The effect of supports on coke deposition on supported platinum and platinum-tin catalysts investigated by FT-IR spectroscopy

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Coke deposit is produced from ethylene on the surface of the platinum and platinum-tin catalysts supported on two various Al_2O_3, SiO_2 and SiO_2-Al_2O_3. The coke amount and the structure depend on the type and the amount of the components introduced onto the catalyst support and on the type of the support. It has been found that the surface area of the support has no significant effect on the type of species in the coke deposit. The analysis of the FT-IR spectra has shown the presence of different species on the surface of the catalysts, including carboxyl groups, pseudo-graphite (polyaromatic) structures, polyphenylene groups, acetyl groups, carbonyl groups of acetone and formate type, enol species.

Keywords: FT-IR, coke deposit, Pt-Sn catalysts, Al_2O_3, SiO_2, SiO_2-Al_2O_3.

INTRODUCTION

Bimetallic catalysts reveal high activity and selectivity in such reactions as reforming, hydrogenolysis and **removal** of pollutants from motor vehicle gas exhaust. The catalysts usually contain platinum at a low concentration and tin. A substantial limitation of the catalytic processes is deactivation related to the appearance of carbon deposit known as coke.

The amount and type of coke depend on many factors, including the conditions of the catalytic process, the method of the catalyst preparation, chemical and phase composition of the catalyst and the type of the support. Our earlier study has shown that the coke deposit formed on the Pt/Al_2O_3 catalyst contained compounds with hydroxyl group[1]. The results reported in[2] have proved that the chemical composition of the deposit depends on the type of the zeolite support. The FT-IR study has shown that the carbonaceous deposit formed over $\gamma - Al_2O_3$ has carboxylate character, while that formed over the HX zeolite is a mixture of the above and conventional (aromatic) coke. The deposit formed over the HZSM-S zeolite is composed mainly of conventional coke, however, the presence of species containing acetyl groups is also detected. **No carbonaceous deposit over zeolite type A was formed**, probably because of the lack of appropriately strong adsorption centres and small pores.

In[3] concerned with Pt/Al_2O_3 catalysts containing Cr(VI), Mo(VI) or W(VI) ions in the amount of 2 or 20 wt.% it has been found that in low-loaded Pt-Me/Al_2O_3 catalysts (Me = Cr, Mo, W) the coke deposit has a more carboxylate character, whereas for the high-loaded catalysts the coke is more aromatic. It has also been established[4] that the coke deposit, obtained from the decomposition of chemisorbed ethylene and **butene-1** used as precursors on Al_2O_3, is of typical carboxylic character. At elevated temperatures a deposit of aromatic character is also formed. The presence of Cl^- ions introduced from HCl or NH_4Cl inhibits the formation of the coke deposit of the aromatic character. For the samples with 2-methylpropane deposited on Al_2O_3 the coke obtained has both carboxylic and aromatic character. The carbonaceous deposit formed on samples with **butene-1** introduced Pt/Al_2O_3 catalysts has a more complex nature. **When increasing the amount of platinum** the carboxylic character of the coke deposit decreases, which indicates that it is related to the presence of Al_2O_3. The study reported in this paper has been undertaken to characterise the coke deposit on Pt catalysts containing a different amount of Sn supported on Al_2O_3 of low and large surface area, on SiO_2 or on amorphous aluminosilicate.

EXPERIMENTAL

The coke deposit on the support of Al_2O_3-Degussa C (100 m^2/g), Al_2O_3-Norton (260 m^2/g), SiO_2 -Cab-O-Sil (289 m^2/g) and SiO_2-Al_2O_3 (296m^2/g) as well as on the catalysts containing Pt and Sn was produced by thermal decomposition of ethylene. The samples were studied by the FT-IR method **using transmission technique** on the Analect FX-6160 spectrometer of a resolution of 2 cm^{-1}. The samples were pressed into pellets under a low pressure and the area of the pellet was close to 2,6 cm^2, while its mass was about 50 mg. The samples were placed in a high-vacuum glass cell with NaCl windows. At first the sample was degassed at 350ºC in the vacuum of 10^{-5} Torr for 1 h, then it was reduced with hydrogen (300 Torr) for 1 h at 350ºC. At the next stage hydrogen was evacuated and ethylene was introduced (10 Torr, 350ºC, 4 hours). After the evacuation of the non-decomposed ethylene and cooling the cell to room temperature the IR spectra were recorded (200 scans).

