Petroleum Res. J. Vol. 15 (2003); P. 65-72, 11 Figs.

FTIR Infra-red Observations of the Adsorption of Ethene, Ethyne and Carbon Monoxide on Supported Platinum Catalysts

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دراسة إمتزاز الإيثين والإيثاين وأول أكسيد الكربون على حفازات البلاتين المدعم باستخدام الأشعة تحت الحمراء

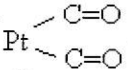
عز الدين أحمد عرفة

تم في هذه الدراسة استخدام تقنية الأشعة تحت الحمراء في تتبع إمتزاز المواد، الإيثين والإيثاين وأول أكسيد الكربون على حفازات البلاتين المدعم على السيليكا والألومينا والماغنيسيا . على ضوء ذبذبات الأطياف المتحصل عليها من تجارب إمتزاز هذه المواد على الحفازات تحت الدراسة وتلك المنشورة على حفازات عناصر المجموعة الإنتقالية الأخرى، تبين أن إمتزاز الإيثين والإيثاين ينتج المركب إيثايليدين ذو التركيب ($-C-CH_3$) كمركب وسيط على أسطح الحفازات العذراء. بيد أن الحفازات التي تم استهلاكها في هدرجة الإيثاين بينت أطيافاً بها ذبذبات تشير لوجود المركبات الوسيطة ذات التركيب PtCH=CHPt ومركبات هيدروكربونية متبلمرة.

كذلك بينت الدراسة أن أول أكسيد الكربون يمتز في صورة خطية على أسطح الحفازات العذراء ويتغير إلى الصورة الجسرية عندما يتم أكسدة الحفازات بالهواء خصوصاً بالحفازات المدعمة على السيليكا .

Abstract: *The adsorption of ethene, ethyne and carbon monoxide on silica-, γ-alumina and magnesia-supported platinum catalysts was studied by Fourier Transform Infrared Spectroscopy (FTIR). On the basis of the observed band frequencies and the reported literature data, assignments have been made for the bands detected in the spectra. The addition of ethene and ethyne to freshly reduced Europt-1(6.0% Pt/SiO_2) resulted in the formation of an ethylidyne (C-CH_3) species as evidenced by the development of bands at 1297 cm^{-1} ($\delta_s(CH_3)$) and 954 cm^{-1} (v(C-C)) in addition to the vs(CH_3) at 3074 cm^{-1}.*

While on ethyne/hydrogen deactivated catalysts, bands characteristics of surface species such as, PtCH=CHPt (band at 1693 cm^{-1}, vs(C=C)) and of hydrocarbon polymeric moieties (bands at 2974-2884 cm^{-1}, $\delta_s(CH_3)$ and 1374 cm^{-1} vs(CH_3)), were detected.

On freshly reduced catalysts, carbon monoxide was found to adsorb in the linear form (Pt–C=O, at v_sC-O (2086 cm^{-1}, 2112 cm^{-1}, depending on support type). Exposure of the catalysts to air tends to convert the linear form of carbon monoxide to bridged form ( $Pt\langle^{C=O}_{C=O}$ *) at v_sC-O (1886 cm^{-1}, observed on silica-supported pt-catalysts).*

INTRODUCTION

Although the chemical nature of the adsorbed species at metal surfaces has been the subject of debate for more than six decades, since the pioneering work of Horiuti and Polanyi[1], it can be said with

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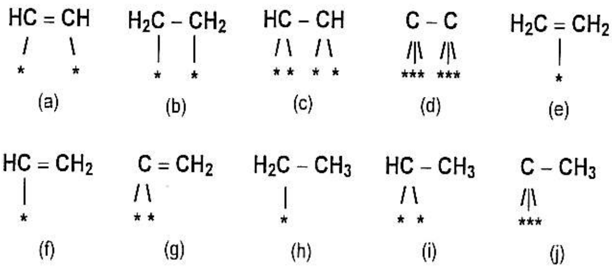

Fig. 1. The adsorption forms of ethane.

