Chemisorptive Properties of Platinum Supported on Zeolite Y Studied by Infrared Emission Spectroscopy

In a recent review article, Bates (1) pointed out that the infrared emission spectroscopy technique (IRES) has provided valuable supplementary information to absorption and reflection studies. IRES has been extensively used for the study of molten salts. Surprisingly, since the pioneer work of Eischens and Pliskin (2), only a small number of publications have been devoted to the investigation of catalytic systems by this technique (3–10).

In a previous paper (11), by using IRES, we have followed the modifications of a V_2O_5 catalyst during its interaction with propene in the temperature range of catalytic reaction. This study was mainly concerned with the changes in the system of vanadium–oxygen bonds and not with the identification of adsorbed species. In the present note, we intend to show the application of IRES to the characterization of species present on a catalytic surface. We have chosen intentionally a system not completely opaque to the infrared radiation in order to compare the results so obtained with those deduced from conventional transmission measurements. By this latter technique adsorbed species are not easily detected in the range of strong absorption bands of the support. Thus, it appears interesting to verify if IRES is able to give additional data for this purpose.

Platinum supported on Y zeolite is the subject of the present study. The chemisorption properties of the metal were examined by adsorption of a test molecule (carbon monoxide) whereas the acidic properties of the support were investigated by pyridine adsorption. The sodium ions of the NaY zeolite (Linde SK 40) were exchanged by $[Pt(NH_3)_4]^{2+}$ ions. The solid was treated at 350°C under oxygen, then under hydrogen according to a procedure already published (12) in order to obtain agglomerates of platinum of ca. 10-Å diameter encaged in the large cavities of the Y zeolite. The reduced sample was then introduced into the cell used for IRES measurements. The cell is described elsewhere (11). As previously stated (11), the effective sample thickness is one of the most critical parameters in IRES. The sample thickness adopted in the present study corresponds to a weight of Pt/NaY sample close to 0.1 mg/cm². The zeolite-supported platinum was reduced again at 200°C under a 100 Torr hydrogen pressure for 1 h and evacuated at the same temperature. After such a treatment, adsorption measurements have shown that the platinum surface is free of adsorbed oxygen (13).

Infrared emission spectra were recorded at 110°C by using a Fourier transform spectrometer (Digilab F.T.S. 14). Every spectrum was obtained within 1 h by setting the resolution at 8 cm⁻¹ and the number of scans at 1000.

Figure 1 shows the single-beam emission spectrum of the Pt/NaY sample recorded at 110°C (spectrum (a)) and the single-
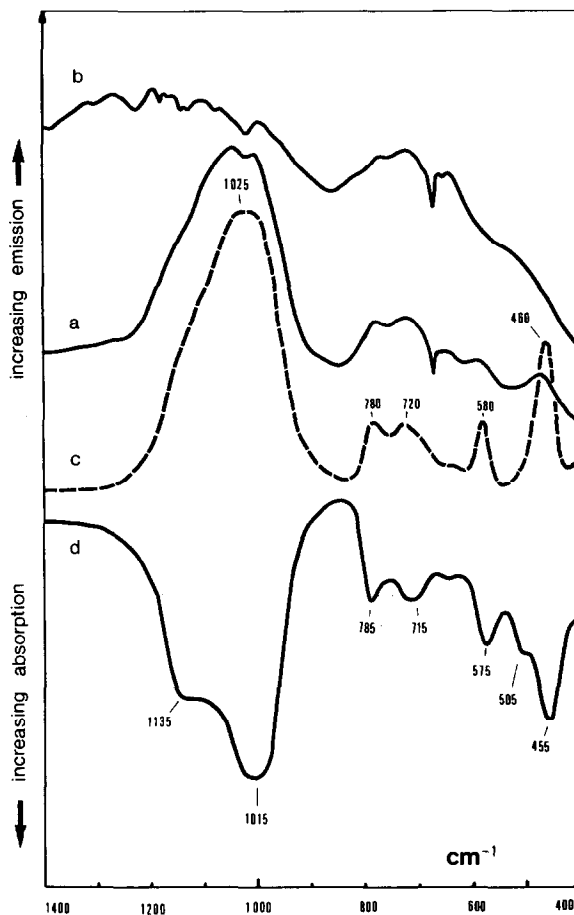
FIG. 1. Infrared emission spectrum of the reduced Pt/NaY sample: (a) Single-beam emission spectrum of the Pt/NaY sample recorded at 110°C under 20 Torr hydrogen pressure; (b) single-beam emission spectrum of the reference black body recorded at 110°C under 20 Torr helium pressure; (c) ratio of spectrum (a) against spectrum (b); (d) transmission spectrum of the Pt/NaY sample in KBr (1 mg/g).