RESULTS AND DISCUSSION

Fig. 1 presents the FT-IR spectrum of ethylene in the **gas phase** prior to its adsorption on the support. The spectrum shows three characteristic bands disappearing after thermal treatment and the formation of the coke deposit. Fig. 2 presents the spectrum of this deposit on the surface of Al_2O_3-Degussa C and on the samples containing different amounts of platinum (0.3 do 9.0 wt. %). The spectra show two distinct bands with the maxima at about 1588 and 1468 cm^{-1}. The first of them in the spectra of the samples containing 0.3 and 3.0 wt. % of platinum is composed of two sub-bands of similar intensity. With increasing the concentration of platinum the band at the higher wave number gradually disappears. The strong bands
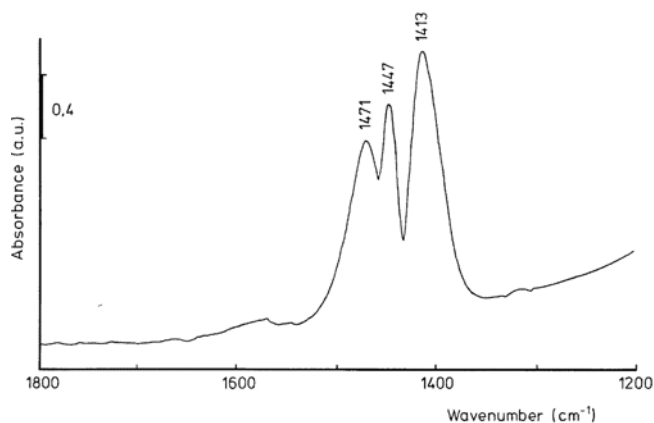
Figure 1. The FT-IR spectrum of gaseous ethylene on Al_2O_3 – Degussa C before desorption

at 1468 cm^{-1} and 1588 cm^{-1} are assigned to the symmetric and asymmetric stretching vibrations of the C-O bond in the carboxyl groups[5]. The band at 1591 cm^{-1} is assigned to the formation of pseudo-graphite structures[6] or polyaromatic structures[7]. The weak bands at 1378 – 1400 cm^{-1} and 1420 – 1432 cm^{-1} are attributed to the deformation vibrations of the C-H bonds in the $-CH_3$ group and to the bending vibrations of the C-H bond, respectively[8]. The spectrum of the sample containing 9.0 wt. % Pt shows only two strong but broadened bands with the maxima at 1572 and 1470 cm^{-1} and weak band at 1380 cm^{-1}. The FT-IR spectrum of the sample with 3.0 wt. % tin and 3.0wt.% platinum supported on Al_2O_3 – Degussa C (Fig. 3) reveals a broad bands with the maxima at 1577 and 1468 cm^{-1}, whose positions and intensities are similar to those in Fig. 2. As it follows from the FT-IR study of the effect of the surface area of the support on the type of the carbonaceous groups formed, the bands recorded for Al_2O_3-Norton (260 m^2/g) (Fig. 4) are similar as those in the spectrum of Al_2O_3-Degussa C (100 m^2/g) (Fig. 3).

The increase of the amount of the components introduced on Al_2O_3-Norton from 0.3 to 0.6 wt % brings about a great increase in the intensity of the bands at 1590, 1572 and 1644 cm^{-1}, while a further increase of the concentration of the active components has insignificant effect on the intensity and positions of these bands. Therefore, it can be concluded that an increase of the surface area of γ-Al_2O_3 from 100 to 250 m^2/g has no significant effect on the type of the coke deposit formed or on its amount, assuming that the area under the band is proportional to the amount of the coke deposited.

