Effect of platinum particle size and catalyst support on the platinum catalyzed selective oxidation of carbohydrates

J.H. Vleeming *, B.F.M. Kuster ‡ and G.B. Marin§

Laboratorium voor Chemische Technologie, Schuit Institute of Catalysis, Eindhoven University of Technology,
PO Box 513, 5600 MB Eindhoven, The Netherlands

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The effect of the platinum particle diameter and the catalyst support was investigated for the aqueous phase selective oxidation of methyl α-D-glucopyranoside, octyl α-D-glucopyranoside and α-cyclodextrin with molecular oxygen. No platinum particle size effect was observed in the platinum particle diameter range of 1.4 to 3.0 nm. The structure-insensitivity is attributed to the high degree of surface coverage by oxygen. The rate of deactivation due to over-oxidation of the catalyst increases to a small extent with decreasing platinum particle diameter. The effect of the catalyst support is much larger than the platinum particle size effect. The turnover frequency for platinum on activated carbon and carbon fibrils supported catalyst is 3–7 times higher than for graphite as the catalyst support. The support effect is attributed to the hydrophilic character of the support.

Keywords: glucopyranoside, selective oxidation, platinum, structure-sensitivity, catalyst support effect

1. Introduction

For the platinum catalyzed selective oxidation of carbohydrates or alcohols, converting hydroxyl groups into aldehyde, ketone or carboxylate groups, the reaction rate per unit surface area of platinum may depend on the platinum particle size. This rate is often expressed as the turnover frequency, i.e. the rate per surface atom. Che and Bennett [1] reviewed the influence of the particle size on the catalytic properties of supported metals, in particular on the turnover frequency. For the selective oxidation of methyl α-D-glucopyranoside over platinum catalysts [2] and for the electro-oxidation of methanol [3] an increase of the turnover frequency with increasing platinum particle diameter is reported. On the other hand other authors report smaller or no particle size effects for the oxidation of ethanol [4] or methanol [5].

The effect of the particle size on the rate reported for the oxidation of alcohols and carbohydrates is generally attributed to the increase of the heat of adsorption of oxygen with decreasing particle size [6,7], resulting in less reactive oxygen species [4] or a relative increase of the fraction of adsorbed oxygen species [3].

If platinum is more easily oxidized with decreasing platinum particle size, deactivation due to over-oxidation of the catalyst will also be larger for smaller particles. Over-oxidation is generally attributed to strong chemisorption of oxygen on the platinum surface [2,8] and can be described by a slow transformation of oxygen adatoms into subsurface oxygen [9]. This effect has indeed been reported for the oxidation of 2-propanol [10], for the oxidation of glucose [11] and for the electrochemical reduction of oxygen [6].

The catalyst support is another important factor determining the rate of carbohydrate oxidation. Firstly, the reaction rate or the extent of over-oxidation may depend on the internal rate of diffusion [12]. Secondly, the support may influence the surface properties of platinum particles due to platinum–support interaction [13–15]. Furthermore, the rate of aqueous phase oxidation may be influenced by the hydrophilic character of the catalyst [16], which is related to the number and nature of the support surface groups.

Often, metal particle size and support effects occur simultaneously. It is almost impossible to vary the metal particle size preserving all the physicochemical characteristics of the support and vice versa. Frequently, metal particle size effects are studied using different supports [2,11], supports with a different BET surface area [5] or catalysts with a different metal loading [6]. Furthermore, catalysts with different metal particle size are obtained by different preparation procedures [3] or by sintering upon high temperature treatments in nitrogen [17] or oxygen [4], which may also change the support or the metal–support interaction. On the other hand, support effects are often disguised by concomitant changes of the metal particle diameter [12], or differences in the distribution of metal particles over the support [11].

This paper deals with the effect of the platinum particle diameter and the catalyst support on the selective oxi-

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* Present address: Institut Francais du Pétrole, BP 3, 69390 Vernaison, France.

‡ To whom correspondence should be addressed.

