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Methanol partial oxidation on carbon-supported Pt and Pd catalysts

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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 H_2 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 O_2/CH_3OH 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.

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

1. Introduction

Methanol partial oxidation is an attractive on-site source of H_2 for fuel cells. This is an exothermic reaction according to equation (1):

$$CH_3OH + \tfrac{1}{2}O_2 \rightleftarrows 2H_2 + CO_2, \quad \Delta H^{\circ}_{298} = -192.5\,\mathrm{kJ/mol} \tag{1}$$

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 H_2 (8) oxidation:

$$CH_3OH + \tfrac{3}{2}O_2 \rightleftarrows CO_2 + 2H_2O \tag{2}$$

$$CH_3OH \rightleftarrows CO + 2H_2 \tag{3}$$

$$CH_3OH + H_2O \rightleftarrows 3H_2 + CO_2 \tag{4}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{5}$$

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \tag{6}$$

$$CO + \tfrac{1}{2}O_2 \rightleftarrows CO_2 \tag{7}$$

$$H_2 + \tfrac{1}{2}O_2 \rightleftarrows H_2O \tag{8}$$

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 O_2/CH_3OH molar ratio [10]. Thus, CO and H_2 were obtained in excess methanol, whereas CO_2 and H_2O formation was favored in excess oxygen. For equimolar amounts of methanol and O_2, the main products obtained were H_2O and CO. For Pt supported on α-Al_2O_3 [13], a decrease in the O_2/CH_3OH molar ratio brought about a decrease in methanol conversion and an increase in H_2 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 O_2. In the former case, the only products obtained were CO and H_2. 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/ZrO_2 with different O_2/CH_3OH molar ratios was also studied [4,5]. The H_2 and CO selectivities depended on methanol conversion and reaction temperature. Catalysts supported on ZrO_2 gave lower H_2 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 N_2 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, $[Pt(NH_3)_4]Cl_2$ or $[Pd(NH_3)_4]Cl_2$ dissolved in water, and $PdCl_2$ 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 H_2 flow for 12 h or, alternatively, in He for 1 h and H_2 for 11 h before characterization or use in the catalytic tests. After pretreatment, catalysts were characterized by H_2 chemisorption at 25 °C, 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 H_2 uptake for Pt and from the irreversible H_2 uptake for Pd, obtained by subtracting the H_2 uptake in the first and second H_2 isotherms. Once the metal dispersion was known, the mean metal particle size, d (nm), was obtained as follows: $d(\mathrm{Pt}) = 1.08/D$ and $d(\mathrm{Pd}) = 1.12/D$.

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

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 $\lambda = 0.1545$ 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 $2\theta = 39.76^\circ$ for Pt and at $2\theta = 40.12^\circ$ for Pd.

XPS measurements were made with an Escalab 200R system (VG Scientific Co.) equipped with Mg Kα X-ray source ($h\upsilon = 1253.6$ eV) and hemispherical electron analyzer. Both fresh catalysts and those previously used for H_2 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 O_2 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 cm^3/min. The mixture contained a methanol molar concentration of 3.8% and O_2/CH_3OH 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 methanol) was passed through the catalyst over the same temperature range and the catalyst was weighed before and after the reaction.

3. Results and discussion

3.1. Characterization of Pt catalysts

Results obtained for the dispersion and mean Pt particle size of catalysts are compiled in Table 3. Mean particle sizes obtained from the different techniques applied to a given catalyst were in good or fairly good agreement with each other. In both types of catalyst, He pretreatment yielded smaller mean particle size versus H_2 pretreatment. The reasons for this difference have been explained elsewhere [14].

Results of XPS studies of supported Pt catalysts have been published and explained in detail elsewhere [14]. Briefly, the XPS pattern of the Pt $4f_{7/2}$ region in the fresh catalysts showed only one component at 72.7–72.9 eV, which can be assigned to Pt^{2+} [28,29]. After He pretreatment of catalysts, a new component at 72.0–72.1 eV appeared in the Pt $4f_{7/2}$ region, which can be assigned to a metallic state of Pt [24]. H_2 pretreatment of catalysts shifted the latter component by 0.5 eV to lower binding energy values, indicating an increase in the Pt particle size as confirmed by H_2 chemisorption, XRD, and TEM measurements.

