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Impact of Pt dispersion on the elementary steps of CO oxidation by O_2 over Pt/Al_2O_3 catalysts

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Abstract

The impact of Pt dispersion (denoted by D) of Pt/Al_2O_3 catalysts on the turnover frequency (TOF) of the CO/O_2 reaction and on the elementary steps involved in the catalytic reaction is studied using transient experiments with either a mass or a FTIR spectrometer as a detector. Similar to literature data, it is observed that TOF decreases with an increase in D. The aim of the present study is to correlate this observation with the modifications of the surface elementary steps of two kinetic models, M1 and M2, developed previously for $D \lesssim 0.6$. The elementary steps considered are (1) adsorption of CO as a linear CO species (denoted by L and involved in models M1 and M2) and as a bridged CO species (denoted by B); (2) the oxidation by O_2 of the adsorbed CO species; and (3) the reduction by CO of the strongly adsorbed oxygen species (denoted by O_{sads}) involved in model M2. It is shown that D has no significant impact on the heat of adsorption of the L CO species and on the mechanism of the reduction of O_{sads} species by CO. For oxidation of the L CO species by O_2, it is shown that there is an induction period in the CO_2 production for $D \gtrsim 0.60$ not observed for a lower dispersion. This is explained by considering that the rate of formation of the Pt sites, which adsorb O_2 during oxidation, depends on D. These sites, which represent a small fraction of the Pt^0 sites, are associated with the B CO species. It is shown that the heat of adsorption of the B CO species increases with an increase in D. It is suggested that it is the removal of the B CO species (by desorption and oxidation) that controls the induction duration.

Keywords: CO/O_2 reaction; Pt/Al_2O_3 catalysts; Surface elementary steps; Pt dispersion; Induction period

1. Introduction

In previous studies [1–5], a specific microkinetic approach to the CO/O_2 reaction on 2.9% Pt/Al_2O_3 catalyst was developed to interpret the evolution of the coverage of the adsorbed species as well as the turnover frequency (TOF) of the reaction in the absence of mass transfers during lighting-off tests. The procedure consists mainly of (a) defining a plausible mechanism with elementary steps such as adsorption of reactants, bimolecular Langmuir–Hinshelwood steps, and desorption of products; (b) studying experimentally each elementary step to obtain the kinetic parameters of interest (i.e., adsorption coefficients, heats of adsorption, rate constants, activation energies, preexponential factors) [1,2,4,6–8], and (c) comparing the experimental curves (coverage of the adsorbed species and TOF during lighting-off tests to the theoretical curves obtained according to the plausible kinetic model) [3,5]. This microkinetic approach leads to new insight into the CO/O_2 reaction; in particular, one may consider the role of each adsorbed CO species (i.e., linear and bridged) in the catalytic process. For instance, we have shown [1–5] that (a) the L CO species adsorbed on Pt^0 sites (the main adsorbed CO species) is oxidized into CO_2 by O_2 at room temperature; (b) L CO species can be considered as the adsorbed intermediate of the CO/O_2 reaction according to two kinetic models, M1 and M2, differing by the nature of the adsorbed oxygen intermediate; and (c) the experimental conditions (P_{CO}/P_{O_2} and reaction temperature) [5] fix the operative kinetic model (either M1 or M2).

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One of the interests of this procedure is to afford the opportunity to study the impact of the catalyst preparation (i.e., Pt dispersion and nature of the support) on the surface elementary steps of the reaction and, in turn, on the TOF. Zafiris and Gorte [9] have proven that the CO/O_2 reaction on Pt particles can be structure sensitive, determining the TOF for Pt particle diameters of 14 and 1.7 nm deposited on a α-Al_2O_3 (0001) single crystal: the higher the Pt dispersion, the lower the TOF, with a $TOF_{14\,nm}/TOF_{1.7\,nm}$ ratio ≈ 10 at $T \approx 602$ K for $P_{O_2}/P_{CO} = 1$. Considering a kinetic model based on (a) competitive chemisorption between the adsorbed CO species (not specified) and the oxygen intermediate and (b) the assumption that the adsorbed CO species predominates ($\theta_{CO} \approx 1$ and $\theta_O \ll 1$), the difference in TOF values is ascribed to the higher heat of adsorption of the adsorbed CO intermediate on the smaller particles. However, it has been shown that the Pt dispersion has no significant impact on the heat of adsorption of the L CO species [10] which can be considered the main adsorbed CO intermediate of the CO/O_2 reaction [1–5]. In the present study, it is shown that the Pt dispersion modifies significantly the L-H elementary step of kinetic model M1, while that of kinetic model M2 is not significantly affected.

2. Experimental

2.1. Analytical procedures for the study of the elementary steps

The procedures were the same as those used in previous studies [1–5]. Mainly, experiments in the transient regime (using either a FTIR or a mass spectrometer as a detector) were performed to characterize the oxidation by O_2 of preadsorbed CO species and the reduction by CO of preadsorbed oxygen species.

The analytical system with the mass spectrometer was composed of various valves to perform switches between regulated gas flows (1 atm total pressure, flow rate in the range 100–600 cm^3/min) passing through the catalyst contained in a quartz microreactor. A quadrupole mass spectrometer permitted determination of the composition (molar fraction) of the gas mixture at the outlet of the reactor during a switch, after a calibration procedure. The temperature was recorded with a small K-type thermocouple ($\phi = 0.25$ mm) inserted in the catalyst sample (weight range ≈ 0.2–0.5 g according to the Pt loading). The exploitation of the data consisted of performing C and O mass balances for determining the evolution of the coverage of the Pt surface as well as the rates of different processes during the experiments [2,4]. For measurement of the Pt dispersion, the amounts of either CO or O_2 chemisorbed at 300 K were obtained after pretreatment of the solids (see below) using a He → 1% CO (or O_2)/2% Ar/He switch as described in [2]. Isothermal oxidation of the adsorbed CO species (denoted by I.O.CO_{ads}) at $T < 353$ K was studied according to the following switches: He → x% CO/2% Ar/He ($t_a \approx 2$ min, $x = 1$ or 2) → He (duration denoted t_d) → x% O_2/y% Ar/He (100 cm^3/min, x and y in the range 1–4). Isothermal reduction by CO of strongly adsorbed oxygen species (denoted by O_{sads}) was studied according to the following switches: He → x% O_2/y% Ar/He ($t_a \approx 2$ min) → He (t_d) → x% CO/y% Ar/He (100 cm^3/min, x and y in the range 1–4). Several successive isothermal cycles constituted by oxidation of the adsorbed CO species/reduction of the O_{sads} species were denoted by O/R cycles. This analytical system was also used to perform lighting-off tests with x% CO/y% O_2/He mixtures providing the change in TOF (in s^{-1}) with reaction temperature. The same sample of catalyst was used for several experiments and due to the progressive decrease in D according to the number of the pretreatments, the Pt dispersion for each experiment performed with the quartz microreactor is given here.

