

Methanol partial oxidation on carbon-supported Pt and Pd catalysts

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Available online 13 March 2007

Abstract

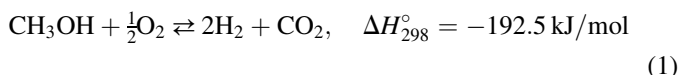
Different Pt and Pd catalysts supported on an activated carbon were prepared by using different metal precursors. Prepared catalysts were pretreated at 400 °C under different atmospheres to decompose the precursor compound and reduce the metal. After pretreatments, the supported catalysts were characterized by H₂ chemisorption, X-ray diffraction, transmission electron microscopy and X-ray photoelectron spectroscopy to know their metal dispersion, particle size, distribution and oxidation state. Afterwards, the catalysts were tested in methanol partial oxidation with two different O₂/CH₃OH molar ratios. Results obtained in this reaction were compared with those obtained for methanol decomposition in inert atmosphere. For Pt catalysts, there was an increase in methanol conversion and hydrogen production and a decrease in carbon monoxide production under oxidizing conditions. Both methanol conversion and partial oxidation reactions appear to be sensitive to Pt particle structure in the particle size range studied. Results obtained under oxidizing conditions differed between Pd and Pt catalysts. Finally, catalytic activity in methanol partial oxidation was more affected by Pt than Pd particle size in the size range studied.

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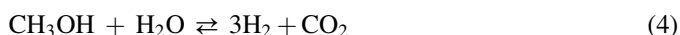
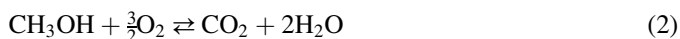
Keywords: Carbon-supported Pt and Pd catalysts; Methanol partial oxidation; Methanol decomposition

1. Introduction

Methanol partial oxidation is an attractive on-site source of H₂ for fuel cells. This is an exothermic reaction according to equation (1):



However, a number of other reactions can take place at the same time. These are mainly methanol total oxidation (2), methanol decomposition (3), steam reforming (4), water-gas shift (5), methanation (6), and CO (7) and H₂ (8) oxidation:



Methanol partial oxidation has been studied with different transition metals as catalysts. Cu-based catalysts have been most widely studied, but other metals such as Pd [1–9], Rh [3,10,11] and Pt [10,12,13] have also been tested. However, there have been fewer studies of this reaction catalyzed by Pt than by Pd. In the case of polycrystalline Pt, the composition of reaction products obtained depended on the O₂/CH₃OH molar ratio [10]. Thus, CO and H₂ were obtained in excess methanol, whereas CO₂ and H₂O formation was favored in excess oxygen. For equimolar amounts of methanol and O₂, the main products obtained were H₂O and CO. For Pt supported on α-Al₂O₃ [13], a decrease in the O₂/CH₃OH molar ratio brought about a decrease in methanol conversion and an increase in H₂ production. Other reactions were also observed, e.g., decomposition and water-gas shift reactions.

Methanol oxidation on Pd films was studied with deficiency and excess of O₂. In the former case, the only products obtained were CO and H₂. The effect of oxygen was to reduce the temperature required for methanol decomposition, and the total

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oxidation reaction predominated in excess oxygen. Methanol partial oxidation on Pd/ZnO and Pd/ZrO₂ with different O₂/CH₃OH molar ratios was also studied [4,5]. The H₂ and CO selectivities depended on methanol conversion and reaction temperature. Catalysts supported on ZrO₂ gave lower H₂ selectivity and higher CO selectivity compared with those supported on ZnO.

Carbon-supported Pt and Pd have been little used in decomposition [14] and partial oxidation reactions despite the wide use of these catalysts in organic synthesis [15–17]. However, there has been some investigation of other metals that are active in the decomposition reaction. Thus, copper oxide supported on activated carbons was shown to be very active in the above reaction at temperatures below 250 °C [18,19]. Importantly, there may soon be an increase in the use of carbon materials as supports for Pt and other metals because of their application in fuel cells [20–23].

The aim of this work was to study the methanol partial oxidation reaction on various carbon-supported Pt and Pd catalysts prepared from different metal precursors. The results were compared with those obtained from the methanol decomposition reaction.

2. Experimental

The activated carbon used as support was obtained from olive stones by chemical activation with KOH. The preparation method was described elsewhere [14]. Particle size of the activated carbon used was between 0.63 and 0.80 mm and its ash content was 0.1%. This activated carbon was characterized by N₂ adsorption at –196 °C and mercury porosimetry. Some characteristics of the support are shown in Table 1.