The character of the FT-IR spectrum of the carbonaceous deposit formed on silica is completely different. It shows weak but detectable bands at 1658, 1623, 1605 and 1546 cm^{-1} (Fig. 5a). The first of them is assigned to the twisting vibration of the C=C bond[8], the second to the stretching vibration of C=O in acetyl groups[9]. The band at 1605 cm^{-1} may characterise the pseudo – graphite structures[6], whereas after Regalbuto and Wolf[10] the last band characterises the polyphenylene structures.

The spectra of the samples obtained by simultaneous impregnation of silica with platinum and tin ions are very complex (Fig. 5), made of a number of weak bands whose interpretation at the present state of knowledge is very difficult. For this reason we will concentrate on those few already described in literature. All the spectra (5b – e) show the bands characteristic of the carbonaceous groups
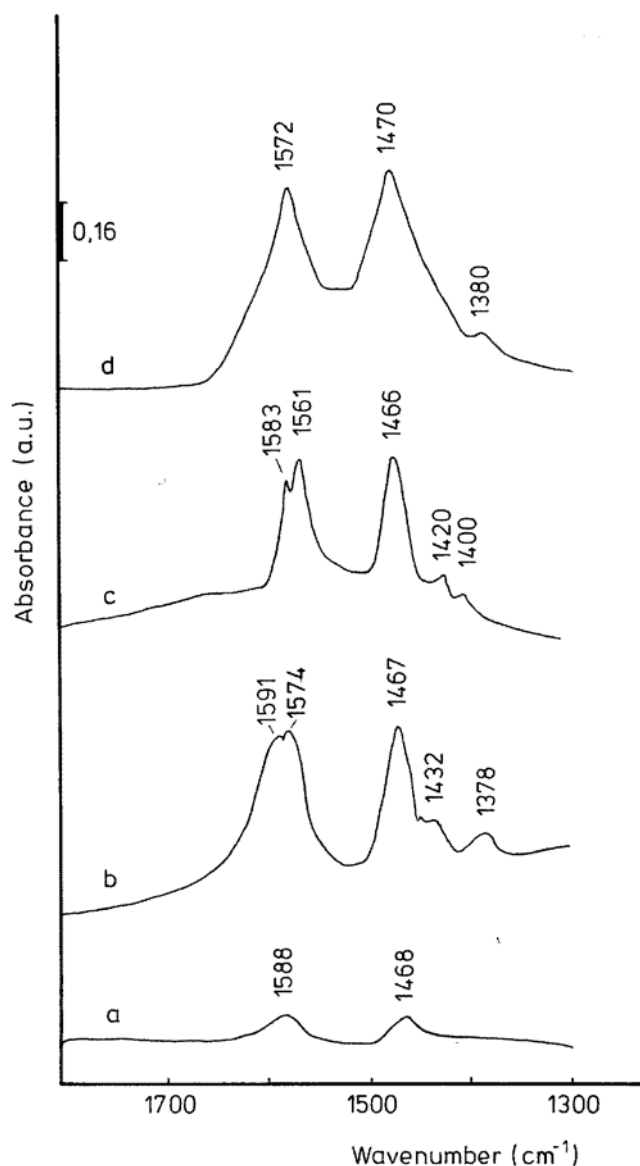

Figure 2. The FT-IR spectra of coke deposit on Al_2O_3 – Degussa C – **a**, 0.3 wt.% Pt/Al_2O_3 – **b**, 3.0 wt.% Pt/Al_2O_3 – **c** and 9.0 wt% Pt/Al_2O_3 – **d**

identified as occurring on pure silica and a number of new bands above the wave number 1700 cm^{-1} and below 1520 cm^{-1}.

