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FT-IR AND TPD STUDIES ON SUPPORT-METAL AND PROMOTER-METAL INTERACTION. Pt AND Pd CATALYSTS

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New CO absorption bands were observed on promoted Pd and Pt catalysts and were attributed to C and O coordination of CO. The possibility of selective coverage of some metal faces by the promoter is discussed. TPD and FT-IR experiments show that the promoters stabilize an acetyl species upon adsorption of acetaldehyde.

1. Introduction

It is well known that the selectivity and activity of transition and noble metal catalysts can be very dependant on the nature of the support, the promoter or additives. Thus, in $CO + H_2$ reactions, hydrocarbons, methanol or C_2 oxygenates can be produced selectivity and in high yields [1,2]. Palladium was considered for a long time as giving essentially methane. But, after the discovery of Poutsma et al. [3] in 1978 that high selectivities in methanol could be achieved on Pd catalysts, it appeared rapidly that many oxide supports or promoters lead to a reasonable activity in almost pure methanol even at atmospheric pressure [4–7]. Kikuzono et al. [8,9] found that palladium catalysts prepared from the precursor complexes of the type M_2PdCl_4 ($M =$ alkali metal) produce methanol selectively even below atmospheric pressure and that the activity for methanol formation depends sharply on the alkali metal cations. Similar methanol selectivities could be obtained with platinum containing catalysts.

Despite numerous works, the problem of the nature of the support effect remains to be solved. Several models have been proposed to account for the influence of promoters and supports.

a) The promoters or supports have an influence on the particle size. However Underwood and Bell [10] have studied in detail the influence of particle size and concluded that it cannot explain entirely the changes in activity and selectivity of a Rh containing catalyst.

b) The promoters stabilize the metal in a higher oxidation state. Van der Lee and Ponec [11] could establish a correlation between extractable rhodium (by acetylacetone e.g. oxidized rhodium) and methanol synthesis. But no such correlation could be found for ethanol formation. On palladium catalysts Driessen et al. [7] have shown the same very nice dependence of the methanol activity versus the palladium on surface concentration.

c) The promoters influence the adsorption state of carbon monoxide
(i) by an enhanced backbonding through the metal
(ii) by an electrostatic effect
(iii) by short range chemical interactions.

Several works have recently appeared showing the presence of a low frequency CO absorption band on rhodium containing catalysts [12–18]. It seemed us interesting to investigate CO adsorption on different metals supports and/or promoters. We want here to report the results obtained on platinum and palladium containing catalysts. Furthermore, acetaldehyde adsorption was studied, to control the possibility of stabilization of presumed reaction intermediates.

2. Experimental

2.1. CATALYST PREPARATION

SiO_2 (Mallinckrodt 100 mesh supplied by Roth) or CeO_2 were impregnated with $Pt(NH_3)_4\ (NO_3)_2$ or $Na_2Pt(OH)_6$ and dried under vacuum. Palladium containing catalysts were prepared from $PdCl_2$ as in ref. [19]. The necessary amount of Pt or Pd precursor was used to obtain 3 weight% metal loadings. Previous to their use the catalysts were calcined in air at 773 K during 6 hrs.

2.2. FT-IR EXPERIMENTS

Samples (15–20 mg) were pressed into 13 mm diameter disks under a pressure of 25 MPa. For chemisorption experiments, their activation was performed by heating at 575 K for 4 hours under 0.1 MPa of hydrogen. After 1 hour of reduction, the hydrogen was pumped off and the cell refilled with H_2. The chemisorption of CO was then achieved by admitting it at room temperature and under a pressure of 10^4 Pa on the evacuated disk. Acetaldehyde was introduced at room temperature on the reduced samples.

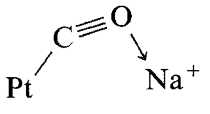
Spectra were recorded using a Nicolet 5DXC spectrometer. Those reported in the figures were subtracted from the reference one and eventually from that of CO or CH_3CHO gas.

