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In situ FT-IR study of CO and H_2 adsorption on a Pt/Al_2O_3 catalyst

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Abstract

Infrared spectra are reported of Pt/Al_2O_3 exposed to CO and H_2 at different conditions. Two broad bands appeared in the spectra at 2180 and 2550 cm^{-1} due to the catalyst Pt/Al_2O_3 itself and became stronger while increasing the temperature. Adsorption of CO on Pt/Al_2O_3 gave an infrared band at 2085 cm^{-1}, and when H_2 was adsorbed, methane was formed due to reaction of H_2 and the pollutant CO, while increasing the temperature, above 673 K for 1 h or so, when the pollutant CO had almost disappeared during the reaction, a band at 2060 cm^{-1} appeared due to H_2 adsorption on Pt/Al_2O_3. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: FT-IR; Pt/Al_2O_3; Adsorption

1. Introduction

The investigation of catalysts under operating conditions is essential for a complete understanding of how catalysts function. Interest in the in situ methods for catalyst investigations has grown in recent years and a number of techniques are now effectively developed. Simultaneously, the complexity of syn-gas reactions over noble metal catalysts is well known, but incompletely understood. Platinum catalysts in CO/H_2 mixtures under high-pressure conditions give predominantly methane, but at lower pressures higher hydrocarbons are also formed. Proposed mechanisms involve carbon monoxide behaving dissociatively or non-dissociatively. The role of hydrogen in F-T synthesis has not been previously investigated. Using infrared spectroscopy to detect associatively adsorbed H_2 on a Pt/Al_2O_3 catalyst were able to relate the hydrogen addition to linear, bridged, or dissociative CO in the adsorbed states. The present in situ FT-IR study of Pt/Al_2O_3 in CO/H_2 mixtures was aimed at simultaneously probing CO adsorption, hydrocarbon formation, and the generation of hydrocarbonaceous intermediates as a function of reaction time, reaction temperature, and CO/H_2 feed ratio.

The adsorption of H_2 is seldom observed because of the low sensitivity of M–H bond formed by the dissociative adsorption of hydrogen. This low sensitivity can be overcome in part by use of Fourier transform-IR instrumentation and the use of newly designed in situ cell (Fig. 1). Dixon and other authors [1–3] reported that in the temperature range of 77–252 K, the adsorption of H_2 on Pt/Al_2O_3 leads to the appearance of the bands at 2120 and 2060 cm^{-1}, in which the band at 2120 cm^{-1} might be caused by the vibration of Pt-H, but the band at 2060 cm^{-1} may be attributed to the vibration of $Pt \cdots H \cdots Pt$, or the trace pollutant CO. In this paper, the effect of trace CO on H_2 adsorption over Pt/Al_2O_3 was effectively investigated and the features of H_2 adsorption on Pt/Al_2O_3 (mainly the band

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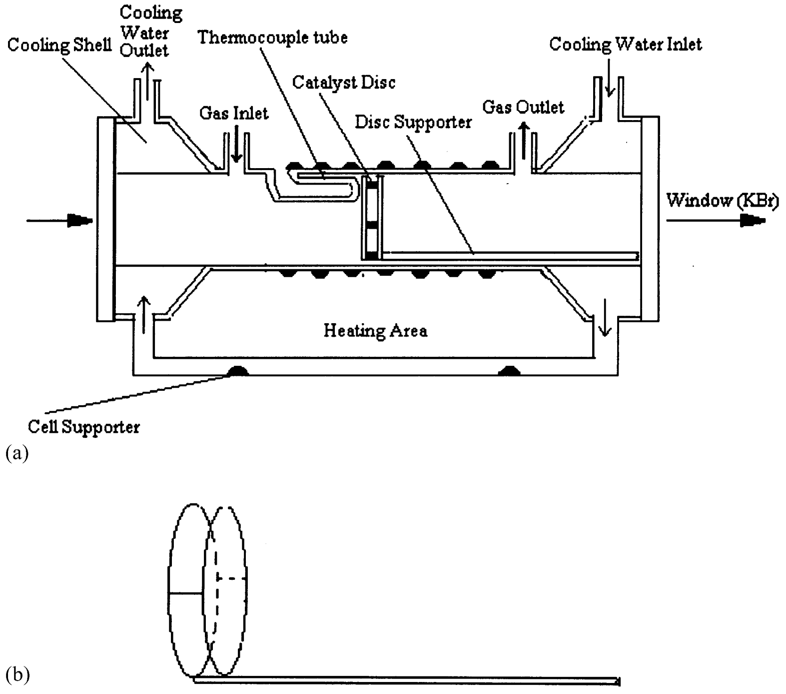

Fig. 1. (a) In situ FT-IR quartz cell (unit: mm); (b) disc quartz-supported.

at 2060 cm^{-1}) were extensively studied by use of in situ IR spectroscopy.

