Pore curvature and support composition effects on the electronic properties of supported Pt catalysts: An infrared spectroscopy study with CO as probe molecule

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Abstract

Supported 1 wt% Pt-based catalyst materials have been used as model systems to study pore curvature and support composition effects on the electronic properties of supported Pt nanoparticles. For this purpose, Pt nanoparticles have been loaded onto microporous (ITQ-1), mesoporous (Si-MCM-41, Si-MCM-48 and Si-SBA-15), macroporous (SiO₂) all-silica supports, as well as onto a macroporous SiO₂ support, impregnated with monovalent (Na⁺, Cs⁺) and divalent (Mg²⁺, Ba²⁺) cations. Time- and temperature-dependent infrared spectroscopy with CO as probe molecule has been used to investigate the adsorption and desorption properties of CO from these supported Pt nanoparticles. At 350 K, a narrow and smooth linear Pt-coordinated C≡O vibration band at 2070 cm⁻¹ was observed for the all-silica catalysts. The IR-CO-TPD results revealed a slightly higher desorption rate for the micro- and mesoporous supports, probably due to larger non-bonding electrostatic interactions between CO and the pore walls. A systematic shift from linear (L) to bridge (B) bonded C≡O upon a decrease of the radius of curvature, which would indicate an increasing electron charge on the supported Pt nanoparticles, is however not observed. In contrast, a relationship between the L:B band intensity ratio and the Lewis acidity of the monovalent and divalent cations, as expressed by the Kamlet-Taft parameter α , was observed for the Pt/SiO₂ catalysts. This effect is less pronounced than for zeolite-supported Pt nanoparticles (J. Phys. Chem. B 2005, 109, 3822–3831), but the results demonstrate that the correlation can be easily transferred from one support type to another, thus providing further guidelines for the design of improved automotive catalysts.

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1. Introduction

The catalytic properties of supported nano-sized noble metal particles are known to be tuneable by changing the chemical composition, porosity and structure of the support material. However, despite many characterization studies that have been undertaken to elucidate the exact nature of this metal-support effect [1–6], many questions still remain, preventing the design of improved catalyst systems based on an intelligent choice of the support material. In principle, three effects of the support on the

catalytic activity of the metal particles can be distinguished: i.e., (1) the support composition, (2) the support pore size and curvature and (3) the presence of promoting elements. In previous papers, we have reported on well-defined Pt nanoparticles supported on a microporous crystalline aluminosilicate material [7–9]. More specifically, we have investigated the effect of monovalent (Na⁺, K⁺, Rb⁺ and Cs⁺) and divalent (Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺) cations on the electronic properties of Pt nanoparticles entrapped in the supercages of zeolite Y. Pt–C≡O temperature programmed desorption infrared spectroscopy (TPD-IR) and atomic X-ray absorption fine structure (AXAFS) studies were used to determine the electron charge on the supported Pt nanoparticles. It was found that the Pt electron density increased with decreasing Lewis acidity of the cation

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introduced in the zeolite matrix. Simultaneously, the CO coverage increased with increasing electron density, which resulted in an enhanced CO oxidation activity.

In order to further shed light insight into the origin of these intriguing metal-support interactions, it is worthwhile to perform a similar systematic study on the effect of the support pore curvature. For that reason, we have decided to investigate the physicochemical properties of supported Pt nanoparticles in a series of catalysts with different curvatures of the support wall by means of CO IR-TPD spectroscopy. To exclude effects of the chemical composition, we have investigated a series of Pt-loaded all-silica supports with an architecture ranging from micropores over mesopores to macropores. ITQ-1 is an all-silica microporous molecular sieve with a pore structure similar to that of zeolite Y [10–12], while Si-MCM-41, Si-MCM-48 and Si-SBA-15 are different mesoporous solids also possessing amorphous silica walls [13,14]. Finally, SiO₂ is an amorphous all-silica material containing macropores. It will be shown that the effect of the pore curvature of an all-silica support on the electron density of supported Pt nanoparticles plays only a minor role. As a consequence, the chemical composition of the support must play the dominant role. For that reason, it was a logical next step to investigate whether the effect on the electronic properties of the metal particles that was obtained by the introduction of promoting cations in Pt/zeolite-Y [7–9], can be transferred to other support materials, such as an all-silica one. For this purpose, we have studied a series of Pt/SiO₂ catalysts loaded with monovalent (Na⁺, Cs⁺) and divalent (Mg²⁺, Ba²⁺) cations. It will be shown that the promoting effect also correlates with the Lewis acidity of the cations under study, although the promoting effect is less pronounced than previously observed for zeolite-based materials.