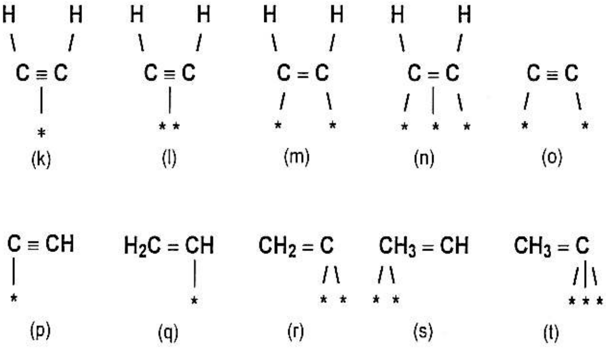

Fig. 2. The adsorption forms of ethyne.

confidence that, so far, these studies have not yet brought about a clear and unambiguous picture of the adsorbed states of even the most simple molecules, such as ethene and ethyne, at these surfaces. Knowledge concerning the adsorbed states of olefins, di-olefins and carbon monoxide has been obtained in part from infrared (I.R.) studies of organometallic chemistry[2] and the application of direct instrumental methods developed by surface physicists[3], such as, AES, LEED, XPS, *etc.*, which have been mainly concentrated on the adsorption of ethene and ethyne on single crystals. However, the application of the results of these methods to inerpret catalytic processes is not straightforward. This is due to the fact that most of these studies are carried out over clean surfaces (generally without hydrogen), under ultra-high vacuum conditions and usually at low temperatures, whereas catalytic reactions take place on surfaces covered with adsorbed species and under several pressures of reactant gases at ambient or elevated temperatures. The other source of information regarding the adsorbed states of unsaturated hydrocarbons and carbon monoxide comes indirectly from the kinetics and product distributions of various processes such as hydrogenation, adsorbed states of unsaturated hydrocarbons and carbon monoxide comes indirectly from the kinetics and product distributions of various processes such as hydrogenation, deuterium exchange and isomerisation of these compounds[4]. Various states of ethene adsorption have been proposed and these are presented in the formulae a-j (Fig.1). The findings of the studies of ethyne adsorption and hydrogenation on metal surfaces led to the postulation of the adsorbed species presented in the structures k-t (Fig.2). The presence of any of these adsorbed species on any particular metal surface is the subject of the literature data reported by many investigators and found to depend on, the metals themselves, their dispersion, oxidation state and the type of the support. A wealth of research has been done in recent years to try to understand the interaction of carbon monoxide with metal surfaces. Primarily this because CO chemisorption is an important step in various industrially important reactions, such as, the methanol synthesis, Fisher-Tropsch process and the formation of alcohols. Secondly, CO has been used widely as a probe for catalyst surface area determination and as a test molecule to distinguish the active centres in the catalytic reactions. The current knowledge of the spectroscopy of adsorbed molecules on catalyst systems originated from the pioneering studies on organometallic compounds[1,5-8]. The C-O stretching frequency of gaseous CO is at 2143 cm^{-1} and this band was observed to shift to between 2000 cm^{-1} and 2100 cm^{-1} after monodentate ligand formation (linear species) and shifts below 2000 cm^{-1} when bi-dentate ligands (bridged species) formed with transition-metal compounds. The so- assigned 'linear' and 'bridged' CO species to adsorb on metal surfaces are depicted in the structures (u-z, Fig. 3).

This paper presents the results of Fourier transform infrared (FTIR) spectroscopy investigation of the nature of adsorbed ethene, ethyne and carbon monoxide on silica-, alumina- and magnesia-supported Pt-catalysts at room temperature (22 ± 2°C) under different conditions and treatments.

EXPERIMENTAL

Apparatus

The apparatus which was employed for *in situ* I.R. experiments consisted of a conventional vacuum system containing a reaction vessel similar to that described previously[9-11] and storage bulbs for the feed stocks of hydrogen, hydrocarbons and carbon monoxide, which maintained at a pressure of ~0.01 Pascal (Pa) by means of a mercury diffusion pump backed with an oil rotary pump. The *in situ* I.R. cell

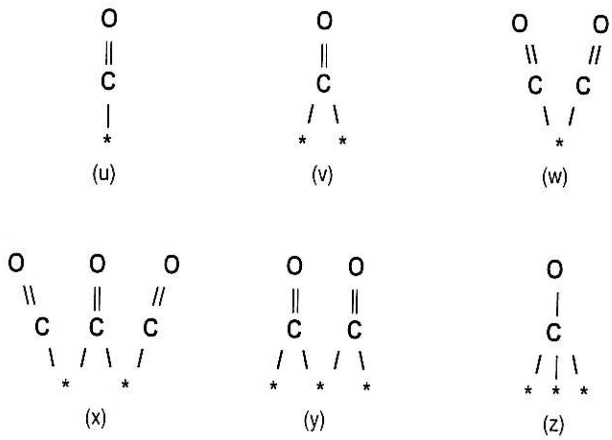

Fig. 3. The adsorption forms of carbon monoxide.