§ Present address: Laboratorium voor Petrochemische Techniek, University of Gent, Krijgslaan 281, B 9000 Gent, Belgium.

dation of carbohydrates. The effects are studied by variation of the platinum particle diameter, pore diameter of the support, size of the carbohydrate, platinum–support interaction, hydrophilic character of the support and that of the carbohydrate. In order to prevent the simultaneous occurrence of two effects, these parameters are varied as much as possible independently from each other. The effect of the platinum particle size is studied for the oxidation of methyl α-D-glucopyranoside (figure 1a) on graphite supported catalysts. Graphite, activated carbon and carbon fibrils supported platinum catalysts are used to study the effect of the pore diameter, platinum–support interaction and hydrophilic character of the support. As the carbohydrates to be oxidized methyl α-D-glucopyranoside, octyl α-D-glucopyranoside (figure 1b) and α-cyclodextrin (figure 1c) are used. The carbohydrate size increases in the order methyl α-D-glucopyranoside $<$ octyl α-D-glucopyranoside $<$ α-cyclodextrin, while octyl α-D-glucopyranoside is the most hydrophobic carbohydrate.

2. Experimental

2.1. Catalysts

In order to study the platinum particle size effect platinum on graphite catalysts were prepared according to the procedure described before [18]. Graphite (Lonza HSAG300) with a BET surface area of 2.96×10^5 m^2 kg^{-1} was used. Reduction was performed by heating batches of 8 g in a helium flow of 0.2 mol s^{-1} (300 Nml min^{-1}) at 373 K for 1 h, followed by treatment in a helium flow at 473 to 1073 K for 2–20 h and reduction in a hydrogen flow at 473 to 773 K for 2–5 h. Due to the gasification of the graphite support [19] the platinum content of the catalyst increased slightly with increasing temperature of treatment from 4.0 wt% at 473 K to 4.3 wt% at 1073 K. For all preparation steps and experiments ultra pure Millipore water (18 MΩ cm) was used.

The effect of the support was studied using a graphite supported platinum catalyst, Pt/G, prepared according to the procedure mentioned before [18] and reduced at 573 K, a carbon fibrils supported platinum catalyst, Pt/CF, and an activated carbon supported platinum catalyst, Pt/C. For the preparation of the Pt/CF-catalyst the procedure [18] was slightly changed. Activation of the carbon fibrils (Hyperion) was performed by boiling the support in concentrated nitric acid at a concentration of 25 kg m^{-3} for 30 min [20]. The final reduction of the Pt/CF-catalyst was performed by flowing hydrogen over a bed of the catalyst at a flow rate of 0.07 mmol s^{-1} (100 Nml min^{-1}) at 553 K for 3 h. The Pt/C-catalyst was supplied by Engelhard (Escat 21).

2.2. Catalyst characterization

The platinum content was determined by UV/VIS spectrophotometry according to a procedure described elsewhere [18].

The BET surface area, S_{BET} (in m^2 kg$_{\mathrm{cat}}^{-1}$), was determined using a Micromeritics ASAP2000 instrument [18]. The catalyst pore size distribution and total specific pore volume was determined by mercury porosimetry using a Carlo-Erba 200 porosimeter or by the Barrett, Joyner and Halenda (BJH) method [21]. The average pore diameter, d_{p} (in m), is calculated from the BET-surface area, S_{BET} (in m^2 kg$_{\mathrm{cat}}^{-1}$) and the specific pore volume, $V_{\mathrm{S,p}}$ (in m^3 kg$_{\mathrm{cat}}^{-1}$), according to:

$$d_{\mathrm{p}} = 4\frac{V_{\mathrm{S,p}}}{S_{\mathrm{BET}}} . \qquad (1)$$

The fraction platinum atoms exposed, FE$^{\mathrm{CO}}$, was determined by CO pulse chemisorption, described elsewhere [18], and calculated with a CO adsorption stoichiometry of 1.

Platinum particle diameter distributions were obtained from the analysis of transmission electron micrographs (JEOL 2000 CX). Details of this procedure are described elsewhere [18].