2. Experimental

2.1. Catalyst preparation

The microporous silica material ITQ-1 has been synthesized according to a recipe of Cambor and co-workers [10–12]. Si-SBA-15, Si-MCM-41 and Si-MCM-48 materials were used as mesoporous silica supports and were prepared according to the method of, respectively, Van der Voort et al. [13,14], Mokaya

and Jones [15] and Baltes et al. [16]. Amorphous SiO₂ was used as a macroporous support and obtained from Aldrich (Davisil 645). The same material was used to prepare Na-SiO₂, Cs-SiO₂, Mg-SiO₂ and Ba-SiO₂ by dry impregnation with aqueous solutions of the corresponding metal nitrates. The following materials were used for this purpose: NaNO₃ (Merck, p.a.), CsNO₃ (Acros, 99.9%), Mg(NO₃)₂·6H₂O (Acros, 99%) and Ba(NO₃)₂ (Merck, p.a.).

Next, 1 wt% supported Pt particles were prepared *via* a dry impregnation step of the support materials with the appropriate aqueous solutions of Pt(NH₃)₄(NO₃)₂. After impregnation and drying at 353 K in N₂ (quality 4.0; Hoekloos) for 8 h, calcination was carried out by drying in a high air flow (30 ml/min) during 12 h followed by increasing the temperature to 573 K at a heating rate of 0.2 K/min, where it was kept for 8 h to achieve complete removal of NH₃/NO₃ prior to reduction. Reduction was performed in a 60 ml/min H₂ (quality 5.0; Hoekloos) flow with a ramp of 5 K/min to 573 K (1 h). After reduction and flushing with N₂ at room temperature, passivation was carried out by increasing the O₂ flow to 10 ml/min to prevent aggregation of Pt particles. The physicochemical properties of the different catalyst materials under study have been summarized in Table 1.

2.2. Catalyst characterization

X-ray fluorescence (XRF) was carried out on all samples to determine the Pt and cation loadings using a Spectro X-lab 2000 instrument (Spectro). N₂ physisorption was performed at 77 K with a Micromeritics ASAP 2400 apparatus (quality 4.0; Hoekloos). Prior to these measurements, the samples were degassed for 24 h at 573 K in vacuum. Surface area, pore volume and pore size distribution were calculated with standard BET theory. High-resolution transmission electron microscopy (HRTEM) was done with a Philips CM 30 UT electron microscope equipped with a field emission gun as the source of electrons, operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions. Extended X-ray absorption fine structure (EXAFS) measurements were carried out at the ESRF (Grenoble, France) at CRG

Table 1
Physico-chemical properties of the catalysts under study

Sample	wt % Pt	Particle size (nm)	Coordination number (N)	Surface area (m ² /g)	Pore volume (ml/g)	Mean pore diameter (nm)
Pt/ITQ-1	1.4	1	6.5	418	0.18	3.2
Pt/MCM-41	0.7	1–4	8.2	947	1.08	2.7
Pt/MCM-48	1.0	1–4	7.6	690	1.15	3.0
Pt/SBA-15	0.7	1	6.5	678	0.90 (0.17 micro)	5.8
Pt/SiO ₂	0.9	1–4	7.9	542	0.23	16
Pt/Na-SiO ₂	1.8	1–2	–	125	<0.01	12
Pt/Cs-SiO ₂	1.2	1–10	8.8	102	<0.01	26
Pt/Mg-SiO ₂	1.7	1–3	–	209	<0.01	7.5
Pt/Ba-SiO ₂	1.3	1–3	7.0	193	<0.01	18

Pt wt % were obtained from XRF, particle size from HRTEM, Pt-coordination number from EXAFS and support surface area, pore volume and mean pore diameter from N₂ physisorption measurements.

DUBBLE (BM26A). The samples were prepared by pressing 0.12 to 0.14 g powder to a self-supporting wafer. Next, the wafer was placed in a treatment cell. Prior to measurement, the sample was dried at 423 K for 30 min in a flow of dry He and then slowly heated to 573 K under a flow of 10% H₂ in He to reduce the passivated Pt. Finally, the samples were measured at liquid N₂ temperature. EXAFS data analysis was carried out with the XDAP program [17].