used is shown diagramtically in figure 4. It contained a catalyst wafer specimen holder, a Nichrome-wire furnace surrounding the outer body of the quartz cell which was capable of heating the wafer sample to 800°C. The temperature in the cell was monitored by an electronic thermometer (Electronics Ltd.- 1602 Cr/Al) coupled to a chromel-alumel thermocouple located in a thermowell close to the sample. Two KBr windows (25 x 4 mm x Barns), sealed in stainless steel rings with Araldite adhesive, were fitted to the two ends of the I.R. cell by stainless steel threaded jackets and sleeves surrounded by a water coolant system to prevent thermal shock to the KBr windows. The cell could be pumped to ~0.01 Pa using the vacuum system. The catalyst powders (~ 0.05g) were pressed in to wafer discs in air (~7 tonnes pressure). The wafers were placed in the I.R. cell and about 500-1000 scans were recorded. This was usually followed by I.R. measurements of the sample after brief evacuation (~ 15 minutes), flushing with He (25 ml min^{-1}), or heating to an elevated temperature.

When direct adsorption of ethene, ethyne or carbon monoxide was required, a diffuse reflectance collector (type DRIFT-Spectra-Tech Inc.) was used. The design of the collector employs 4 flat and 2 spherical reflectors, plus an alignment mirror (Fig. 5). The sample cup (13 mm, i.d.) could be removed (for emptying and filling the catalyst) from the top of the collector, by sliding the ellipsoids out of the way. The collector was connected to a vacuum system for evacuation and handling the

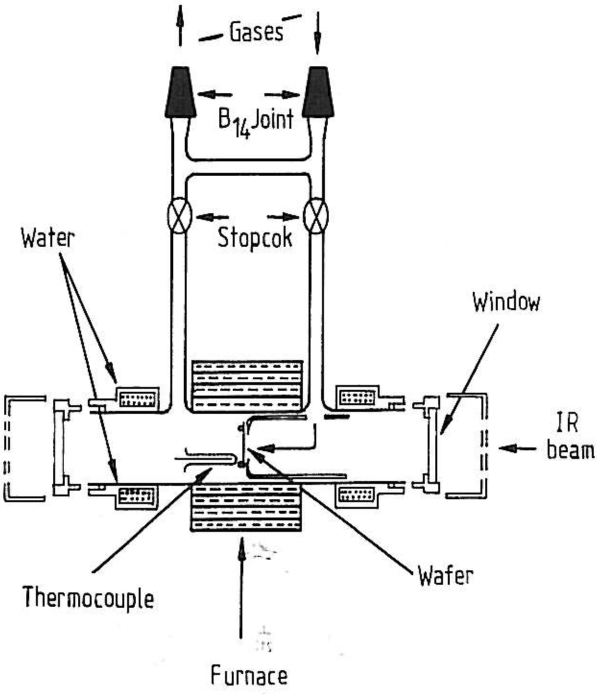

Fig. 4. The *in-situ* I.R. cell.