3.2. Characterization of Pd catalysts

All Pd catalysts were pretreated at 400 °C in He for 1 h and H_2 for 11 h. Mean particle sizes obtained using different techniques are compiled in Table 4. The d_{XRD} and d_{TEM} values were close and slightly lower than those obtained from H_2 chemisorption, which might indicate that chemisorption of this gas was inhibited. This phenomenon has been reported elsewhere with other Pd/C catalysts [25–27]. This would be due to the migration of carbon atoms towards the surface and into Pd crystallites during the pretreatment. The catalyst with highest mean particle size was that obtained using tetrammine palladium chloride as precursor salt.

Palladium core level spectra of Pd(A)/C catalyst are depicted in Fig. 1, as an example. Table 5 shows the binding energy of the Pd $3d_{5/2}$ component and the surface Pd contents obtained from XPS. The fresh Pd(N)/C catalyst showed components at 400.0 and 198.1 eV in N 1s and Cl $2p_{3/2}$ regions, respectively, corresponding to ammonium and chloride ions [28]. Likewise, the fresh Pd(Cl)/C catalyst showed the component at 198.1 eV in the Cl $2p_{3/2}$ region. These peaks disappeared after the pretreatment.

Table 3
Characterization of Pt catalysts

Catalyst	Pretreatment at 400 °C	D_{H_2}	d_{H_2}	d_{XRD}	d_{TEM}
Pt(A)C	He for 12 h	0.36	3.0	n.d.[a]	4.5
	H_2 for 12 h	0.09	11.9	12.4	7.5
Pt(N)C	He for 12 h	0.33	3.2	n.d.	–
	He for 1 h; H_2 for 11 h	0.13	8.2	10.0	–

Dispersion, *D*, and mean particle size, *d* (nm), from H_2 chemisorption, XRD, and TEM.

[a] Non-detected.

Table 4
Characteristics of Pd catalysts

Catalyst	d_{H_2}	d_{XRD}	d_{TEM}
Pd(A)/C	9.2	8.2	7.6
Pd(N)/C	–	12.7	10.8
Pd(Cl)/C	9.4	7.7	6.0

Mean particle size, *d* (nm), from H_2 chemisorption, XRD, and TEM.

In the fresh Pd(A)/C catalyst, two components in the Pd $3d_{5/2}$ region appeared at 335.9 and 337.9 eV. The first component at the lower binding energy corresponded to metallic Pd, and the second one at the higher binding energy corresponded to Pd^{2+}. These values were previously assigned for these oxidation states in this compound [30]. Conversely, in the fresh Pd(N)/C and Pd(Cl)/C catalysts, there was only one component in the Pd $3d_{5/2}$ region, which corresponded to Pd^{2+} in the precursor salts used [31–34].

Therefore, it appears that the acetylacetonate precursor complex was decomposed during preparation of the Pd(A)/C catalyst and the Pd^{2+} was partially reduced to Pd^0. Another possibility is that the Pd complex was decomposed and partially reduced during XPS analysis. Thus, it has been reported [35] that the electron beam can reduce the precursor if the exposure is too long, and that carboxylate type complexes can be partially decomposed when outgassed at ultra-high vacuum and exposed to X-ray radiation [30]. Pd^{2+} was completely reduced

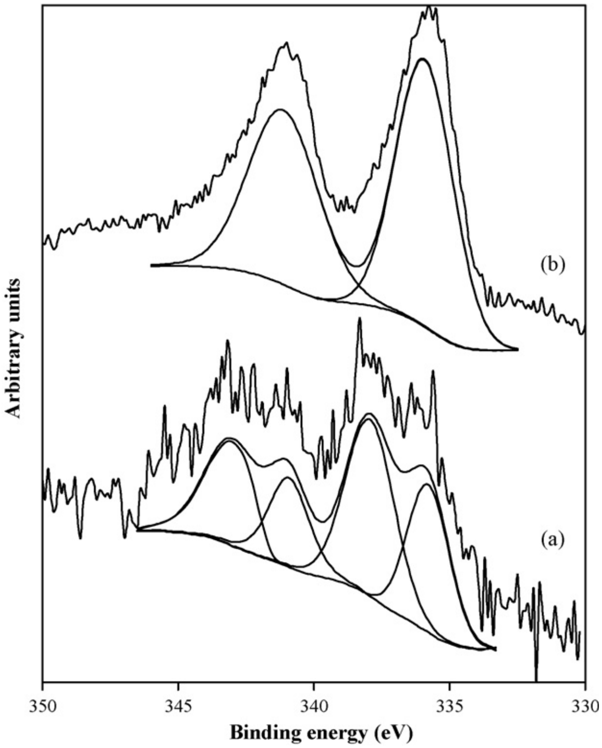

Fig. 1. Palladium core level spectra of Pd(A)/C catalyst: (a) fresh and (b) pretreated.