2.3. TEMPERATURE PROGRAMMED DESORPTION

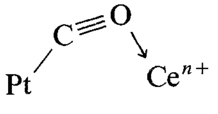
Catalysts samples were charged (500 mg) into a tubular glass reactor (1 cm O.D.) and reduced under hydrogen (2.2% H_2 in N_2, 2 $l \cdot h^{-1} \cdot g \cdot cat^{-1}$ from room temperature to 573 K for Pd, 673 K for Pt during 16 h. After cooling the reactor down to room temperature, the catalyst was exposed to a helium flow (10 $l \cdot h^{-1} \cdot g \cdot cat^{-1}$ for (4–5 h)) and then to acetaldehyde vapor (10 mm Hg). After flushing with He to remove all acetaldehyde from the gas phase, the temperature was raised up to 773 K (6 $K \cdot min^{-1}$) under a carrier flow of helium (4 $l \cdot h^{-1} \cdot g \cdot cat^{-1}$.). A Gow-Mac conductivity cell system allowed the detection of desorbed molecules from the catalytic surface. Desorption products were analyzed and identified by two on-line gas chromatograph fed by heating multi-position sampling valves. Acetaldehyde, acetone, ethanol ... were detected after separation on Porapak R (F.I.D.), carbon monoxide and dioxide on Chromosorb 102 (T.C.D.). Hydrogen, water and formaldehyde were not analyzed. The gases were carefully dried over silica gel and molecular sieve and traces of oxygen were removed by a deoxo-device.

3. Results and discussion

Fig. 1 shows the adsorption of CO on different platinum containing catalysts. For the Pt/SiO_2 catalysts three main bands are observed corresponding to linear (2079 cm^{-1}) and to bridge bonded CO on Pt(100) (1880 cm^{-1}) and Pt(111) (1855 cm^{-1}) faces. On the sodium containing catalyst a new absorption band appears at 1790 cm^{-1} whereas the band at 1880 cm^{-1} almost disappears and the band at 1855 cm^{-1} diminishes. The disappearance of the band at 1880 cm^{-1} suggests that sodium selectivity blocks the bridge bonded adsorption of CO on the Pt(100) face. Such a selective coverage of a particular face of the metal particles has already been observed by Rieck and Bell [20] for palladium on TiO_2. For Pt-Na/CeO_2, two low frequency bands are obtained at 1776 cm^{-1} and 1690 cm^{-1}, whereas on Pt/CeO_2 (not recorded here) only the band at 1690 cm^{-1} is present. These new low frequency absorption bands can be attributed to a C and O coordination of carbon monoxide as already discussed in ref. [17] for rhodium containing catalysts. Comparing with the results obtained in our laboratory [17] and by others [12–16,18], the following proposition can be made:



1790 cm^{-1} (Pt-Na/SiO_2)
1776 cm^{-1} (Pt-Na/CeO_2)



1690 cm^{-1} (Pt/CeO_2)
1690 cm^{-1} (Pt-Na/CeO_2)

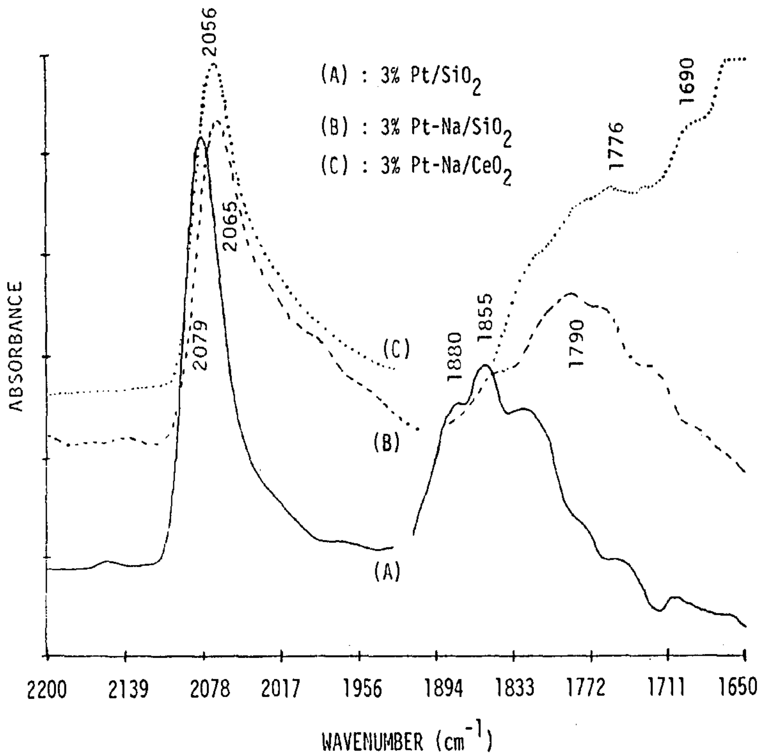


Fig. 1. CO adsorption on platinum containing catalysts.