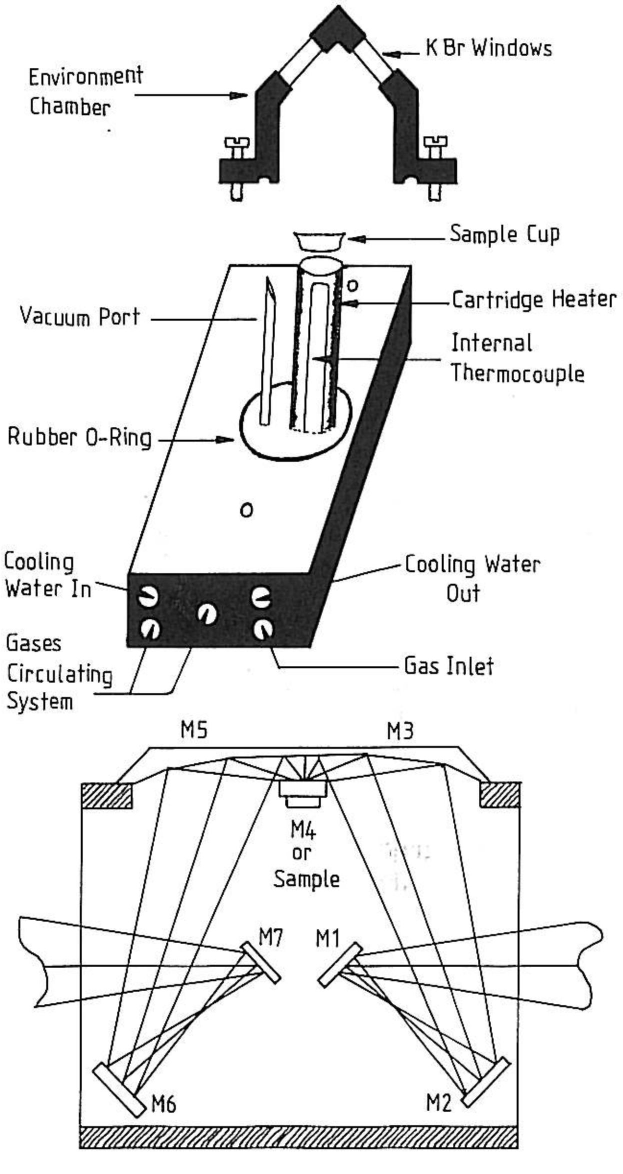

Fig. 5. The diffuse reflectance I. R. cell (DRIFTS).

adsorbate gases. The catalyst samples were heated to the required temperature by an internal cartridge heater.

Catalysts

The catalysts employed in this study are standard reference catalysts, Europt-1, is a 6% (w/w) Pt/SiO_2 catalyst with a total surface area of 185m^2g^{-1} and a pore volume of 0.72 cm^3g^{-1}, prepared by Johnson Matthey Chemicals plc[12]. Europt-3, is a 0.3% (w/w) Pt/Al_2O_3-0.82% Cl catalyst (coded KETJEN-CK 303) with a surface area of 184 m^2g^{-1} and a pore volume of 0.49 cm^3g^{-1}[13]. Another three platinum catalysts supported on silica (Cab-O-Sil), γ-alumina (Degusa, Ltd.) and molybdenum trioxide (Koch-Light, Ltd.) all of 99.9% purity. These catalysts were prepared by impregnation of the aqueous solution of the metal chloride (H_2PtCl_6) containing the required weight of the metal to an aqueous suspension of the support. The excess water was evaporated using a rotary evaporator and the material dried in an air oven at 150°C. These catalysts were characterised as 0.8% (w/w) Pt/SiO_2, 0.8% (w/w) Pt/Al_2O_3 and 0.5% (w/w) Pt/MoO_3 and will be referred to as the impregnated catalysts.

Materials

Hydrogen (H_2) gas (B.O.C., Commercial grade) was used in the catalyst reduction and hydrogenation reactions (deactivation) without further purification. Ethene (C_2H_4) and ethyne (C_2H_2) were degassed at liquid nitrogen temperature (-196 °C) for ~ 15 minutes followed by bulb-to-bulb distillation using liquid nitrogen and methylene chloride + solid CO_2 mixture. Helium (He) and carbon monoxide (CO) (Air products Ltd.) were used as supplied.

Procedures

Two regimes were used for I.R. measurements. In the first, the catalyst samples which had been subjected to C_2H_4, C_2H_2 or CO adsorptions or ((1:3) C_2H_2/H_2) deactivation were examined using a Niolet 5-DXC instrument with the *in situ* cell (Fig. 4) to identify the surface species formed during adsorption or surface interactions and also to examine the effects of various treatments on these species, such as heating or flushing with carrier gases such as He. In the second, direct observation of the adsorption of these molecules by the I.R. system was performed using the diffuse reflectance cell (DRIFTS) (Fig. 5). The procedure used in the 'DRIFTS' experiments was as follows: a background spectrum was acquired using KBr as a diffuse reflector in the Nicolet 5-DXC spectrophotometer at 4 cm^{-1} resolution. A catalyst sample was loaded in the cup of the collector and was reduced in flowing H_2 (30ml min^{-1}) at 250 ± 5 °C for 1h, evacuated briefly (~10 min) at this temperature and then cooled to room temperature (22 ± 2°C). The catalyst was then pulsed with the required adsorbate and after recording the I.R. spectra, the catalyst was subjected to various treatments, such as, evacuation, flushing with He, or heating at elevated temperatures.