The second analytical system with a FTIR spectrometer as detector allowed us to perform similar experiments at $T < 353$ K studying the evolution of the adsorbed CO species. The solids were compressed to form a disk ($\phi = 1.8$ cm, $m = 40$–150 mg) which was placed in the sample holder of a small-internal-volume stainless-steel IR cell (transmission mode) described elsewhere [11]. This IR cell enabled in situ treatments (293–900 K) of the solid, at atmospheric pressure, with the gas flow rate in the range 150–2000 cm^3/min. The IR band intensity of the B CO species was very much lower than that of the L CO species. This made us increase the weight of the pellet in specific experiments for a better characterization of the B CO species (under such conditions the IR transmission was 0 at the position of the IR band of the L CO species).

2.2. Catalysts

The catalysts used in the present study, x wt% Pt/Al_2O_3 (γ-Al_2O_3 (Degussa), BET area 100 m^2/g, incipient wetness method with aqueous solutions of $H_2PtCl_6 \cdot xH_2O$ (Aldrich), drying procedure: 12 h at room temperature and then for 24 h at 373 K, pretreatment: 12 h in air at 713 K) with $x =$ 1.2 or 2.9, were the same than those used to study the impact of D on the heat of adsorption of the L CO species [10]. Considering the aim of the present study, the reduction procedures for the sample were modified as compared with our previous works to decrease D progressively. A fresh reduced solid with the highest dispersion ($D > 0.84$) was obtained according to the following procedure (P1) also used by Li et al. [12]: He (300 K) → He (423 K, 10 K/min) → H_2 (423 K) → H_2 (713 K, 10 K/min) → H_2 (713 K, 30 min) → He (713 K, 5 min) → He (300 K). The same sample of catalyst was used for several experiments and it was reduced before each experiment according to the following procedure (P2): He (300 K) → He (713 K, 10 K/min) → H_2 (713 K, 10 min) → He (713 K, 10 min) → O_2 (713 K, 10 min) → He (713 K, 10 min) → H_2 (713 K, 30 min) → He (713 K, 5 min) → He (300 K). It has been observed that D decreased slightly after two successive P2 procedures (from 0.88 to 0.73 after 10 P2 procedures with 1.2% Pt/Al_2O_3). The stabilized solids were obtained as follows (P3 procedure): after the P2 procedure, CO was adsorbed at 300 K using the switch He → 2% CO/2% Ar/He followed by an increase in the temperature (10 K/min) to 713 K. Then, after a short helium purge, procedure P2 at 713 K was applied. The stabilization pretreatment with CO, which was initially imposed by the procedure for determination of the heat of adsorption [6,8], led to $D \lesssim 0.65$ for 1.2 and 2.9% Pt/Al_2O_3. Then the following pretreatments according to P2 or P3 decreased D very slowly (lower D value = 0.4). It must be noted that (a) D cannot be measured during the FTIR study and (b) the inertia of the IR cell increased the duration of the heating and cooling stages of the pretreatment as compared with the quartz reactor. To correlate the FTIR observations to the change in D, it was considered that the decrease in D (quantified with the quartz reactor) according to the number and nature (P1, P2, P3) of the reduction procedures was also valid for the catalyst pellet used with the IR cell reactor.

3. Results and discussion

3.1. CO uptake and Pt dispersion

The Pt dispersion before each O/R experiment with the quartz microreactor was measured using the switch He → 1% CO/2% Ar/He at 300 K and determining the amount of adsorbed CO from the difference between the Ar and CO molar fractions [2,10]. The accuracy of the experimental procedure is ≈ 1 µmol CO/g of catalyst. The amount of reversible CO chemisorption ascribed in part to the B CO species on stabilized solids [10] is determined by studying CO readsorption according to the following switches: 1% CO/2% Ar/He (duration t_a, total CO uptake) → He (t_d) → 1% CO/2% Ar/He (reversible CO chemisorption). The total CO uptakes are 63 and 107 µmol/g on the fresh 1.2 and 2.9% Pt/Al_2O_3 catalysts, whereas the amounts of reversible CO chemisorption are ≈ 4 and ≈ 5 µmol/g, respectively, for $t_d = 300$ s. The increase in t_d to 15 min does not significantly change the reversible CO fraction. Similar experiments on the stabilized 2.9% Pt/Al_2O_3 indicated a total CO uptake of 78 µmol/g ($D = 0.54$) with a reversible CO chemisorption of 4 µmol/g [2]. Adsorption of 1% CO/2% Ar/He ($P_{CO} = 1$ kPa) at 300 K on the pure Al_2O_3 support leads to reversible CO chemisorption of ≈ 3 µmol/g, indicating a surface concentration of 0.18×10^{17} CO molecules/m^2, in good agreement with that measured by Mao and Vannice [13] on a comparable alumina support and for a similar CO partial pressure (7.9 kPa): 0.72×10^{17} CO molecules/m^2. FTIR studies [14] have evidenced a weakly adsorbed linear CO species on Al^{3+} sites formed by dehydroxylation of the Al_2O_3 surface at high temperatures [13,14] and we have observed (result not shown) the IR band of this CO species at 2202 cm^{-1} on 1.2% Pt/Al_2O_3 at 300 K for $P_{CO} > 5$ kPa (weight of the pellet = 140 mg). The impact of Pt deposition on the amount of CO adsorption on the support is not known. However, it is reasonable to assume that a fraction of the reversible CO adsorption on Pt/Al_2O_3 is due to the support. This means that the amount of reversible CO chemisorption on the Pt particles can be roughly estimated to be in the range 1–2 µmol/g of catalyst according to the metal loading and the reduction pretreatment of the catalyst. On the stabilized 2.9% Pt/Al_2O_3 solid it has been observed that the heat of adsorption of the B CO species (denoted $EB_{\theta B}$) varies linearly with its coverage (denoted θ_B): from $EB_1 = 45$ kJ/mol to $EB_0 = 94$ kJ/mol ($\theta_B = 0.85$ at 300 K for $P_{CO} = 1$ kPa). Assuming nonactivated CO chemisorption and solving numerically, $-d\theta_B/dt = k_d\theta_B$, to determine the theoretical evolution of θ_B with the duration of the desorption, these EB values indicate that θ_B decreases to a quasi-constant value of ≈ 0.25 at 300 K. Considering the amount of reversible CO species, this indicates that the total amount of Pt sites adsorbing the B CO species on a stabilized solid is $\lesssim 6$ µmol/g. This shows that the number of Pt sites adsorbing the B CO species on a stabilized solid represents less than 8% of the total number of Pt sites quantified by the total CO uptake. One may believe that this proportion decreases with the increase in D. FTIR studies [6,8] and the above calculations show that the adsorption of CO at 300 K is due mainly to the L CO species on Pt particles. This permits us to consider the ratio CO/M = 1 using the total CO uptake (this leads to a slight overestimation of D due to the reversible fraction on the support) to determine the dispersion as recently considered by Fanson et al. [15]. Moreover, it has been shown that H_2 and O_2 chemisorption at 300 K on a stabilized 2.9% Pt/Al_2O_3 catalyst give similar D values [2,4]. This is also the situation for the other catalysts. For instance, for the stabilized 1.2% Pt/Al_2O_3, the total hydrogen uptake, 46 µmol H/g, is not significantly different from the total CO uptake, 42 µmol/g. The average particle size according to D is obtained by $d(\text{nm}) \approx 1.1/D$ [16]. D is measured after each reduction procedure using either O_2 or CO chemisorption at 300 K with the quartz microreactor. The evolution of D for the 2.9% Pt/Al_2O_3 catalyst during the stabilization procedure has been studied in detail previously [17].