The band at about 1720 cm^{-1} is typical of the carbonyl groups and the band at 1695 cm^{-1} is assigned to the stretching vibration in the C=C group. On the basis of the interpretation of the bands given by Miyata et al.[11] and Escribano et al.,[12] the bands appearing in the range 1640 – 1634 cm^{-1} can be assigned to the enol species, and the bands from the ranges 1475 – 1462 and 1590 – 1586 cm^{-1} to acetone and formate groups.

Similar very complex spectra of coke deposits have been recorded for the Pt-Sn catalysts supported on aluminosilicate. Fig. 6 presents the spectra of the samples obtained by a simultaneous impregnation of aluminosilicate with Pt and Sn ions. The similarity of the spectra indicates that the character of the carbonaceous deposit on the surface of Pt-Sn/SMR-5 is similar to that forming on the surface of PtSn/SiO_2.
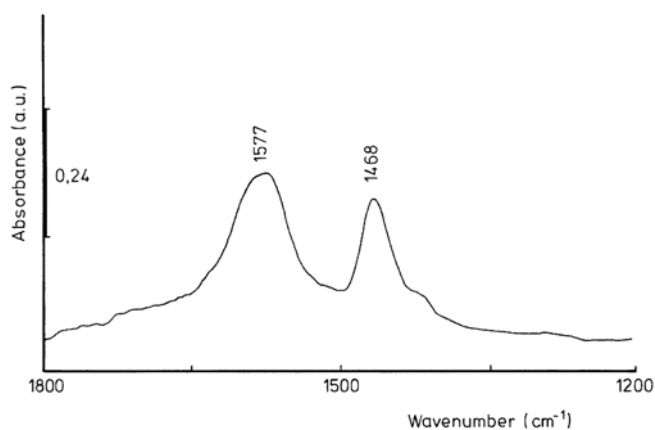
Figure 3. The FT-IR spectrum of coke deposit on 3.0 wt.% Pt – 3.0 wt.% Sn/Al_2O_3 – Degussa C

CONCLUSIONS

The results discussed above have shown that the Pt-Sn catalysts studied of different composition and on different support interact with ethylene in a different way, which leads to the formation of carbonaceous deposits of different chemical composition.

– On the samples Pt/Al_2O_3-Degussa C the coke deposit contains carboxyl groups, -CH_3 groups and the pseudo-graphite or polyaromatic structures.

– The introduction of tin into the samples Pt/Al_2O_3-Degussa C does not cause significant changes in the IR spectrum.

– The character of the coke deposit on the samples PtSn supported on Al_2O_3-Norton of the surface area about 2.5 times greater than that of Al_2O_3-Degussa C is the same as that of the coke deposit on the samples PtSn/Al_2O_3-Degussa C.

– The nature of the coke deposit formed on silica is more complex than that of the coke deposit appearing on aluminium oxides and it contains pseudo-graphite, polyphenylene and acetyl groups.

– The coke deposit formed on the samples PtSn supported on SiO_2 has a very complex character as indicated by the FTI-IR spectrum. Apart from the above mentioned types of the groups, this deposit contains acetone and formate type carbonyl groups and enol species.

– The coke deposit formed on the samples of PtSn supported on SiO_2-Al_2O_3 has a complex composition similar to that of the deposit appearing on PtSn/SiO_2.

As we can see the formation of different coke deposits depends on the composition of the surface species of the examined catalysts.

