300 °C. The reaction products were monitored by a Hewlett Packard 5890 series II gas chromatograph connected to a thermal conductivity detector (TCD). Measurements were recorded at 50 °C intervals (after holding at that temperature for 5 min to avoid obtaining equilibrium between material and oxygen species in the stream) between 200 and 650 °C using a heating rate of 10 °C min^{-1}. After the reaction, the same sample of catalyst was allowed to cool in flowing He, then oxidised in 30 mL min^{-1} O_2 for 1 h at 300 °C, and the catalytic reaction was performed, thereafter, following the same procedure described above. The CH_4 conversion was calculated as follows:

$$CH_4\text{conversion (\%)} = \frac{(CH_4)\text{in} - (CH_4)\text{out}}{(CH_4)\text{in}} \times 100 \tag{1}$$

3. Results and discussion

3.1. Synthesis and characterisation of catalysts

A HR-TEM image shown in ESI Fig. 1A revealed the characteristic structure of HAP, Then, as presented in ESI Fig. 1B, the obtained XRD pattern revealed all the major peaks that correspond to the hexagonal morphology of HAP with the $P6_3/m$ space group (JCPDS 09/0432) [18,19].

Next, metal precursors were applied to the surface of HAP *via* a standard ion exchange approach. EDX analysis was performed to investigate average metal loading and revealed 2–3 wt% for Pd based catalysts and < 6 wt% of Ni content, summarised in Table 2. The BET results showed that sample Pd_O_2 exhibited the highest surface area of 114.6 m^2 g^{-1}. It is interesting to note that Ni-based catalysts showed much lower surface areas than those of Pd loaded HAP, suggesting different interactions between metal and support (Table 2). In view of that, XRD Rietveld analysis was performed to explore the interaction between the Pd metal and the support. Based on the lattice parameters that corresponded to a = b = 9.4 Å and c = 6.9 Å, which were equal to lattice parameters of unmodified HAP, it was clear that after Pd doping