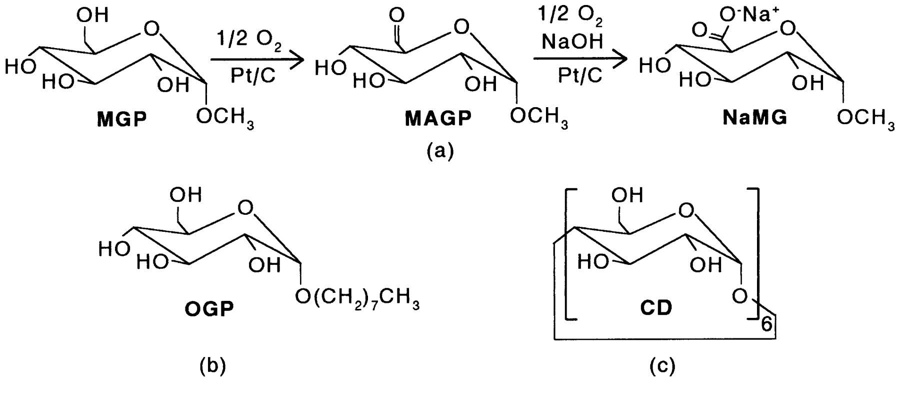

Figure 1. (a) Platinum catalyzed C$_6$-oxidation of methyl α-D-glucopyranoside (MGP) via methyl α-D-6-aldehydoglucopyranoside (MAGP) to sodium 1-O-methyl α-D-glucuronate (NaMG) with molecular oxygen. (b) Octyl α-D-glucopyranoside (OGP). (c) α-cyclodextrin (CD).

2.3. Carbohydrate oxidation reactions

Continuous experiments were performed for the oxidation of methyl α-D-glucopyranoside (figure 1a). Semi-batch reactions were investigated for the selective oxidation of methyl α-D-glucopyranoside (Fluka), octyl α-D-glucopyranoside and α-cyclodextrin (Merck). Octyl α-D-glucopyranoside was prepared from D-glucose (Janssen) and 1-octanol (Aldrich) according to the procedure of Straathof et al. [22]. As a catalyst a cation exchange resin in the H^+-form (K2411 supplied by Bayer) was used. Purity was checked by HPLC and measurement of the clearing point and the specific rotation. The reactions were performed in a three-phase slurry reactor with a liquid volume of 0.35×10^{-3} m^3. The set-up is described elsewhere [9,18]. The continuous experiments were performed under well-defined conditions by control of the temperature, pressure, reaction volume and gas and liquid composition [9]. During the semi-batch experiments the gas feed was continuous, but the liquid inlet and outlet flow rate were equal to zero and the pH was controlled by a titration unit (Radiometer TTT80).

Prior to reaction the catalyst was reduced in water or in 0.1 M $HClO_4$ at 363 K in a hydrogen flow at a flow rate of 1.4×10^{-4} mol s^{-1} (200 ml min^{-1}). Next, in the case $HClO_4$ had been used, the catalyst was washed with oxygen-free water until the filtrate was neutral. Under a nitrogen atmosphere a solution of the carbohydrate and (for the continuous experiments) the oxidation products at the appropriate concentration was added [9,18]. The reactions were started by introducing oxygen into the reactor. The stirring rate amounted to 20 s^{-1} for the oxidation of methyl α-D-glucopyranoside and α-cyclodextrin and 10 s^{-1} for octyl α-D-glucopyranoside in order to reduce the formation of foam.

It was verified experimentally and by calculations that the experiments were not significantly influenced by mass and heat transport limitations. During the continuous experiments irreversible catalyst deactivation due to platinum particle growth, site covering by carbonaceous species or metal leaching did not occur, since it was checked by CO chemisorption that the amount of surface platinum atoms did not change during reaction. Deactivation due to over-oxidation of the catalyst could be completely recovered by an in situ reduction of the catalyst with the carbohydrate [9]. This was performed by replacing oxygen in the feed by nitrogen.

For the continuous experiments the specific rate of consumption of methyl α-D-glucopyranoside, R_w (in mol kg_{cat}^{-1} s^{-1}), is calculated according to:

$$R_w = \frac{F_{v,L}(C^0_{MGP} - C_{MGP})}{W_{cat}}, \qquad (2)$$

in which $F_{v,L}$ is the volumetric liquid flow rate (in m^3 s^{-1}), C^0_{MGP} is the concentration of methyl α-D-glucopyranoside in the feed (in mol m^{-3}), C_{MGP} is the concentration of methyl α-D-glucopyranoside in the reactor (in mol m^{-3}) and W_{cat} is the catalyst mass (in kg).

For the semi-batch experiments the calculation of the initial rate of carbohydrate consumption is based on the initial rate of hydroxide consumption.

The turnover frequency, N (in s^{-1}), is calculated according to:

$$N = \frac{R_w M_{Pt}}{w_{Pt} FE^{CO}}, \qquad (3)$$

where M_{Pt} is the platinum molar mass (in kg mol^{-1}), w_{Pt} the platinum weight fraction (in kg_{Pt} kg_{cat}^{-1}) and FE^{CO} is the fraction of exposed platinum atoms determined by CO chemisorption.