Infrared (IR) measurements were performed on self-supporting catalyst wafers that were pressed from 0.01 to 0.05 g of calcined and reduced sample material. A pressure of 3 bar was applied during 10 s to prevent destruction of the pore structure of the support [18]. The wafer was placed in an IR transmission cell equipped with CaF₂ windows as previously described [19]. The cell was evacuated to 10^{−8} bar followed by drying of the wafer at 323 K overnight prior to reduction by a 10 ml/min flow of H₂ (quality 4.6; Hoekloos). During reduction the temperature was raised from 323 to 573 K where it was maintained for 1 h. Next, the system was switched to vacuum and after 1 h at 573 K, cooled to 323 K at a rate of 3 K/min. In the next step, the catalyst wafer was exposed to 10% CO (quality 4.7; Hoekloos) in He (quality 4.6; Hoekloos) at a pressure of 0.2 bar. After 30 min of static pressure, the system was re-evacuated and after another 30 min, temperature programmed desorption (TPD) was started by increasing the temperature from 323 to 573 K (3 K/min), where it was maintained for 30 min. IR spectra were recorded on a Perkin-Elmer 2000 FTIR instrument with a data point resolution of 4 cm^{−1}. For each spectrum 25 scans were co-added. As a background, the spectrum of the catalyst wafer was taken after drying, reduction and cooling down to 323 K, 2 min prior to CO exposure. During CO adsorption and TPD, time-resolved scanning was carried out by automatically acquiring spectral data every 2 min, using Perkin-Elmer Time-Base software. Intensity data were acquired by calculating the integrated area of baseline corrected spectra using the Perkin-Elmer Spectrum software.

3. Results and discussion

3.1. Catalyst characterization

The physicochemical properties of the catalyst materials under study as obtained with N₂ physisorption, XRF, HRTEM and EXAFS have been summarized in Table 1. The surface area of Pt/ITQ-1 was 418 m²/g with a mean pore diameter of 3.2 nm and a micropore volume of 0.18 ml/g. The surface area of the mesoporous Pt/Si-MCM-41, Pt/Si-MCM-48 and Pt/Si-SBA-15 was 947, 690 and 678 m²/g, respectively. This is a reduction of about 10–20% compared to the BET results obtained prior to Pt impregnation and is attributed to blocking of some of the pore architecture. The corresponding pore diameters were 2.7, 3.0 and 5.8 nm. The results for Si-SBA-15 pointed to a significant amount of 1 nm micropores, next to the 5.8 nm mesopores [13,14]. The amorphous SiO₂ samples exhibited the expected low pore volumes (<0.1 ml/g) and average mean pore diameters larger than 10 nm. The Pt content of the different

catalyst materials as determined by XRF varied between 0.7 (Pt/SBA-15) and 1.7 (Pt/Mg-SiO₂) wt% Pt. The estimated amount of cations in the Pt/Na-SiO₂ and Pt/Mg-SiO₂ samples was 0.5 wt%, while for Pt/Cs-SiO₂ and Pt/Ba-SiO₂ a content of 4 wt% was determined with XRF. The HRTEM pictures revealed that the Pt nanoparticles of the all-silica catalysts are well dispersed. The majority of the particles were about 1 nm with some larger Pt-agglomerates for Pt/Si-MCM-41, Pt/Si-MCM-48 and Pt/SiO₂. The metal ion-impregnated Pt/SiO₂ samples showed Pt clusters of 1–3 nm for Pt/Na-SiO₂, Pt/Mg-SiO₂ and Pt/Ba-SiO₂, while for Pt/Cs-SiO₂ particles up to 10 nm were present. The same observation of larger Pt particles was made previously on the Pt/Cs-Y catalysts [7–9]. To illustrate the Pt particle size and distribution, a selection of HRTEM micrographs of Pt/ITQ-1, Pt/Si-MCM-41, Pt/Na-SiO₂ and Pt/Ba-SiO₂ is presented in Fig. 1.

The Pt coordination numbers determined with EXAFS are in close agreement with the results of HRTEM. For Pt/ITQ-1 and Pt/Si-SBA-15, a coordination number of about 6.5 was found, which corresponds to an average Pt particle size of 1.1 nm, while the values of 7–8 obtained for Pt/Si-MCM-41, Pt/Si-MCM-48 and the Pt/SiO₂ samples point to an average diameter of about 1.5 nm.