2. Experimental

2.1. Catalyst preparation

The Pt/Al_2O_3 catalyst was prepared by impregnating the γ-Al_2O_3 support with solution of $H_2PtCl_6 \cdot 6H_2O$ to yield a nominal 0.6% Pt metal. The impregnated powders were dried at 393 K and calcined at 773 K for 8 h.

2.2. Sorption properties

The surface and structural properties such as surface area, average pore diameter, and pore volume were determined using a gas sorption analyzer using N_2 adsorption at 77.5 K. The accelerated surface area and porosity were analyzed by Micromeritics ASAP 2010 apparatus. Before analysis, samples were degassed under vacuum for 1 h at 373 K and for 3 h at 673 K.

From the adsorption isotherm, surface area was determined using the BET equation. The total pore volume was derived from the amount of adsorption at a relative pressure close to unity, assuming that the pores were totally filled with the liquid nitrogen. The average pore size was estimated from the pore volume, assuming a cylindrical pore geometry using the equation $D_p = 4V_t/S$, where V_t is the total pore volume and S the BET surface area.

The mesopore volume/area and pore distribution curve was obtained from the adsorption branch of the N_2 isotherm by BJH method. For adsorption data, the relative pressure and volume adsorbed data point pairs collected during an analysis were arranged in reverse order from which the points were collected during analysis. All calculations are performed based on a desorption model, regardless of whether adsorption or desorption data is being used.

The micropore distribution and mean pore size were calculated from the gas adsorption using the Horvath–Kawazoe equation, with relative pressure (P/P_0) below 0.01. In the meantime, the t-plot calculation allows quantitative analysis of the area and total volume ascribed to micropores. The mesopore volume was determined by subtracting the micropore volume from the total pore volume.

2.3. In situ IR spectroscopy

A self-supporting disc (50 mg, 13 mm diameter) was prepared by compressing the powder obtained by drying (383 K, 10 h) the catalyst prepared above. This disc was mounted in a self-designed IR quartz cell described as in Fig. 1. The catalyst disc was reduced in situ in H_2, the temperature being raised from ambient to 673 K where it was held for 2 h before evacuation at 673 K and subsequent cooling to reaction temperature. In situ IR spectra of the disc in CO, H_2 at the quoted temperatures and pressures were recorded with a Nicolet Magna-750 Fourier transform-infrared spectrometer. The resolution was 4 cm^{-1} and the disc was at the high treatment temperature quoted unless otherwise stated.

3. Results and discussion

3.1. Sorption properties

The most reliable information about the mesoporous structure of solids comes from lower-temperature nitrogen adsorption isotherms, which enable the calculation of the specific surface area, pore volume, and mesoporous size distribution. The BET surface area of reduced catalyst was 71.03 $m^2\,g^{-1}$ with a total pore volume of 0.23 ml g^{-1} and a mean pore diameter of 13.4 nm. Of interest is that the similar adsorption isothem is type III isotherm, typical of mesoporous solids. The isotherm is characterized by convexity towards the relative pressure axis, commencing at the origin. A type III isotherm is traditionally characteristic of weak gas–solid interactions, which means the isotherm is given by a macroporous solid. This weakness of gas–solid forces will cause the uptake at low relative pressures to be small, but once a molecule has become adsorbed, the gas–solid forces will promote the adsorption of further gas molecules, which is surely the cooperative process, so that the isotherms will become convex to the pressure axis. It means that the catalyst was totally mesoporous with negligible microporosity (pore diameter less than 1 nm).