RESULTS AND DISCUSSION

I.R. of Adsorbed C_2H_4 and C_2H_2

In the DRIFTS experiments, the spectra following the adsorption of C_2H_4 and C_2H_2 on Europt-1 at room temerature are shown in figure 6. The spectrum of the adsorbed species after subtracting the background and gas phase spectra showed a medium band at *ca.* 1297 cm^{-1} and a weak band at *ca.* 954 cm^{-1} in addition to a weak band at *ca.* 3074 cm^{-1}. These bands, which have also been observed by Beebe *et al.*[14] for C_2H_4 and C_2H_2 on Pd/Al_2O_3 at 1333 cm^{-1} for ($\delta_s(CH_3)$), 1088 cm^{-1} for (ν(C-C)) and 2867 cm^{-1} for $\nu s(CH_3)$, have been assigned to the surface ethylidyne species (structure j, Fig. 1; structure t, Fig. 2).

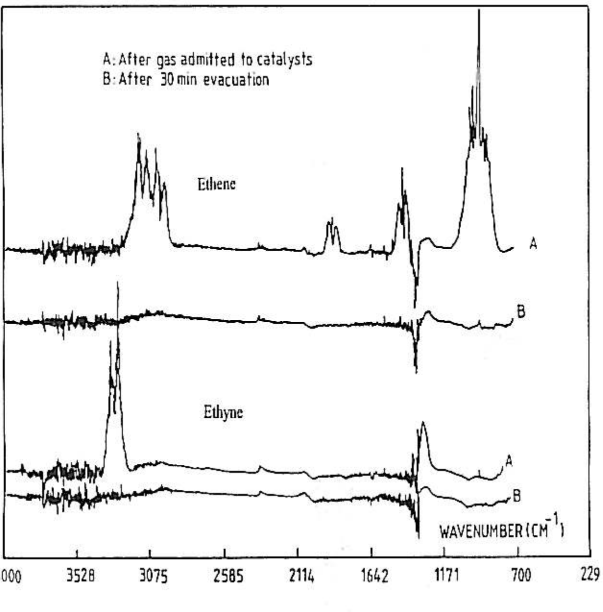

Fig. 6. The I. R. spectra of ethene and ethyne adsorption on Europt-1.

In contrast, when the catalyst samples of Europt-1 and the impregnated 0.8% Pt/SiO_2 had been deactivated by a series of C_2H_2/H_2 and then examined by FTIR, their *in situ* I.R. spectra (Fig. 7) displayed small bands in the region 2974-2884 cm^{-1} and intense bands at 2081cm^{-1}, 1975 cm^{-1}, 1840 cm^{-1}, 1705 cm^{-1}, 1693 cm^{-1} and 1374 cm^{-1}. The bands at 2081 cm^{-1} and 1705 cm^{-1} disappeared as the catalysts were heated to 115°C and flushed with helium for 10 minutes. Based on the literature data [5-8,15-17], the bands at 2974-2884 cm^{-1} and 1374 cm^{-1} were assigned to the CH_3 group and are indicative of the presence of surface alkyl species. While the band at 1693 cm^{-1} has been attributed to C=C stretching and is characteristic of a surface species such as PtCH=CHPt (structure a, Fig. 1; structure m, Fig. 2). The bands at 2081 cm^{-1}, 1975 cm^{-1} and 1840 cm^{-1} are likely to be due to the adsorption of the hydrocarbon molecules on the support material [5].

When ethyne was adsorbed (till saturation) on the various catalysts, gas chromatographic analysis of the gas phase showed that with Europt-1, ethane and ethene were produced. However, with the other catalysts ethene was never observed. From the yields of ethane formed, the average composition of the adsorbed hydrocarbon species at the saturation point was calculated to be $C_2H_{1.6}$ (Europt-1) and $C_2H_{1.8}$ (Europt-3). These observations suggest that a range of adsorbed species is present on these catalysts as a result of an extensive dissociation of the C-H bonds.