3.2. Infrared CO adsorption experiments

The results of the IR-CO temperature programmed desorption are shown in 3D projection in Figs. 2 and 3. The corresponding band maxima, the half band width (HBW) of the linear band and the linear-to-bridge (L:B) intensity ratio at selected temperatures are listed in Table 2. All catalysts show a strong IR-absorption band in the range 2100–2000 cm^{−1} and a weaker one at around 1800 cm^{−1}. The high wavenumber band is commonly assigned to the linear Pt-bonded C≡O stretching vibration, while the lower frequency components are attributed to bridge coordinated types of CO [7–9,19–24]. At higher temperature the band patterns becomes more complex due to reorientation of the CO as result of changing interactions [7–9,24]. In what follows, we will discuss the effects of the pore curvature and the promoting elements separately.

3.2.1. Pore curvature effects

In order to study the effect of the pore curvature of the support material on the electronic properties of the supported Pt nanoparticles, the IR-CO-TPD results of the all-silica microporous (Pt/ITQ-1), mesoporous (Pt/Si-MCM-41, Pt/Si-MCM-48 and Pt/Si-SBA-15) and macroporous (Pt/SiO₂) catalysts have been compared. The linear coordinated CO stretching band is smooth and fairly symmetrical for all compounds. Besides, as listed in Table 2, the HBW at 323 K is rather small (28–37 cm^{−1}), which points to a single type of linear coordinated C≡O and hence to a more or less uniform Pt particle size. This is in line with the results from HRTEM and EXAFS.

At low temperature, the band around 1800 cm^{−1} is also virtually symmetrical, which suggests mainly one type of bridge-bonded CO. At these conditions, the integrated band

Fig. 1. HRTEM micrographs of Pt/ITQ-1 (A), Pt/Si-MCM-41 (B), Pt/Na-SiO₂ (C) and Pt/Ba-SiO₂ (D).

intensity is less than 10% of that of the linear coordinated band (i.e. L:B ratio >10, Table 2) for all catalyst materials, indicating a limited presence of bridged conformations. Furthermore, above 423 K, an absorption band at around 1940 cm⁻¹ grows in, pointing to the formation of bridge-bonded CO. At identical conditions, the position of the linear C≡O band at 323 K is practically the same for all catalyst materials and the shift to lower wavenumber upon increasing the temperature is small (17–23 cm⁻¹). Cooling down to ambient temperature after TPD resulted in a small blue shift of the C≡O band, but different from what has been reported for Pt/SiO₂ by Barth and Ramachandran [23], a gain in intensity was not observed. According to the literature [20], frequency shifts of 20–30 cm⁻¹ can be largely attributed to changes in temperature and for that reason we conclude that the effect of the pore curvature on the C≡O stretching vibration is small. Hence, assuming that the C≡O force constant is inversely proportional to the Pt–C(O) bond strength, one would expect that the CO desorption shows the same picture for all catalyst materials. However, as can be seen from Fig. 2, the IR-desorption patterns are not identical. The main difference is observed in the decrease of the linear band above 523 K. As will be shown later, this is not only caused by CO desorption, but also partly by the conversion of linear into bridge bonded CO conformations, as expressed by the small increase in intensity of the band at 1800 cm⁻¹. The reduction in intensity of the linear CO band follows the order

Pt/Si-MCM-41 > Pt/Si-MCM-48 Pt/Si-SBA-15 > Pt/SiO₂, which is the inverse ranking of the corresponding mean pore diameter (Table 1), although the Pt/ITQ-1 material seems not to follow this trend. In principle, two non-bonding effects might play a role here. The first one is Coulomb interaction between CO and framework oxygen atoms. Regarding the small pore diameter of particularly, Pt/Si-MCM-41, Pt/Si-MCM-48 and Pt/ITQ-1 in relation to the 1 nm Pt particle size, it is plausible to assume that such an electrostatic interaction will play the largest role in the microporous and mesoporous supports. Since these interactions are repulsive, it explains the higher desorption rate for the smaller pore diameter supports. Indeed, one could argue that the small pore volume of ITQ-1 should have been attended with a larger effect, but this can be explained by assuming the Pt nanoparticles to be partly present outside the micropores. The second effect is the increasing contact area of the Pt particles and the support when the pore curvature increases, as schematically visualized in Fig. 4.