3.2. Impact of D on the TOF of the CO/O_2 reaction

TOF has been measured on stabilized (P2 and P3 procedures) and fresh (P1) catalysts according to the following procedure: (a) D is measured using the switch He → 2% CO/2% Ar/He, (b) then three O/R cycles are performed to study the impact of D on oxidation of the L CO species by O_2 [2] and the reduction of O_{sads} species by CO [4], and (c) after a short He purge, a 1% CO/1.75% O_2/3% Ar/He mixture (excess O_2) is introduced (flow rate = 200 cm^3/min, weight of catalyst ≈ 0.5 g) and the reaction temperature is increased linearly (20 K/min) while the molar fractions of CO, O_2, and CO_2 (denoted

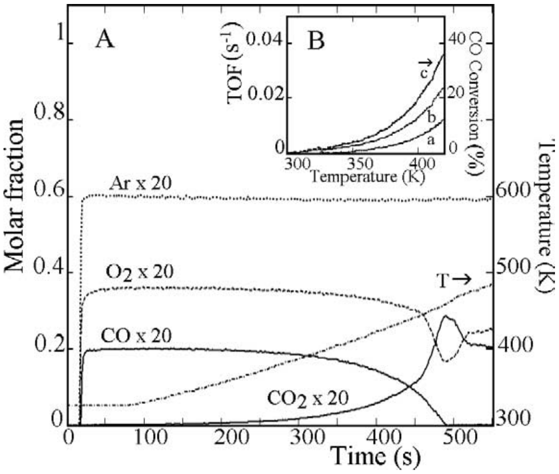

Fig. 1. Evolution of the molar fractions of the gas and of the TOF during lighting-off tests with 1% CO/1.75% O_2/3% Ar/He on 1.2% Pt/Al_2O_3. (A) Molar fractions on a fresh catalyst ($D = 0.88$). (B) TOF for (a) $D = 0.88$ and (b) $D = 0.59$, and (c) CO conversion for $D = 0.59$.

X_{CO}, X_{O_2}, X_{CO_2}) are measured at the outlet of the reactor with the mass spectrometer. Fig. 1A gives the evolution of the molar fractions during the experiment using fresh ($D = 0.88$) 1.2% Pt/Al_2O_3 catalyst until the total oxidation of CO. Similarly to previous observations [5], a strong overshoot in CO_2 production associated with strong O_2 consumption is detected (Fig. 1A) for CO conversions COC% > 60% (COC% $= [(X_{CO})_{in} - (X_{CO})_{out}] \times 100/(X_{CO})_{in}$) due to oxidative removal of the L CO species [5]. As compared with [5], the CO_2 overshoot in Fig. 1A is more discernible due to the lower flow rate (600 cm^3/min in [5]). Oxygen and C mass balances during the lighting-off test indicate that O_2 consumption before the overshoot (COC% $\lesssim 60$) is due only to the CO gas oxidation (the TOF values from the CO and CO_2 signals are equal) while during the overshoot it is due to (a) oxidation of CO_g, (b) oxidation of the L CO species (the TOF from the CO_2 signal is higher than that from the CO signal), and (c) the formation of the O_{sads} species. This O_2 adsorption leads to a change from a Pt surface covered mainly by L CO (denoted Pt–CO surface [5]), where model M1 is operative, to a Pt surface covered mainly by O_{sads} (denoted Pt–O surface [5]), where model M2 is operative. Similar experiments (not shown) have been performed after stabilization of the catalyst to study the impact of D on TOF without observing significant qualitative differences as compared with Fig. 1A. However, the TOF depends on D. For instance, curves a and b in Fig. 1B give the TOF as a function of the reaction temperature for the fresh ($D = 0.88$, P1 procedure) and stabilized ($D = 0.59$, P3 procedure) 1.2% Pt/Al_2O_3 catalyst, respectively, for low CO conversions (Fig. 1B, curve c, for $D = 0.59$). It is clear that the TOF values are higher for the stabilized solid, in agreement with the conclusions of Zafiris and Gorte [9]. Similar observations are obtained for fresh and stabilized 2.9% Pt/Al_2O_3 solid (results not shown). The objective of the present study is to correlate the decrease in TOF with the increase in D to the modifications of the kinetic parameters of the elementary steps involved in the two kinetic models, M1 and M2, of the CO/O_2 reaction.

3.3. Impact of D on the FTIR spectra and the heat of adsorption of the adsorbed CO species

The impact of D on the IR band of the L CO species has been described previously [10] and we summarize the main results to facilitate the presentation. Whatever D, the IR band of the L CO species dominates the IR spectra. At 300 K, the IR band depends on D: 2073, 2066, and 2054 cm^{-1} for $D = 0.44$ (2.9% Pt/Al_2O_3), 0.65 (1.2% Pt/Al_2O_3), and 0.75 (0.1% Pt/Al_2O_3), respectively [10]. These observations are similar to those of Fanson et al. [15] on platinum-supported silica: 2058, 2065, and 2076 cm^{-1} for $D = 0.99$ (0.05% Pt/SiO_2), 0.90 (0.6% Pt/SiO_2), and 0.60 (3% Pt/SiO_2), respectively [15]. This shift is explained [15] considering Blyholder's model [18] for the bonding of CO molecules to Pt surfaces. For small platinum particles (high platinum dispersion), the average number of Pt–Pt bonds per Pt atom is smaller than in the larger particles (low platinum dispersion) and a higher metal electron density is available for backbonding into the $2\pi^*$ orbital of adsorbed CO molecules [15]. The strong IR band intensity of the L CO species as compared with those of the multibound CO species indicates that the L CO species remains a candidate for the adsorbed intermediate of the CO/O_2 reaction on the three Pt catalysts. The impact of D on the heat of adsorption of the L CO species, $EL_{\theta L}$, has been described in [10] using an analytical procedure called adsorption equilibrium infrared spectroscopy (AEIR) [6–8]. This method consists mainly of following the evolution of the IR band of the L CO species at a constant CO partial pressure P_a with adsorption temperature T_a (range, 300–713 K). This allows us to determine the evolution of the coverage of the L CO species, θ_L, with T_a [6–8] in isobar condition. The curve $\theta_L = f(T_a)$ provides $E_{\theta L}$ considering either an adsorption model or the Clausius Clapeyron equation (isosteric heat of adsorption) [6–8]. Whatever D, $E_{\theta L}$ varies linearly with θ_L (generalized Temkin's adsorption model) and the values at high and low coverages are not significantly different considering the experimental uncertainties: $EL_1 \approx 110$ kJ/mol and $EL_0 \approx 210$ kJ/mol at $\theta_L = 1$ and 0, respectively [10]. The AEIR procedure cannot be applied to fresh catalysts ($D > 0.85$) because the sintering of Pt particles during the heating stage in CO/He also contributes to changes in the IR band of the L CO species. The EL_1 value clearly shows that the L CO species can desorb neither in helium nor during its oxidation by O_2 whatever D for $T < 353$ K.