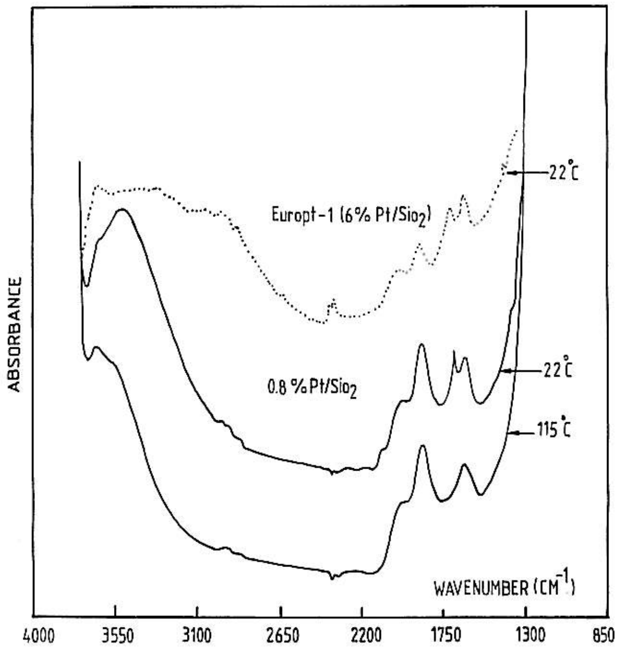

Fig. 7. The I. R. spectra of Pt-catalysts deactivated with C_2H_2/H_2 reactions.

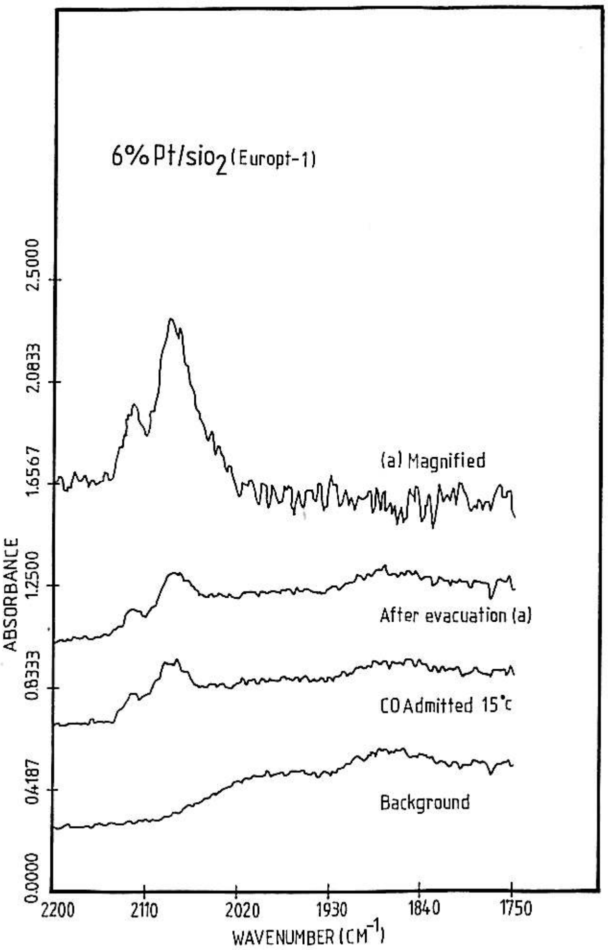

Fig. 8. The I. R. spectra of carbon monoxide adsorbed on Europt-1.

This in turn can lead to two possible processes which may occur independently on the catalyst surface; (i) an extensive dissociation of the adsorbed species to yield multiple bonded species of the form (structures g, i, j, Fig. 1). Figure 6. represents an I.R. evidence for the detection of, ,structure j, following C_2H_4 and C_2H_2 adsorption and hydrogenation on Europt-1 and the impregnated 0.8% Pt/SiO_2 and was reported to exist on Pt (111) surface[16,18]. Consequently, the amount of hydrogen released, together with any hydrogen already present following the reduction process may react with these species to produce C_2H_6 and C_2H_4; (ii) the dissociated species may react with an adsorbed C_2H_4 or C_2H_2 molecule leading to the deposition of polymeric species on the catalyst surface. Such hydrocarbon species have been observed by Avery and Sheppard *et al.*[6,7] on silica-supported Pd- and Pt-catalysts and in this work as shown in the I.R. spectra of adsorbed C_2H_2 on C_2H_2/H_2 deactivated, Europt-1 and the impregnated 0.8% Pt/SiO_2 catalysts (Fig. 7), bands (2974-2884 cm^{-1}, 1374 cm^{-1}).