Table 5
Binding energy values of Pd $3d_{5/2}$ component and surface Pd content, Pd_{XPS}

Catalyst		Pd $3d_{5/2}$ (ev)	Pd_{XPS} (%)
Pd(A)/C	Fresh	335.9 (41)[a], 337.9 (59)	0.9
	Pretreated	335.9	3.8
Pd(N)/C	Fresh	338.0	0.8
	Pretreated	335.7	0.9
Pd(Cl)/C	Fresh	337.2	0.6
	Pretreated	335.9	0.5

[a] Data in parenthesis are the component percentage.

to Pd^0 after pretreatments of the catalysts. The binding energy of the Pd $3d_{5/2}$ component was between 335.7 and 335.9 eV, which corresponds to metallic Pd, as reported elsewhere [30–32,36,37] for Pd catalysts supported on carbons. In contrast, the binding energy reported for bulk Pd is 335.2 ± 0.3 eV [28,31,37–39]. The shift in binding energy to a higher value in carbon-supported Pd might be the consequence of an increased dispersion of Pd particles [31,36].

In the fresh Pd(A)/C and Pd(N)/C catalysts, the Pd_{XPS} value was close to their total Pd content, indicating a good distribution of the metal complex. In the fresh Pd(Cl)/C catalyst, the Pd_{XPS} value was smaller than its total Pd content, which may be due to the higher concentration of the metal complex within the carbon particles. There was practically no change in the Pd_{XPS} value after pretreatment of the fresh catalysts, with the exception of the Pd(A)/C catalyst. In this last case, the Pd_{XPS} value underwent a large increase, indicating that Pd particles were segregated to the outer surface of the support during pretreatment. The decomposition reaction of the acetylacetonate complex may have given the Pd particles sufficient mobility for this segregation.

3.3. Methanol partial oxidation on Pt catalysts

Methanol partial oxidation was carried out at two O_2/CH_3OH molar ratios, 0.5 and 0.2. The only reaction products detected were H_2, H_2O, CO, and CO_2. Effects of the O_2/CH_3OH molar ratio on methanol conversion and product distribution are shown in Table 6 for the He-pretreated catalyst Pt(N)/C as an example. When the molar ratio decreased there was also a decrease in methanol conversion and water selectivity, giving rise to an increase in H_2 selectivity. At the highest O_2/CH_3OH molar ratio, the total oxidation of methanol predominated, due to the high water and CO_2 selectivities. Likewise, oxidation of CO and H_2 from methanol decomposition may also be favored, although preferential oxidation of CO, especially on Pt catalysts, may greatly contribute to the zero CO selectivity. Because of these results, the remaining catalysts were studied at the lowest O_2/CH_3OH molar ratio.

Table 6
Methanol partial oxidation with two different O_2/CH_3OH molar ratios on He-preheated catalyst Pt(N)/C at reaction temperature of 150 °C

	Molar ratio	
	0.5	0.2
Methanol conversion (%)	51	12
Hydrogen selectivity (%)		
H_2O	86	65
H_2	14	35
Carbon selectivity (%)		
CO	0	0
CO_2	100	100

Effects of reaction temperature on methanol conversion and selectivities are shown, as an example, in Fig. 2 for Pt(A)/C pretreated in H_2. The increase in reaction temperature produced a large increase in methanol conversion, with an increase in H_2 and CO selectivities. This suggests that the contribution of steam reforming, Eq. (4), water-gas shift, Eq. (5), and preferential oxidation of CO, Eq. (7), diminishes when the temperature rises. Conversely, methanol decomposition, Eq. (3), appears to be favored with rising temperature due to the increase in CO selectivity.

Results obtained with these Pt catalysts in the methanol decomposition reaction under inert conditions [14] were compared with those obtained in the methanol partial oxidation. The methanol concentration in gas phase was the same in both reactions, as indicated in the Section 2. The only products obtained in the methanol decomposition reaction under inert conditions were CO and H_2.