Similarly to the L CO species, the position of the IR band of the B CO species depends on D. However, it shifts to higher wavenumbers with an increase in D: 1848 cm^{-1} on the fresh 1.2% Pt/Al_2O_3 catalyst (result not shown), 1839 cm^{-1} after two P2 procedures (lower dispersion, inset to Fig. 2), as compared with 1835 cm^{-1} on the stabi-

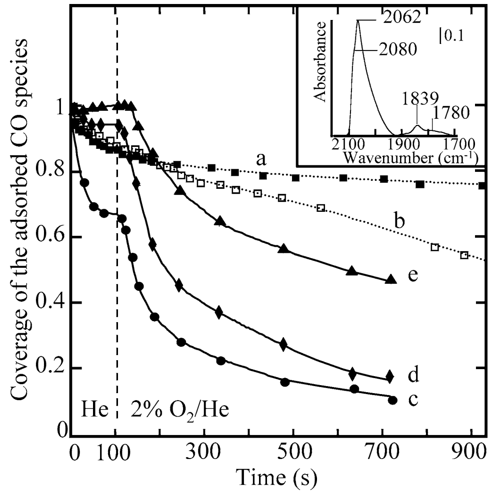

Fig. 2. Evolution of the coverage of the adsorbed CO species at 300 K on 1.2% Pt/Al_2O_3 during desorption in helium and oxidation with 2% O_2/He. (a) θ_B during desorption on a fresh solid (P1 procedure); (b) θ_B during desorption ($t \leqslant 110$ s) and then oxidation on a fresh solid (P1 procedure); (c–e) θ_B, θ_{3FC}, and θ_L, respectively, during desorption ($t \leqslant 110$ s) and then oxidation on a solid with low dispersion (P1 followed by two P2 procedures). Inset: FTIR spectra after adsorption of 1% CO/He at 300 K on 1.2% Pt/Al_2O_3 with high dispersion.

lized 2.9% Pt/Al_2O_3 [8]. The evolution of θ_B (θ_B and θ_{3FC} are obtained after deconvolution of the IR spectra as previously described [8]) according to several experimental parameters reveals that $EB_{\theta B}$ decreases with a decrease in D. Fig. 2, curve a, shows the evolution of θ_B on the fresh 1.2% Pt/Al_2O_3 catalyst with the duration of desorption at 300 K: θ_B decreases from 1 to ≈ 0.78 after 900 s. This curve can be compared with the theoretical curve obtained considering that (a) CO readsorption is negligible (this assumption is erroneous when θ_B decreases rapidly because P_{CO} is not negligible) leading to the differential expression $-d\theta_B/dt = k_d\theta_B$, and (b) the activation energy of desorption, $ED_{\theta B}$, increases linearly with the decrease in θ_B with the rate constant of desorption given by $k_d = 10^{13}\exp(-[ED_0 - (ED_0 - ED_1)\theta_B]/RT])$. The theoretical curve $\theta_B = f(t_d)$ is obtained by solving numerically the differential equation, and reasonable agreement with Fig. 2, curve a is obtained for $ED_0 = 130$ kJ/mol and $ED_1 = 80$ kJ/mol (result not shown). For nonactivated adsorption, these values (which are slightly overestimated due to the readsorption process) correspond to those of the heats of adsorption and they show that $EB_{\theta B}$ is significantly higher on a highly dispersed Pt catalyst than on a stabilized solid [8]. This is confirmed considering the impact of P_{CO} on the intensity of the IR band of the B CO species. After adsorption equilibrium at 300 K on the fresh (P1 procedure) 1.2% Pt/Al_2O_3 catalyst using $P_{CO} = 10$ kPa, it is observed that the switch 10% CO/He → 1% CO/He does not change the IR band intensity on the B CO species (the Pt^0 sites adsorbing the B CO species are saturated for $P_{CO} = 1$ kPa). At the opposite, on a stabilized solid (P3 procedure), the same modification of P_{CO} decreases the IR band intensity, indicating that θ_B is equal to 1 and 0.85 for $P_{CO} = 10$ and 1 kPa, respectively [8] (see also Fig. 3). The AEIR method cannot be apply to measure $EB_{\theta B}$ on fresh 1.2% Pt/Al_2O_3 catalyst due to the change in catalyst surface during the heating in CO. However, after a moderate decrease in D (P1 followed by two P2 procedures) the AEIR procedure has been applied with $P_{CO} = 1$ kPa providing $\theta_B = f(T_a)$ which is compared with that obtained on the stabilized solid (P3) (Fig. 3). The theoretical curves c and d in Fig. 3 are obtained from the generalized Temkin equation [6–8] using $EB_0 = 92$ kJ/mol and $EB_1 = 57$ kJ/mol and $EB_0 = 91$ kJ/mol and $EB_1 = 46$ kJ/mol (same values as on the stabilized 2.9% Pt/Al_2O_3 [8]), respectively. The EB_1 values confirm clearly that $EB_{\theta B}$ increases with an increase in D (roughly for $D > 0.6$).

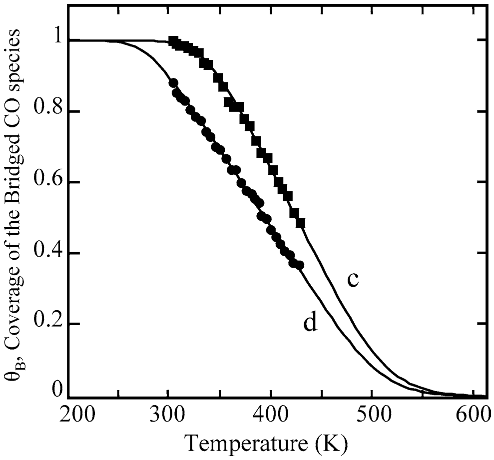

Fig. 3. Determination of the heat of adsorption of the B CO species on 1.2% Pt/Al_2O_3 for different D values at $P_{CO} = 1$ kPa. ■ and ●: experimental coverage of the B CO species for high and low D values; (c, d) theoretical curves obtained by using the AEIR procedure. (See text for more details.)