beam emission spectrum of the reference black body recorded at the same temperature under helium (spectrum (b)). The ratio of (a) against (b) leads to the removal of specific absorption or emissions of the furnace and the beam splitter and gives spectrum (c) which is the emission spectrum of the Pt/NaY sample. The transmission spectrum of the Pt/NaY catalyst obtained by the KBr pellet method is also plotted in Fig. 1 (spectrum (d)). Spectra (c) and (d) are very similar; on both appear various bands previously assigned by Flanigen et al. to silicon (or aluminum)–oxygen vibrations (14).

Deposits used in IRES are thin so that the emission spectrum (Fig. 1c) is closely related to the absorption spectrum (Fig. 1d). Spectrum (d) recorded for a weight of 1 mg of Pt/NaY catalyst on the sample beam. Transmission measurements have also been performed by spraying the Pt/NaY sample on an infrared transparent window in order to reach the same effective sample thickness as for emission spectra. No useful spectra can be recorded. Optical microscope observations have shown that the particles of zeolite occupy a very small fraction of the window area: for such small amounts of catalyst, it

seems impossible to obtain a continuous film and consequently the major part of the transmitted light goes through the free space between the particles.

Pyridine Adsorption

Under 10 Torr pressure, pyridine was allowed to react at 110°C with the reduced Pt/NaY sample. Pyridine in excess was desorbed at 110°C and the emission spectrum was recorded at the same temperature under 10 Torr of helium. The ratio of this spectrum with the emission background of the Pt/NaY sample (Fig. 1, spectrum (a)) is presented in Fig. 2. The range 1700–1300 cm^{-1} is accessible to classical transmission methods and according to the assignments usually proposed the presence of the 1540 cm^{-1} band associated with the 1630 cm^{-1} one shows the formation of pyridinium ions (15). The other weaker bands observed in IRES can be attributed by comparison with transmission measurements to pyridine coordinated to Na$^+$ ions (1595 and 1440 cm^{-1}) (16). The spectral range 900–500 cm^{-1} shows very strong bands due to Si (or Al)–O vibrations. This region has never been

investigated in conventional transmission studies of the acidity of the zeolite. The infrared spectrum of C$_5$H$_5$NH$^+$Cl$^-$ in the solid state presents two strong bands at 755 and 685 cm^{-1} attributed to γ CH vibrations (17). The presence of the 780 and 690 cm^{-1} bands in the emission spectrum of adsorbed pyridine confirms the existence of pyridinium ions at the surface of the zeolite. The formation of pyridinium ions involves the existence of acidic OH groups bonded to the lattice. Since the initial NaY samples do not possess such species, these latter must be generated by the hydrogen reduction of Pt^{2+} ions according to the scheme already proposed for palladium-loaded Y zeolites (18).

$$Pt^{2+} + H_2 \rightarrow Pt(O) + 2H^+ \text{ (bonded to the lattice).}$$

Carbon Monoxide Adsorption

Carbon monoxide was contacted at 110°C with the reduced Pt/NaY sample under 10 or 120 Torr pressure. The emission spectrum was recorded at the same temperature and set in a ratio against the spectrum of the initial Pt/NaY catalyst.
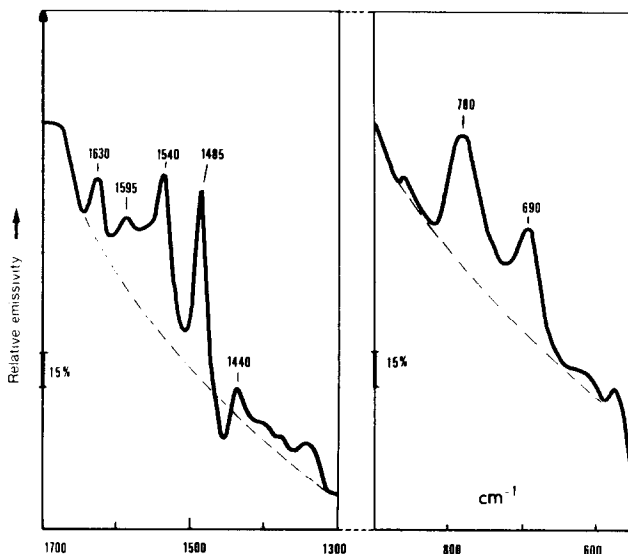