2.4. HPLC analysis

For the continuous experiments the composition of the liquid outlet was determined by on-line HPLC analysis according to the procedure described by Vleeming et al. [9]. For the batch experiments samples of the methyl α-D-glucopyranoside oxidation reactions were analyzed by off-line HPLC analysis according to the procedures given by Schuurman et al. [23]. Reaction mixtures of octyl α-D-glucopyranoside and its oxidation products were analyzed using a 280×4.6 mm reversed phase C-18 ID Lichroma SS column (Chrompack). The eluent consisted of 0.4 v/v 50 mol m^{-3} formate buffer ($pH = 3.45$) and 0.6 v/v methanol. The column temperature was 333 K and the flow rate amounted to 0.5 ml min^{-1}. Refractive index detection was used. In order to avoid crystallization of octyl α-D-glucopyranoside the samples were kept in the autosampler above the Krafft-point [24] at 328 K. The reaction mixtures of the α-cyclodextrin oxidation reactions were not analyzed.

3. Catalyst characterization

Figure 2 shows that the platinum particle diameter increases with increasing temperature of treatment. As a result graphite supported platinum catalysts were obtained with a platinum particle diameter ranging from 1.4 to 3.0 nm. The observed particle growth is in agreement with Bett et al. [25], who demonstrated that in a hydrogen or helium atmosphere temperatures in excess of 873 K were required to bring about more extensive particle growth. This is due to the oxygen-containing surface groups on the support, which hamper platinum particle growth [26].

The fraction exposed (figure 2) remains constant up to a temperature of about 800 K and decreases sharply at higher temperatures. The observation that up to 800 K the d_s^{TEM} increases whereas the FE^{CO} is constant may be due to an increase of the CO adsorption stoichiometry, defined as the number of CO molecules that adsorb on one platinum surface atom, with increasing platinum

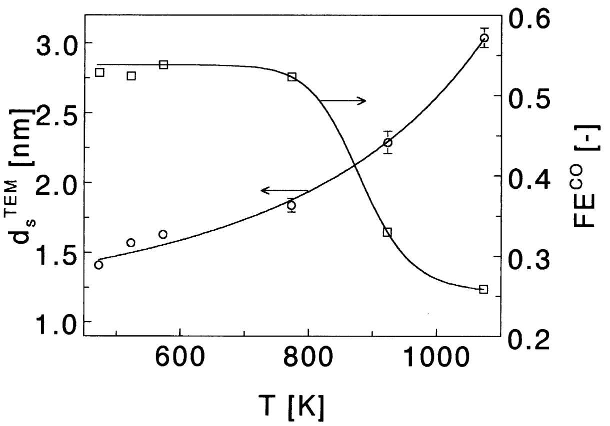

Figure 2. Surface area averaged platinum particle diameter, d_s^{TEM}, and fraction exposed determined with CO chemisorption, FE^{CO}, for the Pt/G-catalysts as a function of the temperature at which they were treated.

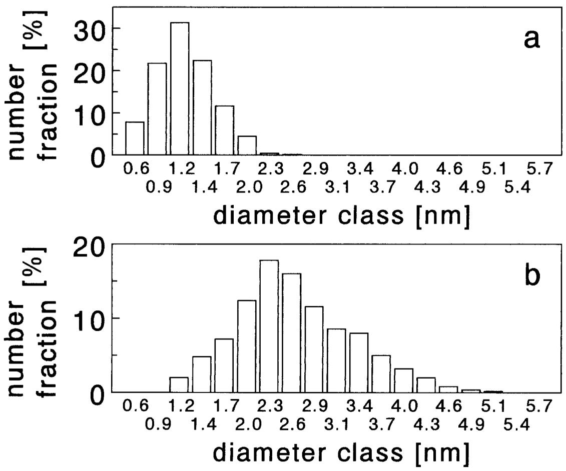

Figure 3. Platinum particle diameter distribution of (a) Pt/G-473, (b) Pt/G-1073 as determined by TEM micrograph analysis.

particle size [18]. Attempts to obtain a well-defined catalyst with smaller particles than Pt/G-473 failed, which is probably due to incomplete decomposition of the platinum precursor or incomplete reduction of the catalyst at a temperature below 473 K.

The platinum particle diameter distributions of the catalyst with the smallest and largest average particle diameter are shown in figure 3. Although the width of the particle diameter distribution increased upon high temperature treatment, the particles are still monodisperse.

From earlier X-ray absorption spectroscopy studies by van den Tillaart et al. [4] it was concluded that in the investigated range of platinum particle sizes the platinum particles are fully reduced prior to reaction and that they have an identical crystal structure.