3.4. Impact of D on the reduction by CO of strongly adsorbed oxygen species

The reduction by CO of strongly adsorbed oxygen species (denoted by O_{sads}) formed by the dissociative O_2 adsorption on the reduced stabilized 2.9% Pt/Al_2O_3 catalyst ($D < 0.6$) has been studied in detail previously [4]. The heat of adsorption of this oxygen species, 175 kJ/mol at $\theta_{O_{sads}} \approx 1$ [2], shows that at 300 K it is removed from the surface only by reduction with CO [4] (no oxygen desorption). After adsorption of O_2 on the Pt catalyst, the IR band of the L CO species, during introduction of 1% CO/He, increases similarly to that observed on a clean Pt surface [4]. However, it is detected at a higher position, 2084 cm^{-1}, as compared with that on a clean Pt surface, 2075 cm^{-1} [4]. This indicates that adsorption of the L CO species is not affected significantly by the presence of O_{sads} species (no competitive chemisorption), in agreement with observations on single crystals [19,20]. The reduction of O_{sads} by CO at $T_r = 300$ K on stabilized 2.9% Pt/Al_2O_3 catalyst ($D = 0.45$) according to the procedure He → 1% O_2/2% Ar/He (formation of the O_{sads}) → He → 2% CO/4% Ar/He (t_r) is characterized by a

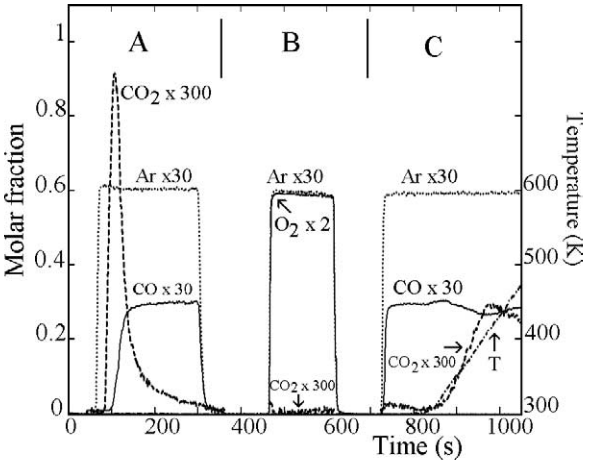

Fig. 4. Molar fraction of the gas during reduction and oxidation at 300 K and TPR of the adsorbed species using 1% CO/2% Ar/He and 2% O_2/2% Ar/He on a fresh 1.2% Pt/Al_2O_3 ($D = 0.88$). (A) Reduction of the O_{sads} species; (B) Oxidation of the adsorbed CO species; (C) TPR of the remaining O_{sads} species.

strong CO_2 peak detected a few seconds after the switch, before the appearance of CO in the gas phase (see [4, Fig. 2]). The C and O mass balances indicate that (a) the CO consumption is due to the CO adsorption and the O_{sads} reduction [4] and (b) some O_{sads} species remain on the Pt surface due to the decrease in the rate of reduction with the decrease in oxygen coverage [4]. The sharp CO_2 peak corresponds to a high rate for the reduction of O_{sads} by CO and mass transfers compete with the surface reaction at $T_r \approx 300$ K while they dominate the titration at higher temperatures [4]. The measurement of the rate constant of oxidation at $\theta_{O_{sads}} = 1$ can be performed only by decreasing T_o: $T_o = 223$ K [4].

Fig. 4A shows the evolution of the molar fractions during the reduction of O_{sads} species formed on fresh 1.2% Pt/Al_2O_3 ($D = 0.88$, oxygen chemisorption) by adsorption of O_2 (Pt–O surface). After 60 s of helium purge, the introduction of CO (Fig. 4A) leads to a strong CO_2 peak without any O_2 desorption, showing that there is no competitive adsorption between O_{sads} and L CO species, similar to the observations at lower D values [4]. The delays between Ar, CO_2, and CO signals come from the fact that CO is strongly adsorbed as a linear CO species on Pt–O before reduction of the O_{sads} species [4]. The comparison between the CO_2 production in Fig. 4A for $D = 0.88$ and that in previous works for $0.4 < D < 0.55$ shows that Pt dispersion has no significant impact on reduction of the O_{sads} species. This agrees with the fact that similar CO_2 production profiles have been observed in several studies on various platinum- and palladium-containing solids (supported catalysts and single crystals) with different dispersions such as 0.12% Pt/SiO_2 ($D = 0.47$) [21], 2% Pt/Al_2O_3 ($D = 0.85$) [22], 1% Pt/SiO_2 ($D = 0.22$) [12], 1% Pd/SiO_2 ($D = 0.15$) [12], Pd(110) [23], and Pt(111) [19,20]. This leads to the conclusions that (a) the L-H elementary step $O_{sads} + L \rightarrow CO_2$ (denoted S3a [5]) of model M2 is not significantly modified by Pt dispersion, and (b) the kinetic model M2 of the CO/O_2 reaction operative at high temperatures in excess O_2 [5] (after the ignition process associated with the oxidative removal of L CO species and with Pt–CO → Pt–O transformation) is not significantly affected by D (structure-insensitive reaction).

3.5. *Impact of D on the oxidation by O_2 of the adsorbed CO species*

After a short helium purge, Fig. 4B shows the evolution of the molar fractions during oxidation at 300 K of the adsorbed CO species formed during the reduction stage (Fig. 4A) of the fresh solid. Fig. 4B differs strongly from our previous observations [2] for $D < 0.5$: there is very little CO_2 production for $D = 0.88$ without any discernible peak, while for lower D values (see Figs. 3–5 in [2]) a strong CO_2 peak is observed on the introduction of O_2. After a He purge, the 1% CO/2% Ar/He mixture is introduced to perform a TPR (Fig. 4C) of the O_{sads} species remaining after Fig. 4A. The reduction is revealed by the CO consumption associated with CO_2 production at $T < 500$ K. Fig. 4C leads to the conclusion that some O_{sads} species remain on the Pt surface after the isothermal reduction, as observed for $D < 0.6$ (see Fig. 9 in [2]). At $T > 500$ K, other reactions such as CO disproportionation and reaction with the OH groups of the support also contribute to the CO consumption. Fig. 4B reveals that oxidation of the adsorbed CO species formed in the course of the reduction stage on a highly dispersed Pt/Al_2O_3 catalyst differs significantly from that on the same solid with a lower dispersion. This oxidation reaction has been studied in more detail after adsorption of CO on reduced solids with different Pt dispersions.

The results and conclusions for oxidation of L CO species on 2.9% Pt/Al_2O_3 catalyst with low dispersion ($D < 0.5$) [1,2] can be summarized as follows. The IR observations during the switches 1% CO/He → He (60s) → x% O_2/He (duration t_o, $x < 50$) [1] show that the L CO species is oxidized at $t_o = 0$ s and that the increase in P_{O_2} increases the rate of oxidation. In agreement with these observations, CO_2 production (quartz reactor) during the I.O.CO_{ads} [2] is characterized by a CO_2 peak at $t_o = 0$ s without any significant CO desorption (no competitive adsorption between oxygen and L CO species). The impact of D on I.O.CO_{ads} must be studied considering that (a) whatever D the IR band of the L CO species dominates the IR spectra (the CO_2 production is mainly linked to the oxidation of this CO species); (b) D affects the IR band position of the L CO species [10,15] without a significant modification of its heat of adsorption (L CO cannot desorb significantly at $T < 353$ K); and (c) D affects the position of the IR band of the B CO species and modifies its heat of adsorption (the higher D is, the higher is the heat of adsorption).