Table 7 shows the activity for methanol conversion, r_{CH_3OH}, and for H_2 and CO production, r_{H_2} and r_{CO}, respectively, at 180 °C in methanol decomposition and partial oxidation reactions. There was an increase in r_{CH_3OH} and r_{H_2} and a decrease in r_{CO} under oxidizing conditions. These results are of interest in the context of the use of methanol to produce H_2 for proton exchange membrane fuel cells, essentially due to the reduction in CO production. The increase in r_{CH_3OH} is a consequence of the contribution of oxidation reactions, Eqs. (1) and (2), and steam reforming, Eq. (4), to methanol decomposition, Eq. (3). The increase in r_{H_2} and decrease in r_{CO} result from water-gas shift reaction, Eq. (5).

Effect of Pt particle size on methanol partial oxidation is shown in Fig. 3, where the turnover frequency (TOF) for methanol conversion and H_2 production is depicted against the mean Pt particle size. TOF values were obtained from the

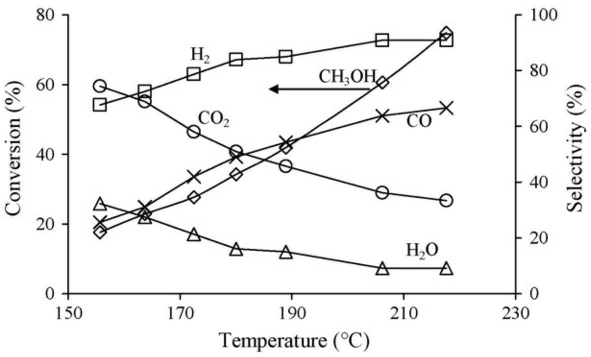

Fig. 2. Methanol conversion and selectivity against reaction temperature for the catalyst Pt(A)/C, pretreated in H_2 at 400 °C for 12 h. O_2/CH_3OH molar ratio = 0.2.

Table 7
Activity of Pt catalysts at 180 °C in methanol decomposition and partial oxidation reactions

Catalyst-pretreatment	d (nm)	Reaction	r_{CH_3OH} (μmol/g s)	r_{H_2} (μmol/g s)	r_{CO} (μmol/g s)
Pt(A)/C–He	3.0	Decomposition	0.52	0.77	0.40
		Partial oxidation	0.99	1.16	0.20
Pt(A)/C–H_2	11.9	Decomposition	1.37	2.30	1.18
		Partial oxidation	2.00	3.04	0.97
Pt(N)/C–He	3.2	Decomposition	0.45	0.66	0.30
		Partial oxidation	1.01	1.23	0.06
Pt(A)/C–He–H_2	8.2	Decomposition	1.03	1.69	0.83
		Partial oxidation	1.50	2.25	0.54

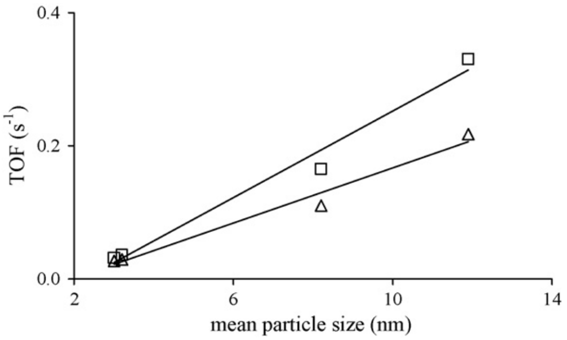

Fig. 3. TOF for methanol partial oxidation at 180 °C against Pt mean particle size. (□) hydrogen production; (△) methanol conversion.

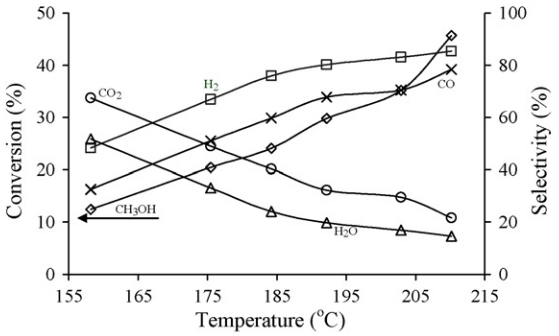

Fig. 4. Methanol conversion and selectivity against reaction temperature for catalyst Pd(N)/C pretreated in He at 400 °C for 1 h and H_2 at 400 °C for 11 h. O_2/CH_3OH molar ratio = 0.2.

respective activity and H_2 chemisorption values. This figure shows an increased activity when the mean Pt particle size of the catalyst is larger, which appears to indicate that the reaction is sensitive to the metal structure of the catalysts within the Pt particle size range studied. Similar results were found for the methanol decomposition reaction, as reported elsewhere [14].