Table 1 shows the characterization results for the platinum catalysts supported on graphite, activated carbon and carbon fibrils. The difference between these catalysts concerning the platinum content, fraction exposed and surface area averaged platinum particle diameter is rather small. However, the pore structure is different. The pore volume of the mesopores of the carbon fibrils support, i.e. in the range from 2 to about 50 nm, is equal to 0.81×10^{-3} m^3 kg$_{cat}^{-1}$, much larger than that of the graphite (0.39×10^{-3} m^3 kg$_{cat}^{-1}$) or activated carbon support (0.18×10^{-3} m^3 kg$_{cat}^{-1}$).

4. Platinum particle size effect

4.1. Initial rate

The extent to which the initial turnover frequency for the continuous oxidation of methyl α-D-glucopyranoside depends on the particle size is very small, as shown in figure 4. Therefore, no platinum particle size effect is concluded, i.e. the reaction shows structure-insensitivity.

The structure-insensitivity is in agreement with Watanabe et al. [5], who did not observe a platinum particle size effect for the electro-oxidation of methanol. Larger particle size effects that were reported for the selective oxidation of methyl α-D-glucopyranoside over platinum catalysts [2], the palladium catalyzed oxidation of glucose [11] and the electro-oxidation of methanol [3] were obtained by use of catalysts with different supports or catalysts prepared via different procedures. Therefore, these reported particle size effects might have been influenced by support effects.

In the present study every effort was made to minimize the influence of support effects. Due to treatment in a hydrogen or helium atmosphere, oxygen-containing surface groups are removed at higher temperature, which leads to a decrease of the hydrophilic character of the support. The importance of the hydrophilic charac-

Table 1
Platinum content, w_{Pt}, fraction exposed measured with CO chemisorption, FE^{CO}, and surface area averaged platinum particle diameter measured with TEM, d_s^{TEM}, BET surface area, S_{BET}, specific pore volume, $V_{S,p}$, and average pore diameter, d_p, for the platinum catalysts supported on graphite, Pt/G, activated carbon, Pt/C and carbon fibrils, Pt/CF, used for the study of the support effect

Catalyst	w_{Pt} (wt%)	FE^{CO}	d_s^{TEM} (nm)	S_{BET} (10^5 m^2 kg$_{cat}^{-1}$)	$V_{S,p}$ (10^{-3} m^3 kg$_{cat}^{-1}$)	d_p (nm)
Pt/G	3.4	0.56	1.70 ± 0.04	1.02	0.97	7.4
Pt/C	5.0	0.47	2.2 ± 0.1	7.62	1.20	3.2
Pt/CF	5.7	0.53	1.8 ± 0.1	2.53	1.58	12.5

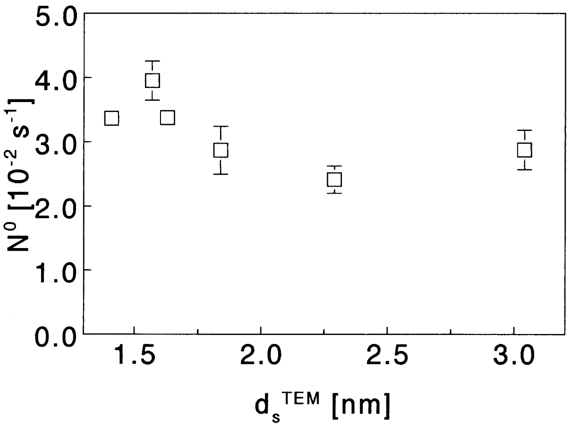

Figure 4. Initial turnover frequency of methyl α-D-glucopyranoside consumption, N^0, as a function of the surface area averaged platinum particle diameter, d_s^{TEM}. Conditions: pH = 8.0, $T = 323$ K, $p_{O_2} = 40$ kPa, $C_{cat} = 2$ kg m^{-3}, $C_{MGP} = 80$ mol m^{-3}, $C_{MAGP} = 1.8$ mol m^{-3}, $C_{NaMG} = 11$ mol m^{-3}.

ter of the support was clearly demonstrated by Hoogenraad et al. [16] for the hydrogenation of nitrobenzene over carbon fibrils supported palladium catalysts. In order to obtain a sufficient hydrophilic character in the present study all catalysts were pre-reduced in 0.1 M $HClO_4$ (at pH = 1) at 363 K. It was observed that after this pre-reduction the catalyst concentration did not decrease due to adhesion of catalyst to the reactor walls. The reduction at a pH of 1 did not lead to changes of the total active platinum surface area compared to reduction at a neutral pH.