In this model, a larger contact area will result in a larger electron withdrawing influence of the acidic support sites on the Pt nanoparticles. As a consequence, the back donation to CO decreases and the Pt–C(O) bond strength becomes weaker, which results in a higher CO desorption rate as observed. According to the literature, a decrease in back donation might also cause a reduced presence of bridge bonded Pt–C≡O [3,7–9], but, as can be seen from Table 2, the linear to bridge intensity ratio (L:B) is

Fig. 2. Time-resolved IR spectra during temperature programmed CO desorption from Pt/ITQ-1, Pt/Si-MCM-41, Pt/Si-MCM-48, Pt/Si-SBA-15 and Pt/SiO₂.

about the same for all catalyst materials. In principle, a decreased back donation to CO and repulsive O···O interactions might lead to a higher C≡O frequency, but as already concluded such correlation is absent. It confirms the conclusion from our earlier studies on Pt/zeolite-Y catalysts, that a high C≡O stretching frequency is not by definition related to a weak Pt–C(O) bonding and vice versa [7–9]. This is also in accordance with the conclusion of Wasileski et al. [25], that there is no simple correlation between the field dependent Pt-bonded C≡O vibration frequency and the Pt–C(O) bonding energy.

Next, we calculated the surface coverage of the different catalyst materials as a function of the desorption temperature

from the integrated intensities of all bands, according to the procedure described before [7]. The result is shown in Fig. 5.

Consistent with the TPD patterns in Fig. 2, all catalysts show a decrease in coverage at higher temperature, but the effect is smaller. This is due to the fact that the intensity decrease observed for the linear band in the TPD pattern (Fig. 2) is partly compensated by the conversion of linear to bridge-bonded CO. According to our conclusions from the study on zeolite-supported Pt nanoparticles [7–9], one could expect the relatively high coverage on Pt/SiO₂ to be attended with a smaller L:B ratio and a lower linear (Pt–)C≡O stretching frequency, but this is not the case. It implies that, next to cation-induced changes of the

Fig. 3. Time-resolved IR spectra during temperature programmed CO desorption from Pt/Na-SiO₂, Pt/Cs-SiO₂, Pt/Mg-SiO₂ and Pt/Ba-SiO₂.

electronic charge on the Pt particles, another effect plays a role in the CO adsorption capacity of supported Pt particles. Apparently, this effect is also not directly linked to the pore curvature of the support.

3.2.2. Chemical composition effects

In order to study chemical composition effects on the electronic properties of supported Pt nanoparticles, IR-CO-TPD patterns of cation-containing Pt/M-SiO₂ catalysts (Pt/Na-SiO₂, Pt/Cs-SiO₂, Pt/Mg-SiO₂ and Pt/Ba-SiO₂) have been measured, together with the reference Pt/SiO₂ material. The results have been compared to the data previously reported for the corresponding zeolite-supported Pt nanoparticles, i.e., Pt/

H-Y, Pt/Na-Y, Pt/Cs-Y, Pt/Mg-Y and Pt/Ba-Y [7–9]. As it appeared, the IR-CO-TPD results of both series of samples show a striking resemblance. Alike the Pt/M-Y catalysts, upon introduction of a cation, the Pt/M-SiO₂ materials exhibit much broader and irregularly shaped bands (Fig. 3). This is illustrated by the HBW of 53–83 cm^{−1} at 323 K, which is considerably larger than the HBW of 29 cm^{−1} as observed for Pt/SiO₂ (Table 2). One explanation could be the presence of different CO-Pt adsorption sites. However, this is unlikely, since the HRTEM and EXAFS results show that, except for Pt/Cs-SiO₂, the average Pt particle size and distribution is about the same for Pt/SiO₂, Pt/Na-SiO₂, Pt/Mg-SiO₂ and Pt/Ba-SiO₂ (1–3 nm). For that reason we assign the observed band broadening

Table 2
Maxima (cm^{−1}) of the linear and bridge coordinated C≡O stretching bands at different temperatures during TPD