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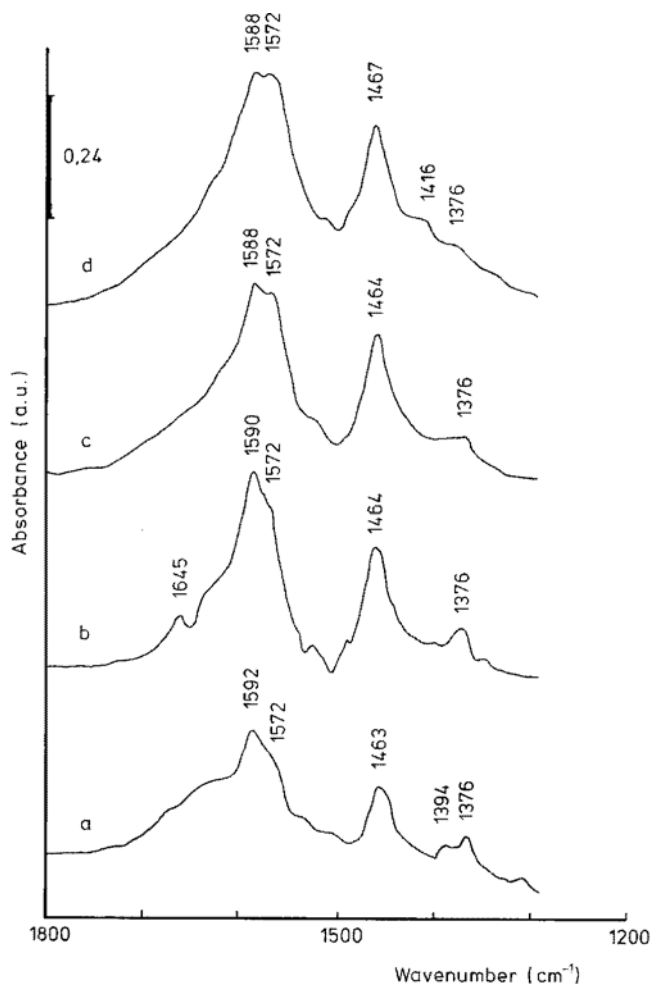(6) Blackmond J. D. G., Goodwin J. G. Jr., Lester J. E.: J. Catal., **1982**, 78, 34.

Figure 4. The FT-IR spectra of coke deposit on Pt – Sn/Al_2O_3 Norton: 0.3 wt% Pt – 0.3 wt% Sn – **a**, 0.6 wt.% Pt – 0.6 wt.% Sn – **b**, 1.0 wt.% Pt – 1.0 wt.% Sn – **c**, 3.0 wt.% Pt – 3.0 wt.% Sn – **d**