The structure-insensitivity for methyl α-D-glucopyranoside oxidation is unlike the results of van den Tillaart et al. [4], who observed a small increase of the turnover frequency of ethanol oxidation for particles smaller than 2 nm, also for graphite supported platinum catalysts. The following explanation can be given to account for this difference.

During the selective oxidation of methyl α-D-glucopyranoside the platinum surface is mainly covered by oxygen [2,9], whereas during ethanol oxidation the degree of coverage is much lower [4,27]. This is caused by the better reducing ability of ethanol compared to methyl α-D-glucopyranoside [28]. It is suggested that, if the reaction is operated under conditions of highly covered surfaces, usually the reaction is structure-insensitive [29]. Whereas, at low surface oxygen coverages structural effects predominate due to the increase of the heat of adsorption of oxygen with decreasing platinum particle diameter [4], at high surface coverages the structural nonuniformaties are overwhelmed by surface interactions [29]. Therefore, since during methyl α-D-glucopyranoside oxidation the surface coverage by oxygen is much higher than during ethanol oxidation, the former reaction is less structure-sensitive.

An alternative explanation to account for the absence of structure-sensitivity for the oxidation of methyl α-D-glucopyranoside is that the relative increase of the degree of coverage by oxygen with decreasing platinum particle size is smaller than for low oxygen coverages. Since oxygen is involved in the rate determining step and the degree of coverage is larger than 0.5 [2,9] the effect of the platinum particle diameter on the initial turnover frequency will be small for methyl α-D-glucopyranoside oxidation. The effect of the platinum particle diameter on the degree of coverage by the other reactant, methyl α-D-glucopyranoside, is assumed to be much smaller, since in a recent kinetic study [9] it was shown that the adsorption of methyl α-D-glucopyranoside must be regarded as physisorption rather than as chemisorption.

4.2. Extent of deactivation

The extent of deactivation by over-oxidation, expressed as the ratio of the turnover frequency and the initial turnover-frequency, N/N^0, increases slightly with decreasing platinum particle diameter as shown in figure 5. This effect was also reported for the oxidation of 2-propanol [10], the oxidation of glucose [11] and the electrochemical reduction of oxygen [6].

The effect of the platinum particle size on the extent of deactivation by over-oxidation is attributed to the increase of the heat of adsorption of oxygen with decreasing particle size [6,7]. Deactivation due to over-oxidation can most adequately be described by the transformation of oxygen into subsurface oxygen [9,30]. Because smaller particles are more easily oxidized [6,7] it is likely that the extent of deactivation by over-oxidation depends on the particle size.

5. Effect of the catalyst support

Figure 6 shows the effect of the catalyst support on the initial turnover frequency for the semi-batch oxida-

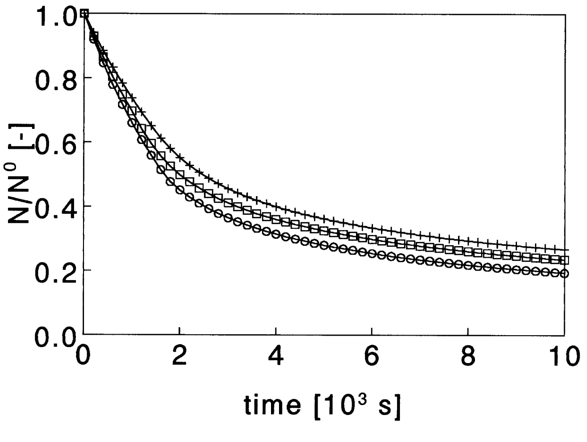

Figure 5. Effect of the platinum particle diameter on the extent of deactivation, expressed as the normalized turnover frequency of methyl α-D-glucopyranoside consumption, N/N^0 for d_s^{TEM} (nm) = (○) 1.41, (□) 1.84, (+) 3.04. Conditions: see figure 4.