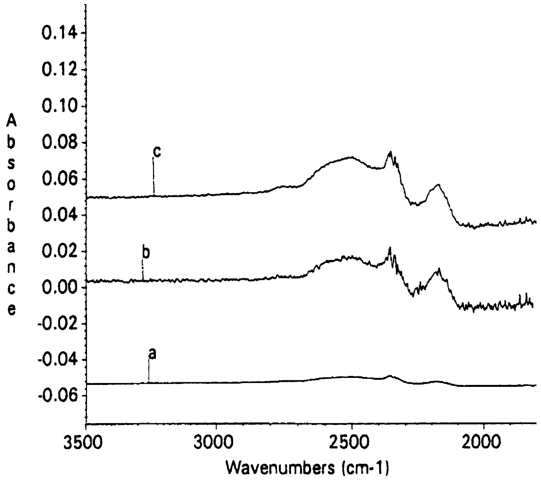

Fig. 2. IR spectra of Pt/Al_2O_3 catalyst at (a) 313 K, (b) 473 K, and (c) 623 K.

3.2. CO adsorption on Pt/Al_2O_3

Before H_2 was adsorbed on Pt/Al_2O_3, the IR absorption of the catalyst, Pt/Al_2O_3 itself, the spectra of pure CO gases, and the adsorption of CO on the Pt/Al_2O_3 catalyst under different conditions was first investigated in order to find the exact band which the adsorbed CO on Pt/Al_2O_3 give rise to.

3.2.1. The IR spectra of Pt/Al_2O_3

To study the adsorption of CO on a Pt/Al_2O_3 catalyst, the spectra of a reduced Pt/Al_2O_3 catalyst at different temperatures was firstly studied. Fig. 2 shows the background IR spectra of reduced Pt/Al_2O_3 itself during the elevation of temperature. The weak bands at ~2550 and ~2180 cm^{-1} are due to the skeleton vibration of the catalyst support when increasing the temperature, and the higher the temperature, the stronger the absorption bands. It shows that no absorption bands are attributable to any of the vibration modes of carbonaceous species polluted by other organic compounds or carbon monoxide, and it means that the surface concentrations of carbonaceous fragments are below the detection limit, therefore, the following results were surely caused by adsorption treatments.

3.2.2. The adsorption of CO on Pt/Al_2O_3

The spectrum (Fig. 3a) of Pt/Al_2O_3 catalyst exposed to CO at 1.0×10^4 Pa pressure and ambient

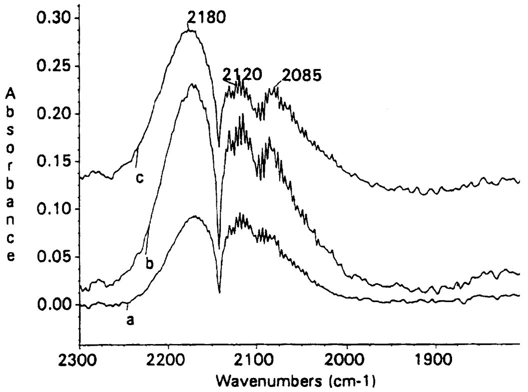

Fig. 3. IR spectra of Pt/Al2O3 catalyst exposed to CO ($P_{CO} = 1.0 \times 10^4$ Pa) at (a) 373 K, (b) 473 K, and (c) 673 K.

temperature contained bands at 2085, 2120, and 2180 cm^{-1}. While evacuating the gaseous CO to 2.0 Pa, the spectra shows that only the band at 2085 cm^{-1} existed (Fig. 4). It means that the bands at 2120 and 2180 cm^{-1} might be caused by gaseous CO and the band at 2085 cm^{-1} may be due to linearly adsorbed CO. Raising the temperature, the band at 2085 cm^{-1} increased gradually, and it reached the strongest intensity at 473 K. According to the literature [4], the band at 2085 cm^{-1} is due to linearly adsorbed CO on Pt/Al2O3, and it would desorb at higher temperature. The spectrum of pure CO gives rise to bands at 2180 and 2120 cm^{-1} (Fig. 5), this just means that when evacuating the system, the CO gas in the cell was removed and the bands at 2120 and 2180 cm^{-1} disappeared accordingly, the linearly adsorbed CO on the catalyst was not desorbed under the vacuum of 2.0 Pa and gave rise to the band at 2085 cm^{-1} in the IR spectra.

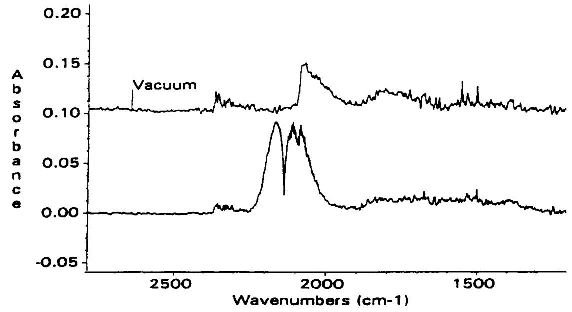

Fig. 4. IR spectra of CO ($P_{CO} = 5.0 \times 10^3$ Pa) adsorption for 10 min, then the system was evacuated.