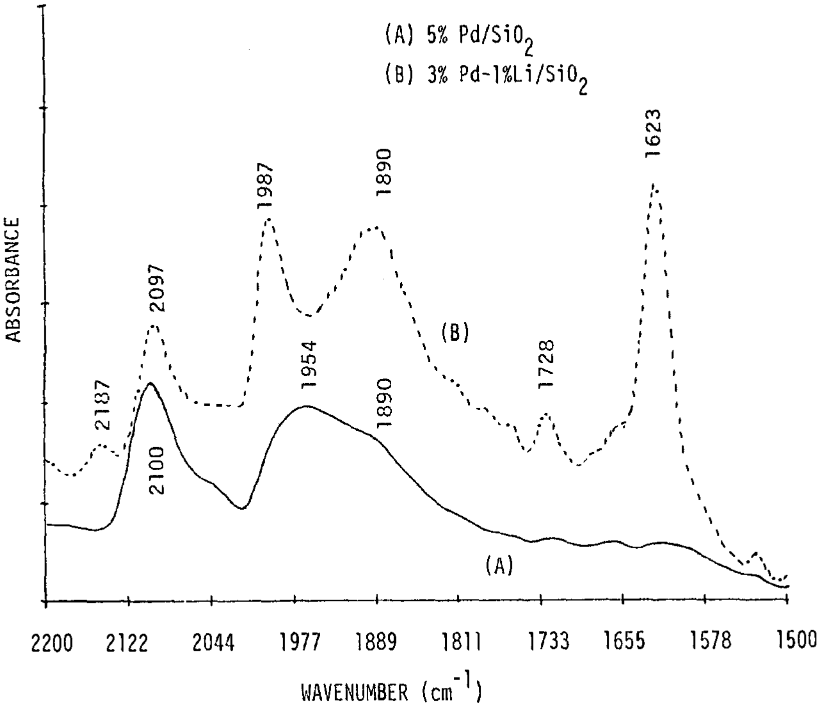


Fig. 2. CO adsorption on palladium containing catalysts.

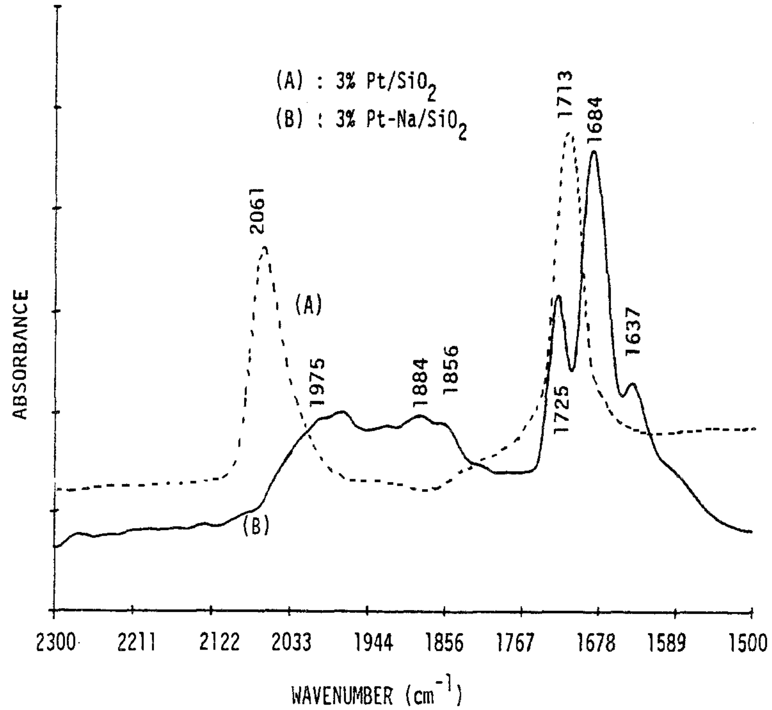
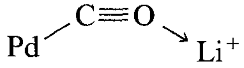


Fig. 3. CH_3CHO adsorption on platinum containing catalysts.