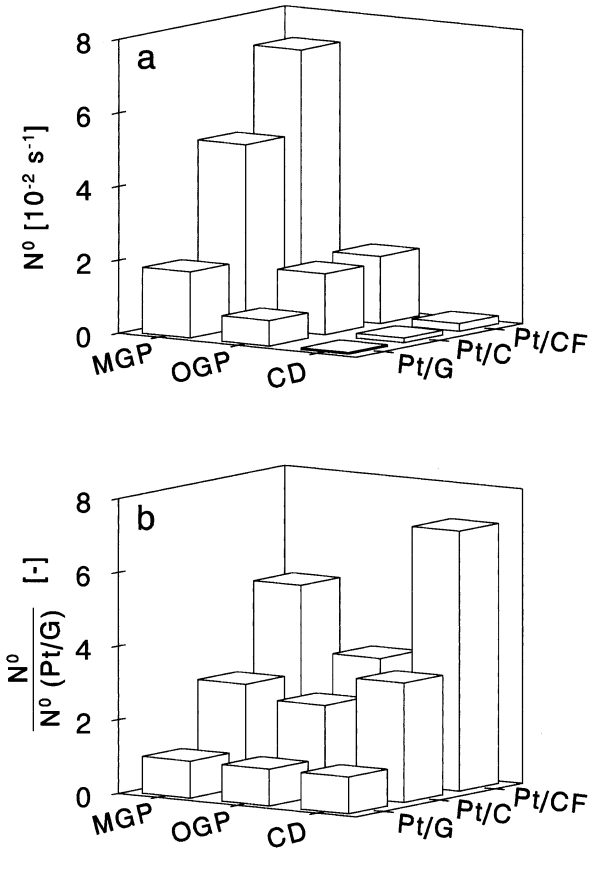

Figure 6. (a) Effect of the catalyst support on the initial turnover frequency for oxidation of methyl α-D-glucopyranoside, MGP, octyl α-D-glucopyranoside, OGP and α-cyclodextrin, CD. (b) Initial turnover frequency relative to that obtained for Pt/G. Conditions: pH = 8.0, $T = 323\,\mathrm{K}, p_{O_2} = 40\,\mathrm{kPa}, C_{\mathrm{cat}} = 2\,\mathrm{kg\,m^{-3}}, C^0 = 100\,\mathrm{mol\,m^{-3}}$.

tion of methyl and octyl α-D-glucopyranoside and α-cyclodextrin. A strong dependence of the turnover frequency on the molecular size of the carbohydrate is observed. Furthermore, the turnover frequency clearly depends on the support, since the turnover frequency for activated carbon is 3–4 times and for carbon fibrils 4–7 times higher than for graphite as the catalyst support. The effect of the support is much larger than the effect of the particle size.

The support effect cannot be due to internal transport limitation. Calculation of the rate of intraparticle oxygen and methyl α-D-glucopyranoside transport showed that the reactions were not significantly influenced by internal transfer limitation. No relation between the pore size distribution, which increases in the order Pt/C < Pt/G < Pt/CF, or the size of the carbohydrate molecule and the increase of the turnover frequency relative to that obtained for the Pt/G-catalyst can be concluded from figure 6b. The strong dependence of the turnover frequency on the molecular size of the carbohydrate is attributed to steric effects upon adsorption on the platinum surface and is discussed in a forthcoming publication [31].

The support effect is not caused by differences in platinum–support interaction either. The platinum–support interaction is assumed to be larger for the graphite supported catalyst due to electron transfer from the graphite to the platinum particles, which are located on the edges of the graphite layers [15]. The difference in the number and nature of the support functional groups may affect the electronic nature of the platinum as well [13]. The degree of oxygen coverage is expected to be higher for the graphite supported catalyst as a result of the more electron-rich platinum surface and a lower turnover frequency is expected. On the other hand, the different electronic structure for the Pt/G-catalyst is expected to affect the rate of deactivation by over-oxidation as well. The effect of the support on the extent of deactivation by over-oxidation during the selective oxidation of methyl α-D-glucopyranoside is, however, negligible, as shown in figure 7. Therefore, even though a lower turnover frequency is observed for graphite, the small effect of the support on the extent of deactivation by over-oxidation indicates that the platinum–support interaction does not play an important role.

The support effect may result from a difference in the hydrophilic character of the catalyst, which is related to the number and nature of the support surface groups. The hydrophilic character will affect the affinity of the catalyst for the aqueous phase as well as the interaction between the support and the carbohydrates.