3.4. Methanol partial oxidation on Pd catalysts

Methanol partial oxidation on Pd catalysts was studied only with an O_2/CH_3OH molar ratio of 0.2. Effects of reaction temperature on methanol conversion and hydrogen and carbon selectivities are plotted in Fig. 4 for catalyst Pd(N)/C, as an example. Similarly to the results obtained with Pt catalysts, higher temperatures produced greater methanol conversion activity and an increase in H_2 and CO selectivities, for the same reasons as explained above for Pt catalysts. These results were also similar to those observed with Pd/ZrO_2 catalysts [3,7,40] but differed in carbon selectivity findings from those obtained with Pd/ZnO catalysts [5,9]. Results obtained in methanol decomposition and partial oxidation reactions at 180 °C with these catalysts are compiled in Table 8. Under oxidizing conditions, the r_{CH_3OH} value slightly increased but both r_{H_2} and r_{CO} values decreased, unlike with the Pt catalysts. Therefore, an increase in H_2 combustion, Eq. (8), water-gas shift, Eq. (3), and CO oxidation, Eq. (7), would explain the results under oxidizing conditions.

The behavior of Pt and Pd catalysts in methanol partial oxidation can be compared at a similar mean metal particle size. Thus, Pt(A)/C pretreated in H_2 (d = 11.9 nm) can be compared with Pd(N)/C (d = 10.8 nm). Likewise, Pt(N)/C pretreated in He–H_2 (d = 8.2 nm) can be compared with Pd(A)/C (d = 7.6 nm). In the first case, the Pt catalyst had a higher r_{CH_3OH} and much higher r_{H_2} compared with the Pd catalyst. In the second case, however, Pt showed only slightly higher r_{CH_3OH} and r_{H_2} values compared with Pd. This might be a

Table 8
Activity of Pd catalysts at 180 °C in methanol decomposition and partial oxidation reactions

Catalyst	d_{TEM} (nm)	Reaction	r_{CH_3OH} (μmol/g s)	r_{H_2} (μmol/g s)	r_{CO} (μmol/g s)
Pd(A)/C	7.6	Decomposition	1.25	2.49	1.25
		Partial oxidation	1.44	2.01	0.95
Pd(N)/C	10.8	Decomposition	1.18	2.18	1.10
		Partial oxidation	1.33	1.55	0.83
Pd(Cl)/C	6.0	Decomposition	1.26	2.32	1.20
		Partial oxidation	1.30	1.68	0.96

consequence of the greater effect of Pt particle size on the activity of these catalysts.

4. Conclusions

Results obtained from methanol partial oxidation on Pt catalysts showed a decrease in methanol conversion and increase in H_2 selectivity with a lower O_2/CH_3OH molar ratio. At the highest O_2/CH_3OH molar ratio, total oxidation of methanol predominated due to high water and CO_2 selectivities. Likewise, CO and H_2 oxidation may also be favored. A higher reaction temperature produced a large rise in methanol conversion and an increase in H_2 and CO selectivities. Comparison between methanol decomposition and methanol partial oxidation results showed an increase in methanol conversion and hydrogen production activities and a decrease in CO production activity under oxidizing conditions. These results are relevant to the use of methanol to produce H_2 for proton exchange membrane fuel cells, essentially due to the lowering in CO production. There was an increase in the TOF for methanol conversion and H_2 production in methanol partial oxidation with larger mean Pt particle size of the catalyst, suggesting that this reaction can be sensitive to the metal structure of the catalysts within the size range studied.

In the case of methanol partial oxidation on Pd catalysts, a higher temperature produced an increase in methanol conversion activity and in H_2 and CO selectivities. Comparison between methanol decomposition and partial oxidation results showed a slight increase in methanol conversion but a decrease in hydrogen and CO production activity under oxidizing conditions, a different result to that found with 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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