3.5.1. *CO_{ads} for $D > 0.6$: experiments with the mass spectrometer as a detector*

Fig. 5 compares the evolution of the CO_2 and O_2 molar fractions at the outlet of the quartz reactor during the

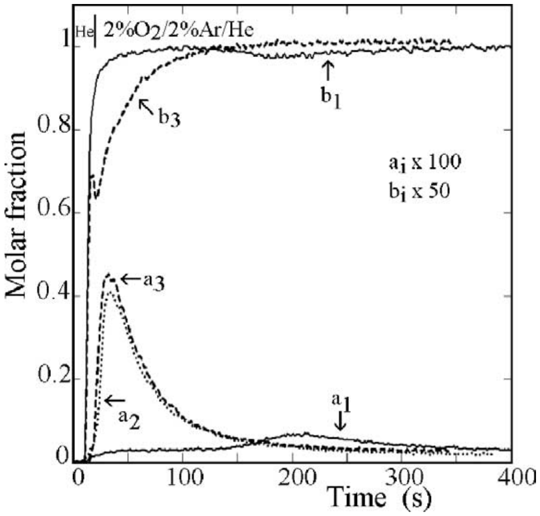

Fig. 5. Molar fractions of the gas during oxidation at 300 K using 2% $O_2/$ 2% Ar/He of the adsorbed CO species on fresh ($D = 0.73$) and stabilized ($D = 0.54$ and 0.48) 2.9% Pt/Al_2O_3. $a_i = CO_2$ and $b_i = O_2$ with $i = 1, 2, 3$ for $D = 0.73$, 0.54, and 0.48, respectively.

$I.O.CO_{ads}$ at 300 K on 2.9% Pt/Al_2O_3 for three dispersion values, $D = 0.73$, 0.54, and 0.48 (experiments performed with the same sample of catalyst: weight 0.5 g), according to the switches He → 1% CO/2% Ar/He (not shown) → He (80 s) → 2% $O_2/2\%$ Ar/He (t_o). For $D = 0.73$, the rate of CO_2 production, RCO_2 (curve a_1), is characterized by a progressive increase for $t_o \lesssim 30$ s followed by a pseudo-stationary value for $\approx 30 \text{ s} < t_o \lesssim 150$ s, and then RCO_2 increases for $\approx 150 \text{ s} < t_o \lesssim 205$ s before a progressive decrease. This leads to a discernible CO_2 peak with a maximum at $t_{mo} = 205$ s. Curve b_1 shows that this peak is associated with O_2 consumption: this eliminated the idea that the CO_2 peak is due to the desorption of adsorbed species (i.e., carbonate species on the Al_2O_3 support). Curves a_2 and a_3 (identical to those observed in [2]) give the evolution of RCO_2 for two lower dispersions: $D = 0.54$ and 0.48, respectively. It can be observed that RCO_2 is detected a few seconds after introduction of O_2 and increases sharply, leading to a CO_2 peak at $t_{mo} = 20$ s. Curve b_3 in Fig. 5 shows that CO_2 production is associated with O_2 consumption, leading to a small negative peak (a smaller amount of catalyst or a lower Pt dispersion [2] suppresses the detection of this negative O_2 peak and the oxygen signal increases progressively). Fig. 5 demonstrates clearly that D significantly affects the rate of CO_2 production from the adsorbed CO species. Several authors [19,24–26] have observed a RCO_2 profile similar to curve a1 in Fig. 5 during $I.O.CO_{ads}$ on metal-supported catalysts. The duration of oxidation before the CO_2 peak is called the *induction period* and its duration (the *induction time*) is denoted by t_m [26]. For $D = 0.73$ and 0.48, the amounts of CO_2 produced in Fig. 5 are ≈ 20 and ≈ 38 µmol/g, respectively, as compared with the total amounts of adsorbed CO, 107 and 71 µmol/g, respectively; this confirms clearly that the higher D is, the lower is the reactivity of the surface for $I.O.CO_{ads}$ (mainly the L CO species). The amount of CO_2 produced during the induction period of curve a_1 is 4 µmol/g, corresponding to a small fraction (≈ 4%) of the total CO uptake.

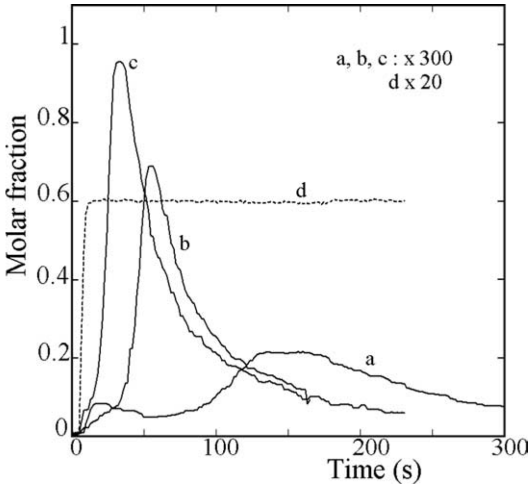

Fig. 6. CO_2 production of the gas during oxidation at 323 K using 2% $O_2/$ 2% Ar/He of the adsorbed CO species on 1.2% Pt/Al_2O_3 catalyst with different Pt dispersions: (a) $D = 0.88$, (b) $D = 0.58$, (c) $D = 0.52$. Curve d: Ar.

The $I.O.CO_{ads}$ performed with the 1.2% Pt/Al_2O_3 catalyst leads to the same qualitative observations. However, for $D = 0.88$, the CO_2 peak at 300 K is very small (i.e., Fig. 4B) and T_o has been increased to 323 K to reveal the impact of D on $I.O.CO_{ads}$. Fig. 6 illustrates CO_2 production for three D values (0.88, 0.58, and 0.52 for curves a, b, and c, respectively) using a 2% $O_2/2\%$ Ar/He mixture after two previous O/R cycles. It can be observed that the higher D is, the longer is the induction period, confirming that the increase in D significantly decreases the rate of $I.O.CO_{ads}$, in particular the L CO species. This is in line with (a) the lower TOF values for the higher dispersion (Fig. 1) and (b) the interpretation of the TOF at low reaction temperatures [3,5] considering the kinetic model M1 which involves oxidation of L CO species according to the elementary L-H step S3 [1,2,5]: L CO + $O_{wads} \to CO_2$. FTIR observations lead to more insight into the modifications of the kinetic parameters of step S3.

3.5.2. $I.O.CO_{ads}$ for $D > 0.6$: experiments with the FTIR spectrometer as a detector

Fig. 7A gives the FTIR spectra observed at 300 K on 1.2% Pt/Al_2O_3 (P1 followed by two P2 procedures) during CO (a) adsorption, (b) desorption, and (c) oxidation according to the switches 1% CO/He → He → 2% O_2/He. Curves c, d, and e in Fig. 2 give the evolution of θ_B, θ_{3FC}, and θ_L during the experiments in Fig. 7. After adsorption of CO the IR band of the L CO species (Fig. 7A, spectrum a) is observed at 2062 cm^{-1} (as compared with 2066 cm^{-1} on the stabilized solid [10]), associated with the IR band of the multibound CO species below 1900 cm^{-1}: i.e., a B CO species at 1839 cm^{-1} and a 3FC CO species at 1800 cm^{-1} [8, and references therein]. The desorption in helium does not modify