Platinum on graphite has the lowest affinity for the aqueous phase, as was observed experimentally. This is probably caused by the lower number of support surface groups that are created by oxidation with sodium hypochlorite (Pt/G-catalyst) than by oxidation with nitric acid (Pt/CF-catalyst) [32]. This is consistent with the lower platinum content of the Pt/G-catalyst obtained upon ion-exchange with the $Pt(NH_3)_4^{2+}$-complex. It was shown by Hoogenraad et al. [16] that freshly prepared

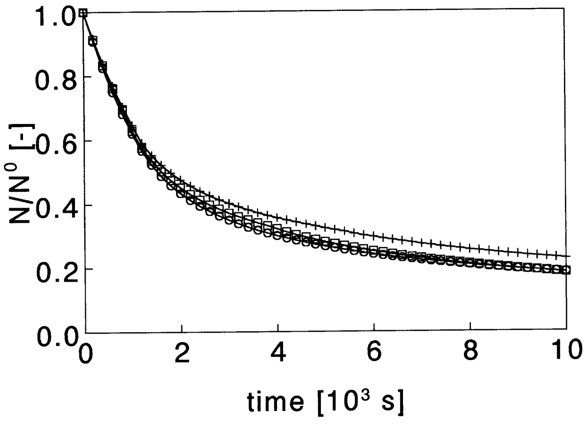

Figure 7. Effect of the catalyst support on the extent of deactivation, expressed as the normalized turnover frequency of methyl α-D-glucopyranoside consumption, N/N^0 for (□) Pt/G, (○) Pt/C, (+) Pt/CF. Conditions: pH = 8.0, $T = 323$ K, $p_{O_2} = 40$ kPa, $C_{\mathrm{cat}} = 2$ kg m^{-3}, $C_{\mathrm{MGP}} = 83\,\mathrm{mol\,m^{-3}}$, $C_{\mathrm{MAGP}} = 1.8\,\mathrm{mol\,m^{-3}}$, $C_{\mathrm{NaMG}} = 10\,\mathrm{mol\,m^{-3}}$.

carbon fibrils supported catalyst displayed a higher affinity for the aqueous phase than the activated carbon supported catalyst. Therefore, the hydrophilic character is expected to increase in the order graphite $<$ activated carbon $\leqslant$ carbon fibrils, which coincides with the increase of the turnover frequency (figure 6). Therefore, the hydrophilic character of the support, which determines the affinity of the catalyst for the aqueous phase can well explain the observed support effect.

A smaller hydrophilic character of the support may also affect the physisorption of the carbohydrate on the support. An increase of this carbohydrate–support interaction may result in an increase of the surface diffusion of the carbohydrate. Indeed, in figure 6 a small effect is observed for the least hydrophilic reactant, octyl α-D-glucopyranoside, and the least hydrophilic support, graphite. The increase of the turnover frequency on the Pt/C- and Pt/CF-catalysts relative to that on the Pt/G-catalyst is slightly smaller for octyl α-D-glucopyranoside, because the interaction between graphite and octyl α-D-glucopyranoside is expected to be relatively larger.

The adsorption of relatively large carbohydrate molecules on the platinum surface will also be affected by the amount and nature of the support functional groups in the vicinity of a platinum particle, because the size of a hydrated carbohydrate molecule is comparable to the diameter of a platinum particle. The interaction of the support groups with the carbohydrate molecule will determine the orientation of the hydroxyl groups of the carbohydrate towards the platinum surface and influences the adsorption of the carbohydrate on a platinum site [31]. This can have a strong effect on the turnover frequency.

In summary, it is proposed that the support effect is mainly caused by differences in hydrophilic character and adsorption properties of the support. This influences the affinity of the catalyst for the aqueous phase and the adsorption of carbohydrates on the platinum surface, due to interaction of the carbohydrate with the support functional groups located near the platinum particles.

6. Conclusions

The catalyst support has a much stronger effect on the turnover frequency than the platinum particle diameter for the investigated platinum catalyzed selective oxidations of carbohydrates.

In the platinum particle diameter range of 1.4 to 3.0 nm no variation of the initial turnover frequency is observed for the selective oxidation of methyl α-D-glucopyranoside. The structure-insensitivity of the reaction is attributed to the high surface coverage by oxygen. The extent of deactivation due to over-oxidation increases to a small extent with decreasing particle size, which is explained by the increase of the heat of adsorption of oxygen with decreasing platinum particle diameter.

The initial turnover frequency for the activated carbon or carbon fibrils supported platinum catalyst is 3–7 times higher than for graphite as the catalyst support. This is attributed to the lower number of support surface groups for the graphite supported catalyst, which results in a decrease of the hydrophilic character and a lower affinity for the aqueous phase. Furthermore, the support surface groups strongly influence the adsorption of carbohydrates on platinum particles, due to interaction of the carbohydrate with the support functional groups located near these particles. The support effect is not caused by internal transport limitation, apparent from the independence of the turnover frequency on the pore diameter of the support for carbohydrates of different molecular size. Also, no effect of the platinum–support interaction was observed.

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