Sample	HBW	L:B	Linear Pt-C≡O band at						Bridged Pt-C≡O band at			
	323 K	323 K	323 K	373 K	473 K	573 K	473 K	573 K	323 K	373 K	473 K	573 K
Pt/ITQ-1	37	10.3	2071	2069	2060	2050	1950	1950	1829	1820	1839	1832
Pt/MCM-41	33	14.1	2070	2069	2062	2061	1938	1938	1850	1840	1812	1812
Pt/MCM-48	28	11.5	2070	2069	2061	2053	1940	1937	1816	1819	1829	1830
Pt/SBA-15	29	12.4	2069	2068	2060	2046	1936	1936	1826	1825	1825	1828
Pt/SiO ₂	29	11.1	2070	2069	2063	2052	1940	1939	1833	1820	1818	1818
Pt/Na-SiO ₂	65	4.0	2055	2052	2035	–	1961	1948	1767	1768	1790	1820
Pt/Cs-SiO ₂	83	3.6	2033	2029	1997	–	1950	1951	1786	1786	1785	1790
Pt/Mg-SiO ₂	54	8.9	2066	2065	2058	2041	1940	1941	1815	1815	1815	1816
Pt/Ba-SiO ₂	53	4.4	2064	2063	2054	2046	1950	1936	1763	1765	1816	1819

Half band width (HBW, cm^{−1}) of the linear Pt-CO band and linear to bridge (L:B) intensity ratio at 323 K.

Fig. 4. Schematic representation of a supported Pt nanoparticle in different silica cages and the corresponding non-bonding electrostatic interactions between the silica wall and a linearly adsorbed CO molecule. Reference is made to the related materials under study in this work based on their mean average pore diameter.

to different C≡O orientations as a result of local non-bonding electrostatic interactions within the support. As outlined in our previous work on promotion effects in Pt/M–Y catalyst systems [7–9], attractive ion–dipole interactions with charge compensating framework cations play a major role in this process. It also explains the larger complexity of the Pt–C≡O bands as a result of the presence of both cation-affected and “free” C≡O positions. Besides, the increasing band complexity at higher temperature can be attributed to reorientation of C≡O as a result of changing interactions. Identical to the Pt/M–Y catalysts, this phenomenon is particularly visible in the IR-CO-TPD pattern of Pt/Na–SiO₂, Pt/Cs–SiO₂ and Pt/Ba–SiO₂ from the increasing intensity of the band at 1950 cm^{−1}. This band has been tentatively assigned by Gandao et al. [24] to bridge-bonded Pt–CO species affected by (Mg²⁺) cations in the near vicinity of the supported Pt particles.

The positions of the Pt–C≡O vibration bands during TPD are listed in Table 2. Again, alike for the Pt/M–Y catalyst systems, the linear C≡O band position decreases upon introduction of the metal cations in the same order as their

position in the periodic system, i.e., Na > Cs and Mg > Ba. Besides, the red shifts show the same trend as for the Pt/M–Y samples [7–9]. Once more, this points to a correlation between the Pt/C≡O vibrational frequency and the electronic properties of the supported Pt nanoparticles as induced by the mono-valent and di-valent cations. This is illustrated by the plot of the red shift of the linearly Pt-coordinated C≡O bands compared to gas-phase C≡O (positioned at 2143 cm^{−1}) versus the cation radius-to-charge ratio of the four different elements [26,27] in Fig. 6. Evidently, the Pt/M–SiO₂ samples show the same trend as the previously reported Pt/M–Y catalysts, confirming the correlation of a high red shift with a large cation radius-to-charge ratio. Similar conclusions can be drawn for the effect of the cations on the IR linear to bridge (L:B) intensity ratio. Alike the Pt/M–Y compounds, the L:B values of the Pt/M–SiO₂ catalysts at 323 K (3.6–8.9) are lower than the L:B value of Pt/SiO₂ (11.1). Plotting of the L:B intensity ratio as a function of the Lewis acidity of the cations, as shown in Fig. 7, reveals exactly the same trend as reported for the Pt/M–Y samples.

Fig. 5. CO coverage on all-silica supported Pt nanoparticles as a function of the desorption temperature: (○) Pt/ITQ-1, (△) Pt/Si-MCM-41, (●) Pt/Si-MCM-48, (x) Pt/Si-SBA-15 and (◆) Pt/SiO₂.

Fig. 6. Red shift of the C≡O stretching vibration of linearly bond CO on cation impregnated Pt/M–SiO₂ (◆) and Pt/M–Y (□) catalysts compared to the gas phase C≡O frequency as a function of the cation radius-to-charge ratio.