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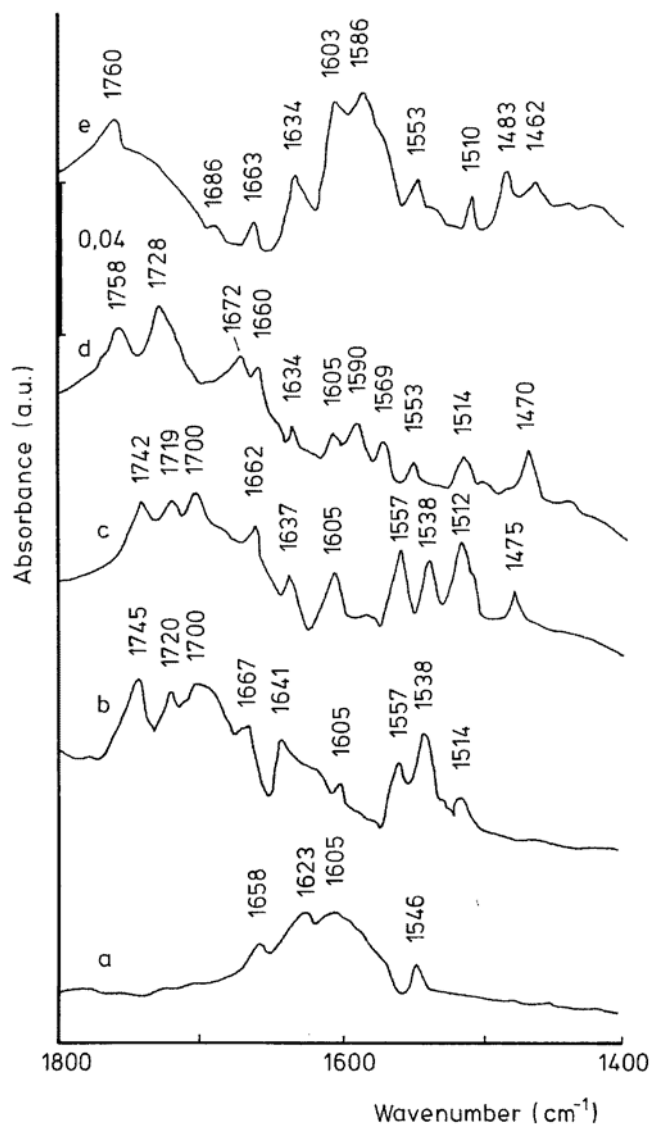**Figure 5.** The FT-IR spectra of coke deposit on SiO$_2$ – **a**, and Pt – Sn/SiO$_2$: 0.3 wt.% Pt – 0.3 wt.% Sn – **b**, 0.6 wt.% Pt – 0.6 wt.% Sn – **c**, 1.0 wt.% Pt – 1.0 wt.% Sn – **d**, 3.0 wt.% Pt – 3.0 wt.% Sn – **e**
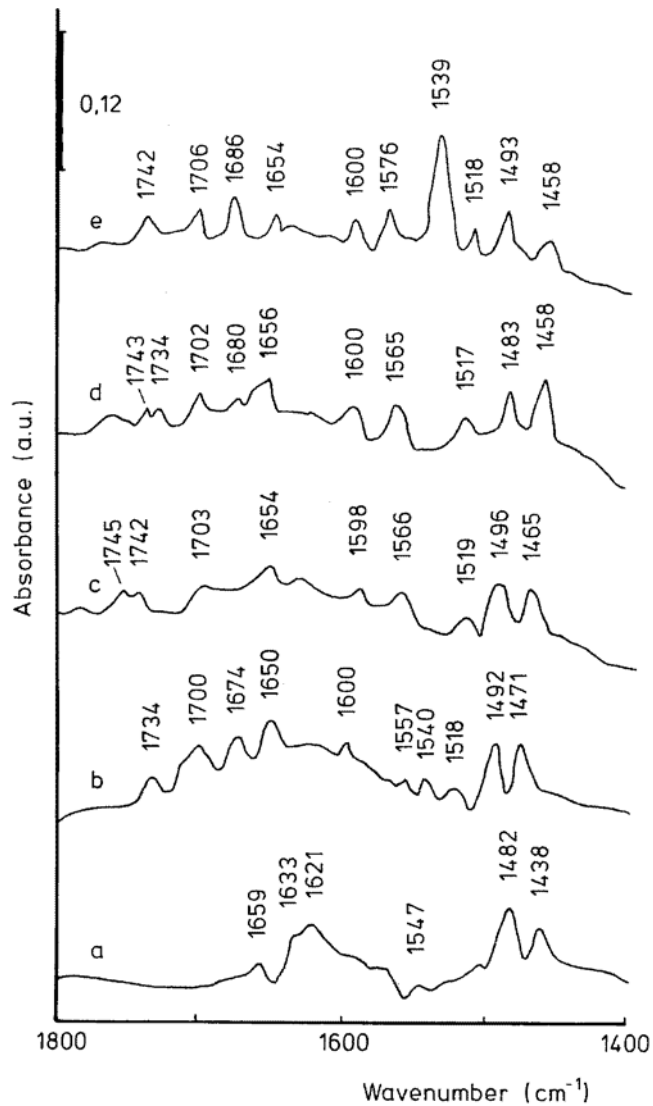
Figure 6. The FT-IR spectra of coke deposit on SiO$_2$ – Al$_2$O$_3$ – **a**, and Pt – Sn/SiO$_2$ – Al$_2$O$_3$: 0.3 wt.% Pt – 0.3 wt.% Sn – **b**, 0.6 wt.% Pt – 0.6 wt.% Sn – **c**, 1.0 wt.% Pt – 1.0 wt.% Sn – **d**, 3.0 wt.% Pt – 3.0 wt.% Sn – **e**