Fig. 2 represents the FT-IR spectra obtained on palladium containing catalysts. On Pd/SiO_2 three bands are observed at 2100 cm^{-1} (linear CO) 1954 cm^{-1} (bridge bonded CO on Pd(111)) and 1890 cm^{-1} (three centered bonded CO on Pd(111)) [21]. For Pd-Li/SiO_2, the band at 1954 cm^{-1} almost disappears and a band corresponding to CO adsorbed on the Pd (100) face appears at 1987 cm^{-1}. For its part the band at 1890 cm^{-1} is increased. Again these changes suggest a selective partial coverage of the Pd(111) face by Li$^+$ forcing the disappearance of the two centres bridged CO adsorption on the Pd(111) and the adsorption as three centre bridge bonded species on this same face.

Here arises the possibility of the selective blocking of special faces of the metal particles depending on the metal and on the promoter. This assumption must however be controlled and are under investigation in our laboratory. A new adsorption band at low frequency can here also be seen at 1728 cm^{-1} for Pd-Li/SiO_2 and could be attributed to a



$$\mathrm{Pd{-}C{\equiv}O{\rightarrow}Li^+}$$

species.

Upon adsorption of acetaldehyde on Pt/SiO_2 bands at 2061 cm^{-1} and 1837 cm^{-1} show that acetaldehyde is partly decomposed into CO at room temperature (fig. 3). However the mean band is situated at 1713 cm^{-1}. TPD experiments (fig. 4) show that ethanol and acetaldehyde are evolved from this catalyst at the same

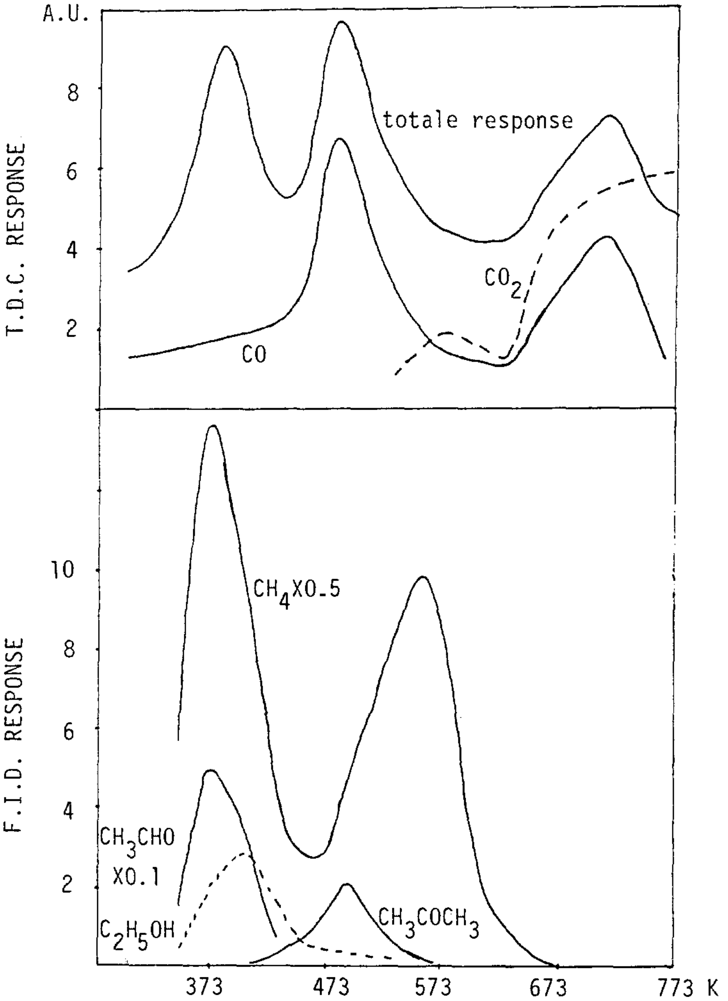


Fig. 4. TPD adsorption of CH_3CHO on 3% Pt/SiO_2.