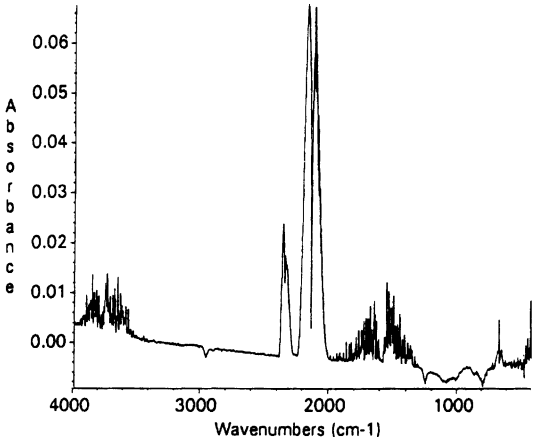

Fig. 5. IR spectra of pure CO; $P_{CO} = 5.0 \times 10^3$ Pa.

On the reduced Pt/Al2O3 catalyst, CO was introduced at 1.0×10^4 Pa, 313 K for 10 min, evacuated to 2.0 Pa in order to evacuate the CO gas in the cell, heating the catalyst under the vacuum at the rate of 4°C up to 623 K. From the spectra, CO adsorption at room temperature on such a catalyst gives rise to a broad band at 2085 cm^{-1} (Fig. 6), and it shifted to lower wave number on increasing the temperature and to 2075 cm^{-1} at 473 K. Heating to 623 K, this band almost disappeared due to the desorption of adsorbed CO. When CO was linearly adsorbed on Pt/Al2O3, on

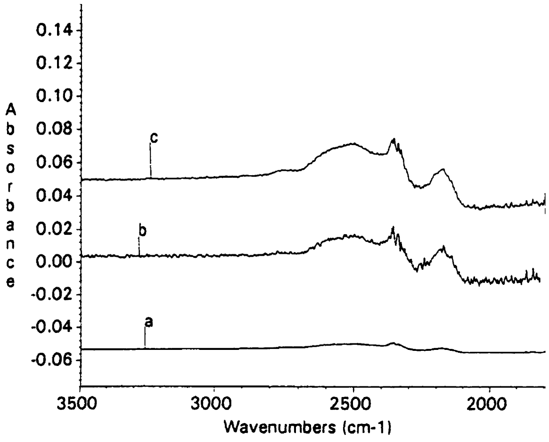

Fig. 6. In situ IR spectra of adsorbed CO on Pt/Al2O3 catalyst; $P_{CO} = 4.0 \times 10^4$ Pa.

the surface of the catalyst, d–π bands were formed and the ν_{CO} was related to the feedback of d–π [5], and the dissociation of adsorbed CO is the first step in the methanation reaction which in simplified form contains the following reaction step [6–8]:

$$CO + * \rightarrow CO_{(ad)} \tag{1}$$

$$CO_{(ad)} \rightarrow C_{(ad)} + O_{(ad)} \tag{2}$$

While increasing the temperature, the concentration of adsorbed carbon (Pt-C) increases, this strengthens the antidonating effect of surface Pt atoms and results in the band, due to adsorbed CO (ν_{CO}), shifting to lower wave numbers.

3.3. Adsorption of H_2 on Pt/Al_2O_3

The adsorption of H_2 on Pt/Al_2O_3 gives a broad infrared band at 2085 cm^{-1} (Fig. 7). With increasing temperature ($H_2 = 5.0 \times 10^4$ Pa), the spectra were similar to Pt-CO adsorption given in Fig. 6. As temperature was elevated, there were no obvious band shifts, but the band at 2085 cm^{-1} became weaker, as band at 3020 cm^{-1} due to the formation of gaseous methane became apparent [9]. Of interest is that no carbon dioxide was simultaneously formed but some surface hydroxyl species at 3500–3600 cm^{-1} were formed. It means that the adsorbed hydrogen, $H_{(ad)}$, formed in the H_2 reduction can interact with surface carbon species and oxygen species formed by the decomposition of CO to form gaseous methane and surface hydroxyl groups or water. A mechanism involving the formation of methane and surface hydroxyl species would be compatible with the present results [10]. It could be explained as follows:

$$CO_{(ad)} \rightarrow C_{(ad)} + O_{(ad)}$$

$$O_{(ad)} + 2H \rightarrow H_2O \tag{3}$$

$$C_{(ad)} + 4H \rightarrow CH_4 \tag{4}$$

In this case, the disproportionation of CO may not have occurred. The adsorbed CO decomposes to form surface oxygen and carbon species on the catalyst, and the oxygen and carbon species directly react with hydrogen to form H_2O and methane. If trace CO is present in the hydrogen gases over Pt/Al_2O_3 catalyst, the pollutant CO would hydrogenate to form methane.

Fig. 8 shows the effect on the IR spectra of the exposure of Pt/Al_2O_3 to hydrogen (4.0×10^4 Pa) at 473 K. The band at 2085 cm^{-1} was observed due to adsorption of CO on Pt/Al_2O_3 (Fig. 8a); we believe this band was mainly caused by the adsorbed pollutant CO. After increasing the temperature to 773 K and holding at this temperature for 1 h, the pollutant CO was effectively hydrogenated and the concentration of CH_4 (A_{3020}) attained was constant. This indicated that the pollutant CO had almost disappeared on lowering the temperature to 473 K. Fig. 8b shows that a new band appeared at 2060 cm^{-1}, which is assigned vibration of the surface Pt···H···Pt band formed

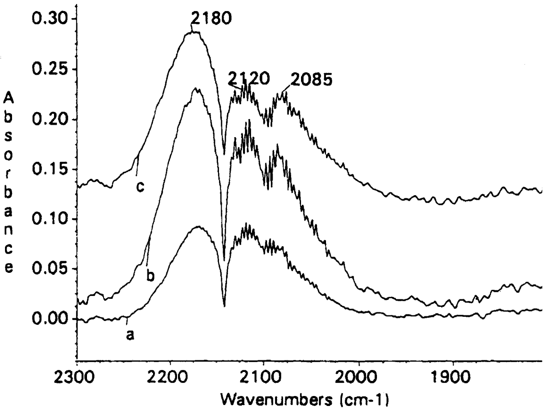

Fig. 7. In situ IR spectra of adsorbed H_2 on Pt/Al_2O_3 catalyst; $P_{H_2} = 4.0 \times 10^4$ Pa.

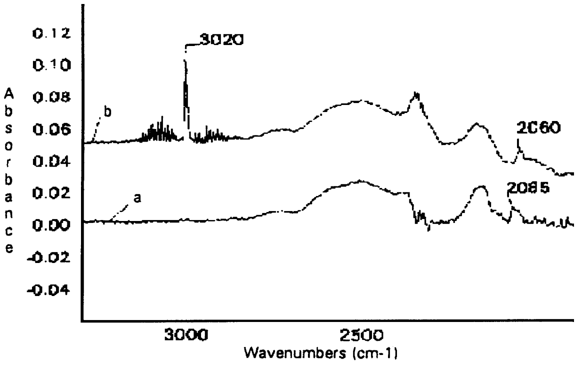

Fig. 8. IR spectra of H_2 adsorption on Pt/Al_2O_3: (a) spectra of 473 K during the process of elevation of the temperature; (b) spectra of 473 K during the process of decrease of the temperature after keeping 773 K for 30 min.

by the decomposition of hydrogen on Pt/Al_2O_3 catalyst.

4. Conclusions

1. While elevating the temperature, the Pt/Al_2O_3 catalyst gives rises to bands at 2180 and 2550 cm^{-1} caused by the skeletal vibrations of the catalyst, and the higher the temperature, the stronger the absorption bands.
2. The IR spectra of CO adsorption on Pt/Al_2O_3 at 0–1.0 atm give rise to the band at 2085 cm^{-1}. This band shifts to lower wave number because of the dissociation of adsorbed CO to form adsorbed carbon, $C_{(ad)}$, and the band becomes weak due to the adsorbed CO desorption.
3. The band at 2060 cm^{-1} is the vibration of the surface $Pt\cdots H\cdots Pt$ band on Pt/Al_2O_3 catalyst; this band is formed by the decomposition of hydrogen. In many conditions, this band is always covered by the nearby band of adsorbed trace CO at 2085 cm^{-1}.

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