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Impact of the support on the heat of adsorption of the linear CO species on Pt-containing catalysts

Prisca Pillonel, Salim Derrouiche, Abdennour Bourane, François Gaillard,
Philippe Vernoux, Daniel Bianchi*

Laboratoire d'Application de la Chimie à l'environnement (LACE), UMR 5634, Université Claude Bernard Lyon 1, Bat. Raulin,
43 Bd du 11 Novembre 1918, 69622 Villeurbanne, France

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Abstract

It has been previously shown that the individual heats of adsorption of each adsorbed CO species (linear, bridged and three-fold coordinated) on Pt/Al_2O_3 catalysts can be obtained from the change of their characteristic IR bands with the adsorption temperature T_a (in the range of 300–800 K) at a constant CO partial pressure P_a according to a procedure denoted adsorption equilibrium infrared spectroscopy. In the present study, this procedure is used to reveal the impact of the nature of the support TiO_2, CeO_2 and Y_2O_3/ZrO_2 (two solids with high (104 m^2/g) and low (14 m^2/g) BET surface area) on the heat of the adsorption of the L CO species that dominates the CO adsorption. These reducible supports have been selected because of their expected interactions with Pt particles according to different SMSI effects. In the wavenumber range characteristic of the L CO species on Pt sites, the FT-IR spectra are dependent on the nature of the support: two strongly overlapped IR bands are detected with an intensity ratio depending on the support. However, it is shown that the nature of the support only has a slight impact on the average heats of adsorption of the L CO species (<20 kJ/mol as compared to Pt/Al_2O_3).

Keywords: Heat of adsorption; Linear CO species; FT-IR spectra; Platinum catalysts

1. Introduction

To improve the understanding of the CO adsorption on supported metal catalysts in the view of a microkinetic approach of the catalytic reactions involving CO, an effort must be performed to characterize each adsorbed CO species (denoted X). We have previously shown [1,2] that the heats of adsorption (abbreviation HA or HsA) of each CO species adsorbed on a 2.9% Pt/Al_2O_3 catalyst (X = linear, bridged and three-fold coordinated CO species, denoted by L, B and 3FC, respectively) can be determined using an analytical procedure denoted by adsorption equilibrium-infrared spectroscopy (AEIR) [3]. The evolutions of the IR band intensities of each X CO species with the adsorption temperature T_a at a constant partial CO pressure P_a allow us to determine the evolutions of their coverages θ_X with T_a and then the curves $\theta_X = f(T_a)$ provide the HsA of each adsorbed CO species at several coverages denoted EX_θ [1–3] according to an adsorption model. It has been observed [2] that the HsA of the three adsorbed CO species on a 2.9% Pt/Al_2O_3 catalyst (Pt dispersion $D < 0.6$) linearly decrease with the increase in their coverage: (a) from EL_0 = 206 kJ/mol to EL_1 = 110 kJ/mol for the L species; (b) from EB_0 = 94 kJ/mol to EB_1 = 45 kJ/mol for the B species and (c) from $E3FC_0$ = 135 kJ/mol to $E3FC_1$ = 104 kJ/mol for the 3FC species. The AEIR method presents several advantages as compared to conventional methods such as isosteric method, TPD and microcalorimetry as previously discussed [1–3]. Two of them are that the heats of adsorption are determined (a) under adsorption equilibrium conditions (similarly to isosteric methods) and (b) from a single experimental isobar (at the opposite of isosteric methods) as justified in a recent study [4]. This strongly simplifies the

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* Corresponding author.
E-mail address: daniel.bianchi@univ-lyon1.fr (D. Bianchi).

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determination of the HsA and facilitates the studies of their modifications by varying specific parameters of the catalyst preparation such as the salt precursor of the metal particles (with or without chlorine) [5,6] or the platinum dispersion [7]. In the present study, the AEIR method is used to reveal the impact of the support: CeO_2, TiO_2, and $0.08Y_2O_3/0.92ZrO_2$ (in molar fractions) on the HsA of the L CO species adsorbed on Pt^0 sites. The reducible TiO_2 and CeO_2 supports have been selected because they are the best candidates to create some interactions with the Pt^0 sites via the SMSI effects appearing by using a high reduction temperatures [8,9]. It is expected that SMSI effects modify significantly the HsA of the linear CO species that is the main adsorbed CO species formed whatever the support and the reduction temperature for $T > 473$ K. The Y_2O_3/ZrO_2 support has been selected for its well-known ionic conductivity: the composition with 0.08 molar fraction of Y_2O_3 provides a stabilized solid (denoted YSZ) and the highest conductivity [10] due to the presence of oxygen vacancies linked to the substitution of Zr^{4+} by Y^{3+}. Moreover, this support has been widely used to develop the electrochemical promotion of catalytic reactions (EPOC) also denoted NEMCA effect (non-Faradaic electrochemical modification of catalytic activity) by Vayenas et al. [11–13]. This process consists to control the work function of the metal (Pt, Pd, Rh) deposited on the YSZ surface by the migration of O^{2-} from the solid due to an applied potential. In turn, this modifies the catalytic activity of the metal such as for the oxidation of hydrocarbons [14] and CO [15] ascribed to a change in the binding energies of the adsorbed species. Recently, in the absence of applied potential, the Vayenas group [16,17] has shown that there is a “self-driven NEMCA effect” for supports with a high work function such as YSZ (i.e., 5.14 eV) and this process is candidate to create an impact on the HsA of the linear CO species.