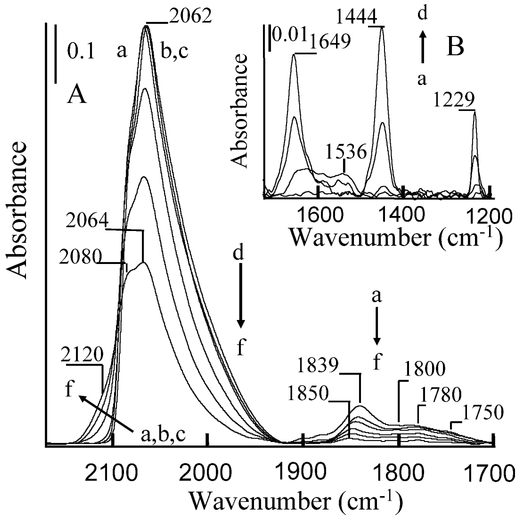

Fig. 7. FTIR spectra of adsorbed CO species at 300 K on 1.2% Pt/Al_2O_3 (pretreated according to P1 followed by two P2 procedures). Part A: (a) 1% CO/He; (b) after 110 s in helium; (c–f): after 30, 70, 220, and 600 s in 2% O_2/He, respectively. Part B: (a) in He before adsorption, (b) in 1% CO/He, (c, d) after 40 and 600 s in O_2, respectively.

the IR band of the L CO species (spectra a and b), whereas the IR band of the B CO species decreases progressively as shown in Fig. 2, curve c, for $t \leqslant 110$ s. Introduction of O_2 does not significantly change the intensity and position of the IR band of the L CO (spectrum c, Fig. 7), whereas those of the B and 3FC species decrease more rapidly than during desorption (curves c and d, Fig. 2, for $t \geqslant 110$ s), associated with a shift to higher wavenumbers for the B CO species (from 1839 to 1850 cm^{-1}) (Fig. 7A). A progressive decrease in the IR band of L CO in the presence of O_2 (Fig. 7A, spectra d–f) is observed after a delay of ≈ 40 s (curve e, Fig. 2) from introduction of O_2. This shows that similar to the observations for $D \lesssim 0.6$ [1,2], the L CO species is oxidized on a highly dispersed Pt catalyst and it is the kinetic parameters of the L-H elementary steps that are modified. The decrease in the IR band at 2062 cm^{-1} leads to better detection of a shoulder at 2080 cm^{-1} (Fig. 7) also observed on the 2.9% Pt/Al_2O_3 catalyst with $D < 0.5$ (see [1, Figs. 1–3]). Similarly to a stabilized 2.9% Pt/Al_2O_3 catalyst, a shoulder develops at $\approx$ 2110–2120 cm^{-1} during I.O.CO_{ads} (Fig. 7, spectra d–f). It is due to a linear CO species adsorbed on Pt^{2+} sites (IR band at 2120 cm^{-1} [1]). This indicates that a small fraction of the Pt^0 sites are oxidized into Pt^{2+} during I.O.CO_{ads}. However, this adsorbed CO species does not contribute to CO_2 formation during O_2 titration [1]. The decrease in θ_L during the oxidation process (Fig. 2, curve e) is delayed from those of θ_B and θ_{3FC}. This shows that CO_2 production during the induction period in Figs. 5 and 6 is due initially to oxidation of the B and 3FC CO species, while oxidation of the L CO species contributes to the final part of the induction and to the CO_2 peak (Figs. 5 and 6). Curve b in Fig. 2 shows the evolution of θ_B according to 1% CO/He → He (110 s) → 2% O_2/He on the 1.2% Pt/Al_2O_3 catalyst with the highest dispersion (P1 procedure). Comparison of curves b and c in Fig. 2 clearly reveals that the higher D is, the lower is the rate of oxidation of the B CO species, whereas comparison of curves a (desorption in helium) and b indicates that the rate of disappearance of the B CO species increases in the presence of O_2 due to oxidation of the B CO species. Three IR bands at 1649, 1444, and 1229 cm^{-1} (Fig. 7B) increase with the duration of oxidation. They indicate the adsorption of a fraction of the CO_2 formed by I.O.CO_{ads} as carbonate species on the Al_2O_3 support. This shows that it is difficult to perform accurate C and O mass balances during the first O/R cycle with the quartz reactor.

The results in Figs. 4–7 lead to the conclusion that the higher D is, the lower are the rates of oxidation of the L and B CO species. We have shown that whatever the CO/O_2 ratio, the kinetic model M1, involving oxidation of L CO species, fixes the TOF of the catalytic reaction at low temperatures for stabilized solids ($D < 0.55$). It is reasonable to assume that the lower the rate of oxidation of the adsorbed CO intermediate, the lower the TOF. This is the qualitative explanation of the impact of D on TOF (Fig. 1). In turn, the interpretation of the presence or the absence of an induction period during I.O.CO_{ads} on highly ($D \gtrsim 0.6$) and lowly ($D \lesssim 0.6$) dispersed solids, respectively, may allow explanation of how D modifies the TOF. A qualitative explanation of the induction period can be provided by considering literature data [21–28]. However, it must be noted that the first conclusion of the present study is that there exists a clear relationship between the value of D and the absence or presence of an induction period in CO_2 production during I.O.CO_{ads}. Other experimental parameters, such as T_o, determine the duration of the induction period [24–26], and they are studied in more detail in a separate article. To our knowledge this impact of D on the induction period has not been considered previously.

3.6. *Interpretation of the induction period according to literature data*

The presence of an induction period during I.O.CO_{ads} has been observed on Pt- as well as on Pd-supported catalysts [21–28]. On reduced 1% Pt/SiO_2 catalyst, Li et al. [12] observe an induction period of $t_m = 109$ s at $T_o = 353$ K that decreased with an increase in T_o ($t_m = 4$ s at $T_o = 468$ K). They suggest that the dissociative adsorption of O_2 required to initiate the reaction is strongly inhibited at low temperatures by the adsorbed CO species. On 8% Pd/Al_2O_3 catalyst, Zhou and Gulari [26] observed that the duration of the induction period is an exponential function of T_o: $\ln(t_m) = f(1/T_o)$ is a straight line with a positive slope. The authors [26] used the slope to determine an activation energy of 90 kJ/mol for the process involved in the induction. They consider that this value eliminates the involvement of mass transfers in the induction process [26]. On 9.1% Pt/Al_2O_3 catalyst, Dwyer and Bennett [24] observed that the induction period at 393 K decreases from 35 to 5 s with an increase in the flow rate of a 2% O_2/Ar mixture from 9.5 to 114 cm^3/min, respectively. This is interpreted [24] as the dependence of the net desorption rate of adsorbed CO species on the residual CO partial pressure in the IR cell reactor (influence of the design of the IR cell). This means that the desorption of CO species allowing the adsorption of O_2 is considered to be in a pseudo-adsorption equilibrium during the induction period. The above interpretations of the induction period point out the role of desorption of an adsorbed CO_{ads} species in the induction period. On Pd/Al_2O_3, Zhou and Gulari [26] provided another interpretation considering the impact of an argon purge before oxidation on the t_m value. They observed that t_m strongly decreased from 110 to 25 s for 0 and 15 min of desorption in argon, respectively, without a significant impact on the amount of CO_2 formed during the oxidation. The authors suggest [26] that the Ar purge is associated with a restructuring of the adsorbed CO species in a more compact and energetically favorable state and/or a reconstruction of the catalyst surface. However, another interpretation could be that the argon purge allows the desorption of an adsorbed CO species present in a very small amount on the metal surface and different from the one that dominates CO_2 production. The removal of this adsorbed CO species creates the sites that activate O_2 (i.e., O_{wads} species in our interpretation [1,2]) for oxidation of the main adsorbed CO species.