An adsorption method was used to prepare 2 wt.% Pt/C and 1 wt.% Pd/C catalysts, ensuring that Pt and Pd catalysts contained approximately the same proportion of metal atoms. The preparation method was explained in detail elsewhere [14]. The metal precursors used were [Pt(acac)₂] or [Pd(acac)₂] dissolved in tetrahydrofuran, [Pt(NH₃)₄]Cl₂ or [Pd(NH₃)₄]Cl₂ dissolved in water, and PdCl₂ dissolved in a HCl solution. The exact metal content of the supported catalysts was determined by burning a portion of the supported catalyst in air flow at 800 °C until constant weight. The designation of the catalysts, the precursor salt used, and their exact metal contents are shown in Table 2.

Catalysts were pretreated at 400 °C in either He or H₂ flow for 12 h or, alternatively, in He for 1 h and H₂ for 11 h before characterization or use in the catalytic tests. After pretreatment, catalysts were characterized by H₂ chemisorption at 25 °C,

Table 1
Surface area and porosity of the support

| | |
|---------------------------------------|------|
| S_{BET} (m ² /g) | 1291 |
| Micropore volume (cm ³ /g) | 0.51 |
| Mean micropore width (nm) | 0.64 |
| Mesopore volume (cm ³ /g) | 0.22 |
| Macropore volume (cm ³ /g) | 0.37 |
| Particle density (g/cm ³) | 0.65 |

Table 2
Designation of catalysts

| Catalyst | Precursor salt | Metal content (%) |
|----------|---|-------------------|
| Pt(A)C | Pt(acac) ₂ | 2.0 |
| Pt(N)C | [Pt(NH ₃) ₄]Cl ₂ | 2.0 |
| Pd(A)C | Pd(acac) ₂ | 1.1 |
| Pd(N)C | [Pd(NH ₃) ₄]Cl ₂ | 1.2 |
| Pd(Cl)C | PdCl ₂ | 1.1 |

transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). All of these techniques are described elsewhere [14]. It was assumed that one H atom was chemisorbed on one surface metal atom in both Pt and Pd catalysts. The dispersion, *D*, was obtained from the total H₂ uptake for Pt and from the irreversible H₂ uptake for Pd, obtained by subtracting the H₂ uptake in the first and second H₂ isotherms. Once the metal dispersion was known, the mean metal particle size, *d* (nm), was obtained as follows: $d(\text{Pt}) = 1.08/D$ and $d(\text{Pd}) = 1.12/D$.

TEM observations were made with a Zeiss EM10C electron microscope at 80 kV. Magnification was 100,000×. Micrographs obtained were analyzed by an image program, counting ≥2000 particles. The mean particle size was obtained by this procedure.

XRD was carried out with Philips PW 1710 equipment, using Cu Kα radiation at λ = 0.1545 nm and Ni filter. The *d*-value was obtained from peak broadening by using Sherrer's equation. The maximum intensity diffraction peak was selected at 2θ = 39.76° for Pt and at 2θ = 40.12° for Pd.

XPS measurements were made with an Escalab 200R system (VG Scientific Co.) equipped with Mg Kα X-ray source (*hν* = 1253.6 eV) and hemispherical electron analyzer. Both fresh catalysts and those previously used for H₂ chemisorption were analyzed by XPS. Survey and multi-region spectra were recorded at C 1s, O 1s, N 1s, Cl 2p, Pt 4f, and Pd 3d photoelectron peaks. The internal standard peak for determining binding energies was that of carbon C 1s (284.6 eV).

Methanol partial oxidation was carried out in a U-glass microreactor in which 0.20 g of the supported catalyst was placed. Reactant gas, a mixture of O₂ and He (diluent), was introduced after pretreatment of catalysts at 400 °C in the appropriate atmosphere and then cooling to the reaction temperature. Flows were controlled by mass flow controllers at a total flow of 60 cm³/min. The mixture contained a methanol molar concentration of 3.8% and O₂/CH₃OH molar ratios of 0.5 or 0.2.

Reaction temperatures ranged from 150 to 210 °C. Reaction products were analyzed by mass spectrometry using a Balzers model MSC200 apparatus. The reactant mixture passed through the catalysts for 30 min before analysis of reaction products. Selectivities were calculated as carbon or hydrogen in products/carbon or converted hydrogen. Methanol decomposition was also studied using the same experimental procedure and equipment but with no oxygen in the reactant mixture.

Support gasification did not occur within the temperature range used to study the methanol partial oxidation reaction. This was checked by blank tests in which an air flow (without

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