Fig. 7. Relation between IR L:B intensity ratio and Lewis acidity of the cations Na⁺, Cs⁺, Mg²⁺ and Ba²⁺ impregnated onto the SiO₂ (◆) and zeolite-Y (□) support as expressed by the Kamlet Taft parameter α .

As explained previously [7], the Kamlet–Taft parameter α is a measure for the Lewis acidity of the cations and reflects the ability of a cation to accept an electron pair. Therefore, weak Lewis acid elements, such as Na⁺ and Cs⁺, have a small α -value and induce a relatively large electron charge on the framework oxygen atoms and hence on the supported Pt nanoparticles. For these elements, the net result is an increasing occupation of the d-levels, an increasing back donation in the CO molecular orbital with $2\pi^*$ character and eventually an increasing red shift of the linear C≡O band and a decreasing infrared L:B ratio. Obviously, the effect of an element with a high α -value, such as Mg²⁺, is much smaller and in line with the results of an IR–CO adsorption study on the promoting effect of manganese in titania-supported cobalt Fischer–Tropsch catalysts [28].

Finally, we calculated the CO surface coverage of the Pt/M–SiO₂ catalysts from the integrated C≡O band intensities as a function of the desorption temperature. The results are shown in Fig. 8.

As appears, the CO coverage (i.e. the summed integrated area of all CO bands) decreases only slightly with the

Fig. 8. CO coverage on supported Pt nanoparticles as a function of the desorption temperature: (◆) Pt/SiO₂, (●) Pt/Na–SiO₂, (×) Pt/Cs–SiO₂, (△) Pt/Mg–SiO₂ and (○) Pt/Ba–SiO₂.

temperature and less than suggested by the 3D TPD patterns in Fig. 3. It follows that desorption is minimal and that the linear bonded CO converts to the two and threefold coordinated form. Furthermore, the relative amount of adsorbed CO is the highest on Pt/Mg–SiO₂ and the lowest on Pt/Na–SiO₂ and Pt/Cs–SiO₂ with the value for Pt/Ba–SiO₂ in between. It is clear that, even though the coverage for Pt/Cs–SiO₂ is probably relatively too low, due to the larger Pt nanoparticles and hence a smaller Pt-surface area, the CO coverage correlates inversely proportional with the L:B ratio and the red shift of the linear Pt–CO band (Table 2). These results are identical to what we observed for the Pt/M–Y compounds and confirm the earlier conclusion that promoting elements can be used to affect the electron density of supported Pt particles.

4. Conclusions

The results of this characterization study demonstrate that time-resolved IR spectroscopy is a useful tool to study temperature programmed desorption effects of CO as probe molecule to unravel electronic properties of supported Pt nanoparticles. The new data largely confirm the conclusions from our previous study on promotion effects in zeolite-supported Pt nanoparticles that IR parameters, like the CO surface coverage and the position, shape and relative intensity of the linear and bridge Pt-bonded C≡O stretching vibration, can be used to determine the electronic properties of supported Pt nanoparticles. It is concluded that pore curvature effects are very small. The band positions, shifts and L:B ratio differ hardly, although desorption seems to decrease with the mean pore diameter due to repulsive non-bonding interactions and/or the larger contact area between the Pt particles and the support. The results for the cation-containing Pt/M–SiO₂ catalysts are consistent with the results, previously obtained for zeolite-supported Pt nanoparticles. The red shift of the linear Pt-coordinated C≡O vibration compared to that of gas-phase CO increases with an increasing cation radius-to-charge ratio, while a decrease in the L:B ratio correlates with a decreasing Lewis acidity, as expressed by the Kamlet–Taft parameter α . Although principally different, both observations can be attributed to an increasing electron charge on the framework oxygen atoms and hence to an increasing electron density on the supported Pt nanoparticles upon decreasing α -value. Furthermore, the correlation of the CO coverage with the electron density on Pt is present though less prominent as for zeolite-supported Pt nanoparticles.