2. Experimental

2.1. Preparation of the Pt-containing catalysts

2.1.1. Pt/TiO_2

A 2.9% Pt/TiO_2 was prepared by the incipient wetness method. TiO_2 (Degussa P25, 85% anatase [8], BET area 50 m^2/g) was impregnated using an appropriated amount of aqueous solution of $H_2PtCl_6 \cdot xH_2O$ (Aldrich). After drying in air 24 h at room temperature and then 12 h at 383 K, the powder is treated 4 h in air at 713 K.

2.1.2. Pt/CeO_2

A 1% Pt/CeO_2 was similarly prepared by using as support the ceria HAS-5 from Rhodia (110 m^2/g).

2.1.3. Pt/YSZ

Two YSZ supports (with the same Y_2O_3 content: 8 molar%) have been used with different BET areas. For the comparison with previous measurements on Pt/ZrO_2 [18], an aerogel support has been prepared according to the procedure developed by Teichner and coworkers [19] and Pierre and Pajonk [20] in line with the preparation of a pure ZrO_2 aerogel support [21]: an appropriated amount of an aqueous solution of $Zr(CH_3CH_2CH_2O)_4$ was introduced at 300 K into an methanol solution of $Y(CH_3COO)_3 \cdot xH_2O$ leading to the formation of a gel. The solvent was evacuated in supercritical conditions in an autoclave containing an appropriated amount of CH_3OH as follows: the autoclave was purged and pressurized with N_2 (1.5×10^7 Pa) at 300 K then the temperature was progressively increased (2.3 h) from 300 to 577 K. At this final temperature, the pressure was decreased to 10^5 Pa and then T was decreased to 300 K (≈2 h). This provided an aerogel solid [19,20] that was crushed and then treated in air at 873 K during 6 h (heating rate 7 K/min) to remove the adsorbed carbonaceous species coming from the preparation. This preparation led to an oxide support (denoted YSZ-HS) with a BET area of 104 m^2/g. The second support was a commercial stabilized product from TOSOH with a BET area of 14 m^2/g (denoted YSZ-LS). In agreement with the BET measurements, the XRD spectra of the YSZ supports (not shown) presented well defined peaks of the cubic phase for YSZ-LS indicating that it was well crystallized while the same peaks were very broad for YSZ-HS, indicating that the solid was mainly amorphous. The two supports were impregnated with Pt (1 wt.%) using the incipient wetness method with an appropriated amount of aqueous solution of $H_2PtCl_6 \cdot xH_2O$. After the drying procedure the solids are treated in air at 743 K.

It must be noted that to study specifically the SMSI impact on the HsA of the L CO species a Pt precursor free of chlorine should be more appropriated [9,22]. However, on the Al_2O_3 support [6], it has been shown that the presence of residual Cl decreases by 10–20 kJ/mol the HsA at high coverages while it has no impact at low coverages.

2.2. Analytical procedure

For the FT-IR studies, the different catalysts were compressed to form a disk (Ø = 1.8 cm, m = 40–120 mg) which was placed in the sample holder of a small internal volume stainless steel IR cell in transmission mode described elsewhere [23] allowing in situ treatments (293–800 K) of the solid, at atmospheric pressure, with a gas flow rate in the range of 150–2000 cm^3/min. Before the CO adsorption, the solid was treated in situ (200 cm^3/min) according to the following procedure: He, 298 K → He, 713 K → O_2, 713 K (0.2 h) → He, 713 K (0.2 h) → H_2, 713 K (0.5 h) → He, 713 K (0.2 h) → He, 300 K → CO adsorption. Literature data [8,9,24] indicate that (a) a reduction temperature $T_r > 600$ K must be used on Pt/TiO_2 for the appearance of SMSI (considering the decrease in the CO (or H_2) adsorption capacity of the Pt particles as the accepted criterion for SMSI [9,22,24]) and (b) the higher T_r the stronger the SMSI [24]. According to [24], $T_r = 713$ K