FIG. 2. Infrared emission spectrum of the pyridine irreversibly adsorbed at 110°C on the reduced Pt/NaY sample.
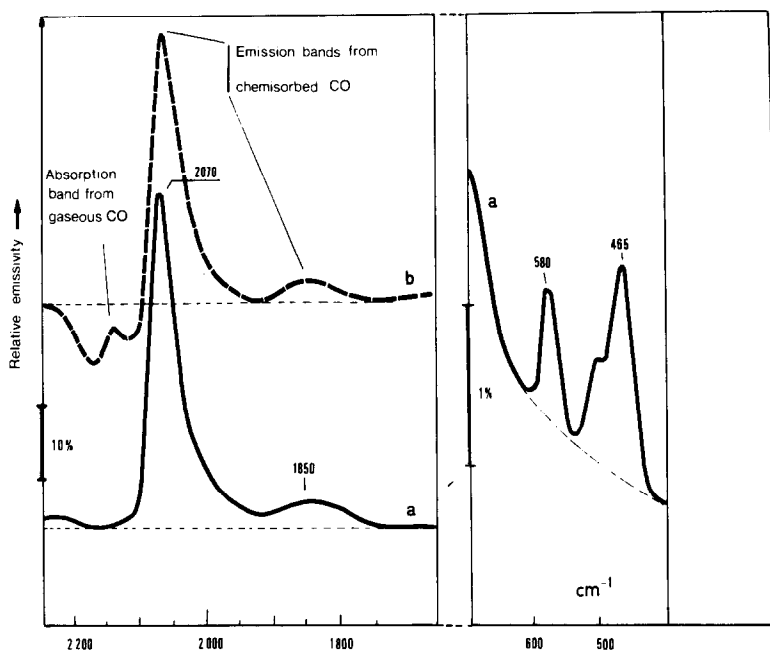
FIG. 3. Infrared emission spectra of carbon monoxide adsorbed on the Pt/NaY sample under a pressure of 10 Torr (spectrum (a)) or 120 Torr (spectrum (b)).

Figure 3 shows the spectrum of carbon monoxide adsorbed on the Pt/NaY sample. For the 10 Torr CO pressure experiments (spectrum (a)), two bands (2070 and 1850 cm^{-1}) are detected in the vicinity of 2000 cm^{-1}, and both correspond to energy emitted from the sample. These two bands have already been observed at the same frequencies and with similar intensity ratio for platinum supported on Y zeolite (19) in transmission measurements. They have been attributed to νCO vibrations of carbon monoxide adsorbed on platinum in the linear (2070 cm^{-1}) and in the bridged form (1850 cm^{-1}) (20). Spectrum (b) was recorded under 120 Torr CO pressure. The same features are observed for the emission bands of CO adsorbed on platinum. In addition, the spectrum of gaseous CO was detected, but this molecule produces bands in absorption; i.e., gaseous carbon monoxide absorbs energy emitted from the Pt/NaY sample. Consequently, it can be concluded *that only adsorbed species* are able to give an emission spectrum. As in the case of pyridine adsorption, emission

and transmission measurements give similar information in the available spectral range.

Because of the strong absorption bands due to the lattice, the metal–carbon vibrations have never been investigated in classical transmission measurements of CO adsorbed on zeolite-supported metals. In our IRES measurements of CO adsorbed on Pt/NaY, two bands at 580 and 465 cm^{-1} have been detected. In a study of CO adsorption on Pt films (20), very weak bands at 570 and 477 cm^{-1} have been observed and, respectively, assigned to a bending mode of chemisorbed CO and to the stretching vibration of the Pt–C bond. Blyholder and Sheets (21), by depositing platinum particles in a hydrocarbon oil film, have found a band at 480 cm^{-1} after CO adsorption. They attributed this absorption to a Pt–C stretching mode and their interpretation was supported by the frequency shift of the 480 cm^{-1} band when $C^{18}O$ was used instead of $C^{16}O$ (21).