3.7. *Qualitative interpretation of the impact of D on oxidation of the L CO species*

Whatever D, CO_2 production due to I.O.CO_{ads} is associated mainly with oxidation of the L CO species, which is the most important adsorbed CO species (B and 3FC CO species contribute to less than 8% of the total CO uptake). For the stabilized 2.9% Pt/Al_2O_3 catalyst ($D < 0.5$), we have shown [1,2] that in the presence of O_2, the rate of disappearance of the L CO species is due only to its oxidation. The $EL_{\theta L}$ value at high coverage indicates that there is no desorption while there is no competitive adsorption with O_2. The oxidation rate of the L CO species depends on O_2 partial pressure [1,2], indicating that the oxygen intermediate is weakly adsorbed on some free Pt sites of the surface. It has been suggested [1,2] that these sites are those liberated by the desorption of B CO species. This species, which has a low heat of adsorption at high coverages for $D < 0.5$ [8], desorbs during the helium purge before the isothermal oxidation. According to these views, the rate of disappearance of the L CO species (controlled by the elementary L-H step (S3), L CO + $O_{wads} \rightarrow CO_{2ads}$) is given by [1,2,5]

$$-\frac{d\theta_L}{dt} = k_3\theta_L\theta_{O_{wads}}, \tag{1}$$

where $\theta_{O_{wads}}$ is the coverage of the O_{wads} species and k_3 is the rate constant of step S3. FTIR results have shown [10] that (a) $EL_{\theta L}$ is not modified by D, and (b) the EL_1 indicates that the L CO species cannot desorb at $T < 353$ K. This leads to the conclusion that it is not a modification of θ_L by the increase in D that explains the induction period. The impact of D on the rate of oxidation must concern k_3 or/and $\theta_{O_{wads}}$.

Data in the literature strongly support the view that the induction is linked to the desorption of an adsorbed CO species [23,24], in particular considering the interpretation of the impact of the gas flow rate [24]: effect on the net desorption rate. This is valid only if it is assumed that the heat of adsorption of the desorbing CO species is (a) not very low (i.e., > 70 kJ/mol; otherwise it must desorb in a few seconds at 300 K) and (b) not very high (i.e., < 110 kJ/mol; otherwise the species does not desorb at 300 K). For instance, considering a rate of desorption of $k_d = 10^{13}\exp(-E_d/RT)$, simple calculations show that at 300 K the coverage θ is 0 after a desorption duration < 1 s for $E_d = 70$ kJ/mol ($\theta = 0$ after 40 s of desorption for 80 kJ/mol), whereas $\theta = 1$ after 10 min for $E_d = 110$ kJ/mol ($\theta = 0.97$ after 10 min for $E_d = 100$ kJ/mol). The above range of E_d values (70–90 kJ/mol) (a) does not correspond to that of the L CO species (> 110 kJ/mol) and (b) agrees with that of the B CO species (< 90 kJ/mol [8] and $\lesssim 130$ kJ/mol according to the coverage for $D < 0.6$ and $D \approx 0.88$, respectively). Finally, the view that the induction period comes from the desorption of the B CO species is in agreement with (a) the literature data (in previous studies [23,24] on Pt-containing solids, the nature of the adsorbed CO species was not considered) and (b) our first suggestion [1,2] that it is the sites liberated by the removal of the B CO species that activate the O_{wads} species.

This interpretation suggests that the longer induction period on highly dispersed Pt particles is due to the fact that $EB_{\theta B}$ at high coverages increases with D and that for a given duration of helium purge there are more free sites at low dispersion than at high dispersion. This leads to a larger amount of O_{wads} species at the beginning of the oxidation for lower D values. However, Fig. 2 (curves c and d) shows that the introduction of O_2 increases the rate of disappearance of the B and 3FC CO before the decrease in θ_L (curve e). Zhou and Gulari have observed a similar situation for I.O.CO_{ads} on Pd/Al_2O_3 [26]. However, it is the L CO species that decreases faster than the B CO species on Pd [26]. This supports the view that CO_2 production during the initial stage of the induction period is due to oxidation of the B and 3FC CO species (progressive decrease in their coverages), while oxidation of the L CO species contributes to the final part of the induction and to the CO_2 peak. This indicates that the oxidation of the B and possibly of the 3FC CO species contributes to the formation of Pt sites that activate O_2 as the O_{wads} species involved in step S3. In summary, it must be considered that the impact of D on the duration of the induction period is linked mainly to the rate of formation of the specific Pt sites activating O_{wads}. This rate depends on two reactions: the desorption and the oxidation of the B (and possibly of the 3FC species). The point of interest is that the removal of B and 3FC species (by desorption and oxidation) creates these specific Pt^0 sites, while the removal of L CO species (by oxidation, step S3) allows the adsorption of strongly adsorbed oxygen species O_{sads} that are not reactive (see [1, Fig. 7]) at low coverages with the remaining L CO species. In a separate article, a kinetic model is developed to interpret quantitatively the duration of the induction period in line with a previous work on the hydrogenation of adsorbed carbonaceous species on Fe/Al_2O_3 catalyst [29].

4. Conclusion

Transient experiments employing mass and FTIR spectrometers as detectors have been used to study the impact of the Pt dispersion of Pt/Al_2O_3 catalysts on the elementary steps involved in the CO/O_2 reaction. It has been shown that D values in the range 0.4–0.88 have no impact (a) on the heat of adsorption of the L CO species and (b) on the mechanism and kinetic parameters of the reduction by CO of strongly adsorbed oxygen species. This leads to the conclusion that kinetic model M2 [5] controlling the CO/O_2 reaction on a Pt surface covered by oxygen (Pt–O surface) does not depend on dispersion.

On the other hand, the oxidation of L CO species by O_2 depends on D, for $D \gtrsim 0.6$, an induction period is observed (not detected for $D \lesssim 0.6$). This induction period has been qualitatively interpreted by a lower rate of formation (by desorption and oxidation of the B/3FC CO species) of specific Pt^0 sites (in small number on the Pt surface) adsorbing the O_{wads} species. The impact of D on the elementary step S3 of kinetic model M1 [3,5] for the CO/O_2 reaction on a Pt surface covered by CO (Pt–CO surface) is correlated to the decrease in TOF with increase in dispersion [9].

The present study on the impact of Pt dispersion on the elementary steps of model M1 (which controls TOF at low temperatures) focuses on the importance of a small number of specific Pt sites (linked to the B CO species) on the rate of the L-H elementary step implicated in the CO/O_2 reaction at low temperature. This reveals one of the difficulties of the microkinetic approach of a catalytic reaction. We have to characterize the impact of a small fraction ($\lesssim 8\%$) of the Pt sites on the CO/O_2 reaction. This requires us to find adapted analytical procedures to discern those sites from the other Pt sites. In this line, the correlation established in the present study between the formation of those sites and the induction period shows that the study of the parameters influencing this induction period (in addition to the Pt dispersion) offers a way of characterization. This is described in a separate article.

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