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References

- [1] L.M. Kustov, D. Ostgard, W.M.H. Sachtler, *Catal. Lett.* 9 (1991) 121.
- [2] J.T. Miller, D.C. Koningsberger, *J. Catal.* 162 (1996) 209.
- [3] D.C. Koningsberger, D.E. Ramaker, J.T. Miller, J. de Graaf, B.L. Mojet, *Top. Catal.* 15 (2001) 35.
- [4] G.E. Arena, G. Centi, *Top. Catal.* 30/31 (2004) 147.
- [5] I. Sobczak, J. Grams, M. Ziolk, *Micropor. Mesopor. Mater.* 99 (2007) 345.
- [6] A.Y. Stakheev, Y. Zhang, A.V. Ivanov, G.N. Baeva, D.E. Ramaker, D.C. Koningsberger, *J. Phys. Chem. C* 111 (2007) 3938.
- [7] T. Visser, T.A. Nijhuis, A.M.J. van der Eerden, K. Jenken, Y. Ji, W. Bras, S. Nikitenko, Y. Ikeda, M. Lepage, B.M. Weckhuysen, *J. Phys. Chem. B* 109 (2005) 3822.
- [8] A.M.J. van der Eerden, T. Visser, T.A. Nijhuis, Y. Ikeda, M. Lepage, D.C. Koningsberger, B.M. Weckhuysen, *J. Am. Chem. Soc.* 127 (2005) 3272.
- [9] T. Visser, T.A. Nijhuis, A.M.J. van der Eerden, K. Jenken, Y. Ji, Y. Ikeda, M. Lepage, B.M. Weckhuysen, *Stud. Surf. Sci. Catal.* 158 (2005) 1239.
- [10] M.A. Cambor, C. Corell, A. Corma, M.J. Diaz-Cabanas, S. Nicolopoulos, J.M. Gonzalez-Calbet, M. Vallet-Regi, *Chem. Mater.* 8 (1996) 2415.
- [11] A. Corma, C.R.A. Catlow, G. Sastre, *J. Phys. Chem. B* 102 (1998) 7085.
- [12] M.A. Cambor, A. Corma, M.J. Diaz-Cabanas, C. Baerlocher, *J. Phys. Chem. B* 102 (1998) 44.
- [13] P. Van Der Voort, P.I. Ravikovitch, K.P. de Jong, M. Benjelloun, E. Van Bavel, A.H. Janssen, A.V. Neimark, B.M. Weckhuysen, E.F. Vansant, *J. Phys. Chem. B* 106 (2002) 5873.
- [14] P. Van Der Voort, P.I. Ravikovitch, K.P. de Jong, A.V. Neimark, A.H. Janssen, M. Benjelloun, E. van Bavel, P. Cool, B.M. Weckhuysen, E.F. Vansant, *Chem. Commun.* (2002) 1010.
- [15] R. Mokaya, W. Jones, *Chem. Commun.* (1997) 2185.
- [16] M. Baltes, K. Cassiers, P. Van der Voort, B.M. Weckhuysen, R.A. Schoonheydt, E.F. Vansant, *J. Catal.* 197 (2001) 160.
- [17] M. Vaarkamp, J.C. Linders, D.C. Koningsberger, *Physica B* 208/209 (1995) 9825.
- [18] E. Geidel, H. Lechert, J. Dobler, H. Jobic, G. Calazferri, F. Bauer, *F. Micropor. Mesopor. Mater.* 65 (2003) 31.
- [19] M. Vaarkamp, B.L. Mojet, M.J. Kappers, J.T. Miller, D.C. Koningsberger, *J. Phys. Chem.* 99 (1995) 16067.
- [20] N. Sheppard, T.T. Nguyen, *Adv. Infrared Raman Spectrosc.* 5 (1978) 67.
- [21] C. Hippe, R. Lamber, G. Schulz-Ekloff, U. Schubert, *Catal. Lett.* 43 (1997) 195.
- [22] A. Bourane, D. Bianchi, *J. Catal.* 218 (2003) 447.
- [23] A. Barth, A. Ramachandran, *J. Catal.* 125 (1990) 467.
- [24] Z. Gandao, B. Coq, L.C. de Ménorval, D. Tichit, *Appl. Catal. A: Gen.* 147 (1996) 395.
- [25] S.A. Wasileski, M.A. Weaver, M.T.M. Koper, *J. Electroanal. Chem.* 500 (2001) 344.
- [26] N.N. Greenwood, N.N. Earnshaw, *A Chemistry of the Elements*, Pergamon Press, Oxford, 1984.
- [27] Y. Marcus, *Ion Properties*, Marcel Dekker, New York, 1997, p. 193.
- [28] F. Morales, E. de Smit, F.M.F. de Groot, T. Visser, B.M. Weckhuysen, *J. Catal.* 246 (2007) 91.