I.R. of Adsorbed CO

The DRIFTS spectra of the adsorption of CO on the different catalysts are shown in figure 8 ,(Europt-1), figure 9, (0.8% Pt/SiO_2, 0.5% Pt/MoO_3) and figure 10, ((Europt-3) and 0.8% Pt/Al_2O_3). The spectra of adsorbed CO on Europt-1 showed a band at 2086 cm^{-1} and a companion shoulder at 2122 cm^{-1}, while, on the 0.8% Pt/SiO_2 and 0.5% Pt/MoO_3 catalysts, CO adsorption, produced a single sharp band at 2086 cm^{-1}. On Europt-3 and 0.8% Pt/Al_2O_3 catalysts, CO adsorption gave rise to bands at 2124 cm^{-1}, 2086 cm^{-1} and 2070 cm^{-1}. These bands disappeared completely by evacuation of the Europt-3 catalyst, while only thermal treatment (up to 250 ± 5 °C) was required to remove the adsorbed CO from the 0.8% Pt/Al_2O_3 catalyst (except for those species corresponding to the 2124 cm^{-1} band, which shifted towards the lower frequency region at *ca.* 2115 cm^{-1}). Based on the literature data[2,14-20] and the DRIFT -I.R. bands observed on all the catalysts used in this work, the bands at 2086 cm^{-1}, 2122 cm^{-1} and 2124 cm^{-1} are characteristics of the linear form of adsorbed CO (structure u, Fig. 3) and such species have been assigned to adsorp on terrace sites[19].

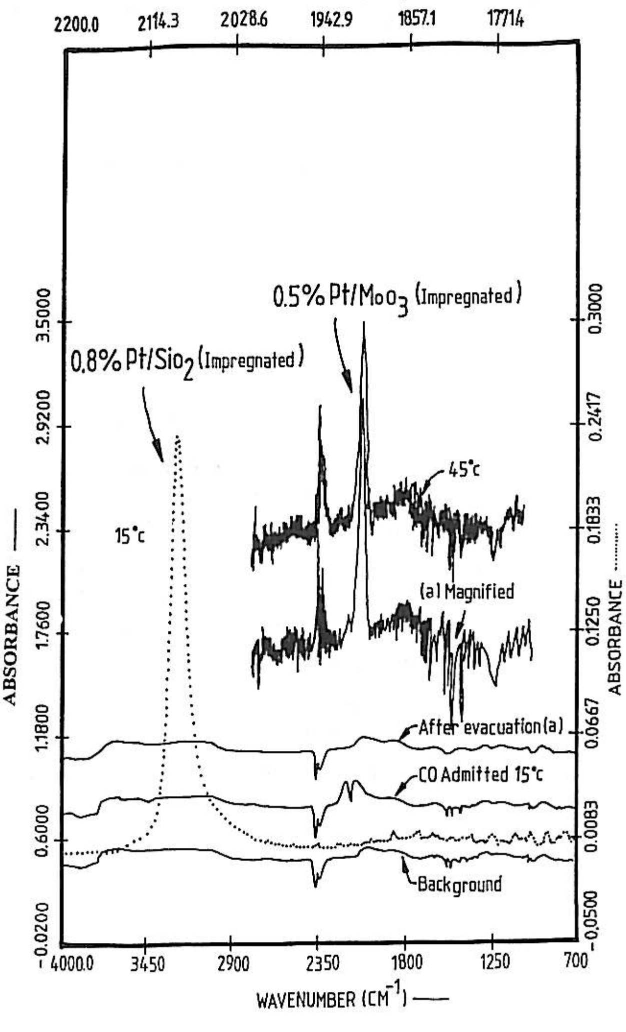

Fig. 9. The I. R. spectra of carbon monoxide adsorbed on Pt-catalysts.