The adsorption of CO on Pt(111) surfaces has been studied by electron-energy-loss spectroscopy (EELS). It has been

found (22, 23) that CO is molecularly adsorbed on two adsorption sites, namely, the on-top and the bridge sites. At low coverages, two loss peaks at 476 and 2085 cm^{-1} are present. These peaks saturate with increasing coverage whereas two new peaks at 380 and 1855 cm^{-1} develop. The peaks at 2085 and 476 cm^{-1} were attributed (22, 23), respectively, to the C–O stretching vibration and to the Pt–C stretching vibration of carbon monoxide linearly adsorbed on platinum atoms. The 1855 and 380 cm^{-1} bands are due to the corresponding vibrations of CO bonded between two platinum atoms. It is worth noting that by adsorption on C$_2$H$_4$ on Pt (111) surfaces, a band at 467 cm^{-1} has been detected by EELS and also attributed to a ν Pt–C vibration (24).

More ambiguous is the assignment of the 580 cm^{-1} band observed in our IRES measurements. The 580 cm^{-1} band cannot be a ν Pt–C band corresponding to bridged carbon monoxide since the EELS measurement has detected such a vibration at 380 cm^{-1}, unfortunately not available in the spectral range of our spectrophotometer (4000–400 cm^{-1}). Garland et al. (20) have attributed a 560 cm^{-1} band to a δ Pt–CO mode, whereas Blyholder and Sheets (21) have postulated a partial oxidation of the platinum (or an incomplete reduction) with the formation of Pt–O species responsible for the 560 cm^{-1} band; indeed, they found such a band after addition of oxygen to the platinum surface covered by CO. Controversially, Blyholder and Tanaka (25), during the interaction of CO and Fe particles at temperatures down to 43 K, observed a 570 cm^{-1} band and they attributed it to a δ Fe–CO vibration.

According the conclusions proposed by Blyholder and Sheets (21), the 580 cm^{-1} band observed by IRES would be a ν Pt–O vibration. This adsorbed oxygen could arise either from an incomplete reduction of the Pt/NaY sample or from a side reaction between the platinum particles

and the carbon monoxide. The first hypothesis must be ruled out since volumetric measurements have shown that the platinum was completely reduced under our experimental conditions, of activation (13). The second hypothesis might explain the formation of Pt–O bonds if we assume a limited dissociation of CO during the recording of the emission spectrum at 100°C under CO. Such dissociations, at moderate temperature, have been already mentioned in the cases of Ni/SiO$_2$ (26) and Rh/NaY samples (27).

Nevertheless, the 580 cm^{-1} band might be a δ Pt–CO vibration if we consider the "metal surface selection rule" proposed by Pearce and Sheppard (28). For CO groups bonded normal to the platinum surface, this δ Pt–CO vibration would be expected to give a dipole change parallel to the surface (28) and, therefore, this vibration would absorb or emit weakly the infrared radiation. This observation could explain why Ibach et al. (22, 23) do not detect the δ Pt–CO vibration for CO linearly adsorbed on the Pt (111) planes whereas this vibration was found between 505 and 540 cm^{-1} in organometallic complexes such as cis-[PtX$_2$COPBu$_3$], where X is a halogen (29). For the small particles involved in the Pt/NaY catalyst (mean diameter ca. 10 Å), it is less sure that the "metal surface selection rule" remains valid. In such a case, a δ Pt–CO vibration might be active in infrared and might produce a band at 580 cm^{-1}.

In conclusion, our IRES results obtained on a supported metal (Pt/NaY) are in rather good agreement with the previous attributions; i.e., the 2070 cm^{-1} band is due to the ν CO vibration of CO adsorbed in the linear form (Pt–CO) whereas the 1850 cm^{-1} band is assigned to a ν CO vibration of CO bonded between two platinum atoms (Pt$_2$–CO). The 465 cm^{-1} band is attributed to a ν Pt–C vibration associated with CO linearly adsorbed.

Two attributions can be proposed for

the 580 cm^{-1} band: (i) a δ Pt–CO vibration mode allowed by the small metal particle size, (ii) a ν Pt–O vibration, adsorbed oxygen being formed by the dissociation of the carbon monoxide molecule.

In the spectral range where the samples are transparent to infrared radiation, the information obtained from emission and transmission methods is similar. In the range of lattice vibrations of the support, the use of very thin samples, which is not possible by transmission techniques, allows one to obtain additional data which reinforce the previous assignments. Moreover, infrared emission spectroscopy allows the study of real catalysts in the conditions of the catalytic reaction, i.e., in the presence of the reactants and at the temperature of the reaction (high-temperature use).

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