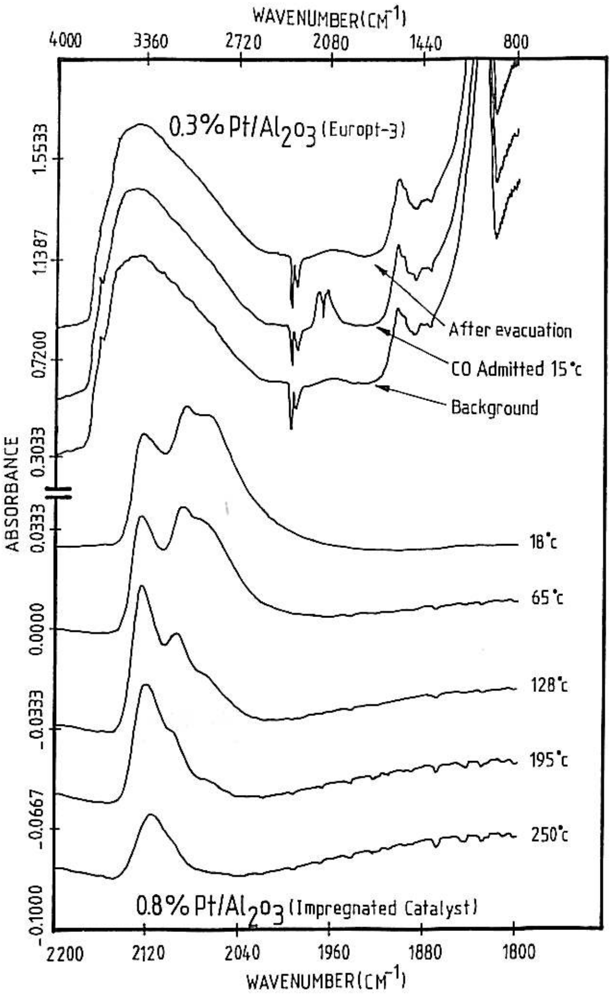

Fig. 10. The I. R. spectra of carbon monoxide adsorbed on Pt-catalysts.

The catalyst samples of Europt-1, Europt-3 and 0.8% Pt/SiO_2 which were first subjected to CO adsorption (untill it showed a saturation plateau) were subsequently examined by the IR spectroscopy using the *in situ* cell. As it can be seen from the spectra (Fig. 11), these catalysts contained moites which are characteristics of chemisorbed hydrocarbon species as indicated by the bands at 1685 cm^{-1} (C=C), 1632 cm^{-1} (C-C) and 1440 cm^{-1} (CH_3 group). The band at 1685 cm^{-1} appeared as the catalyst (Europt-1) was heated at elevated temperatures followed by evacuation. Interestingly, these species were likely to be evolved by the reaction of CO with the H_2 which may be retained on the catalyst metal and/or on the support after the reduction process.

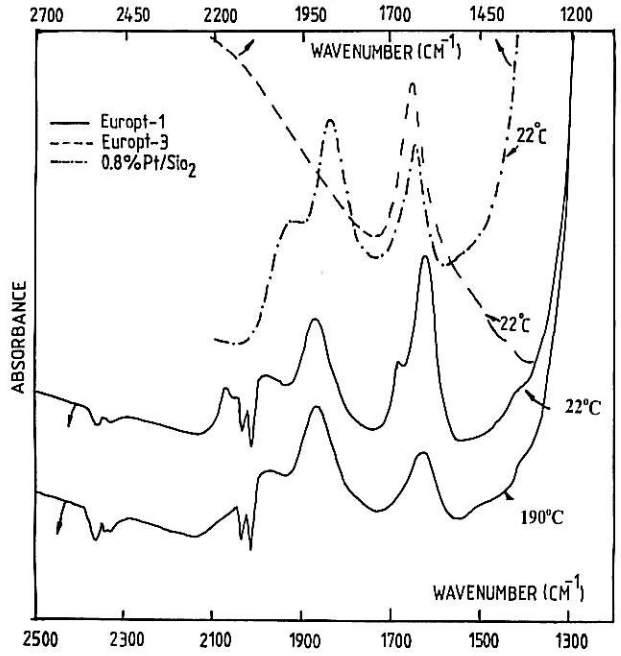

Fig. 11. The I. R. spectra of Pt-catalysts deactivated with CO adsorptions.

A band at 1886 cm^{-1} has also appeared in the spectra of Europt-1 and the impregnated 0.8% Pt/SiO$_2$ (Fig. 11) which is representative of the adsorbed bridged form of carbon monoxide. This observation is likely to suggest that upon the exposure of these catalysts to air (oxidation), the linearly adsorbed CO detected in the DRIFT-I.R. experiments plausibly converted to the bridged form (structure v, Fig 3). Such bridged species have been detected on oxidized platinum Group metals[19,20].

CONCLUSIONS

In conclusion, an I.R. evidence has been obtained for the formation of an ethylidyne (C-CH$_3$) species upon the exposure of freshly reduced Europt-1(6.0% Pt/SiO$_2$) catalyst to ethene or ethyne, while bands characteristics of hydrocarbon polymeric species were detected on ethyne/hydrogen deactivated catalysts. On freshly reduced catalysts, carbon monoxide was found to adsorb in the linear form. Exposure of the catalysts to air tends to convert the linear form of carbon monoxide to bridged form.

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