temperature (373 K) as the band at 1713 cm^{-1} disappears. We therefore attribute this band to physisorbed acetaldehyde. On $Pt\text{-}Na/SiO_2$, the bands corresponding to adsorbed CO are observed at 1975 and 1884 cm^{-1} and correspond to bridge bonded CO. Besides a band at 1725 cm^{-1} corresponding to physisorbed acetaldehyde, a new band appears at 1684 cm^{-1}. This band increases upon heating to 333 K and begins to disappear at 393 K.

The TPD spectrum (fig. 5) after acetaldehyde adsorption on $Pt\text{-}Na/SiO_2$ shows that acetone and $C_3^=$ hydrocarbon are evolved at 393 K. This low temperature acetone desorption peak cannot be ascribed to the decomposition of a surface acetate which would occur at a much higher temperature and with codesorption of CO_2. We therefore propose that this peak could be due to the scavenging of an acetyl species (evidenced by the band at 1684 cm^{-1} in FT-IR)

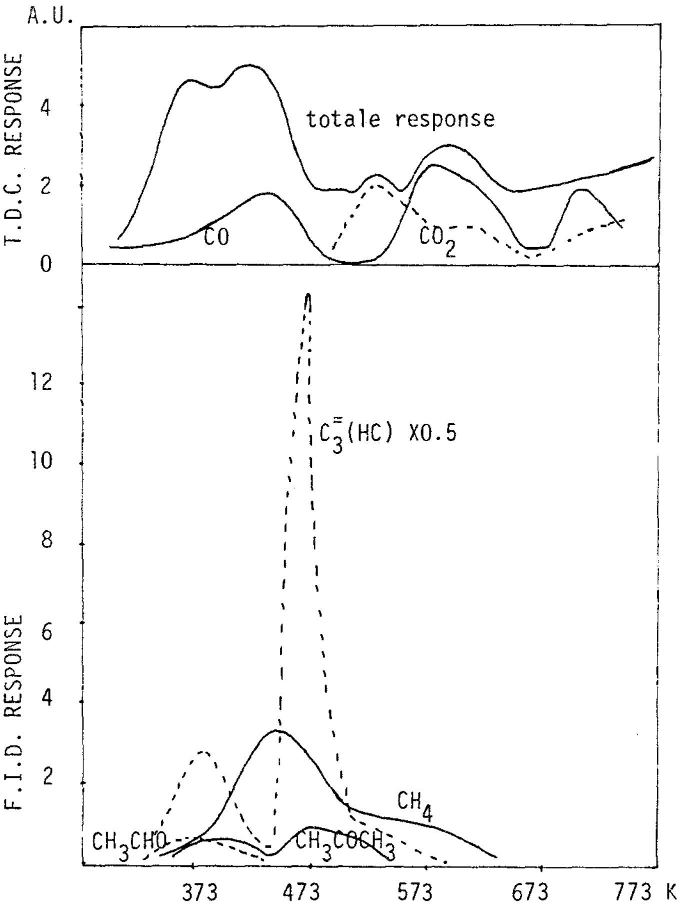


Fig. 5. TPD after adsorption of CH_3CHO on 3% Pt-Na/SiO_2.

by surface CH_x entities produced by acetaldehyde decomposition. This assumption is reinforced by the simultaneous desappearance of the 1684 cm^{-1} band (393 K) and the maximum of the desorption peak of acetone in the TPD spectrum. A higher temperature (473 K) acetone and $C_3^=$ hydrocarbon desorption peak corresponds to the decomposition of an acetate species.

4. Conclusion

Our experiments on Pd and Pt containing catalysts show that a new adsorption mode of CO exists also on metals and supports other than those shown for Rh containing catalysts. This C and O coordinated CO might be the key intermediate for CO + H_2 reactions on promoted catalysts. Furthermore it is shown that for Pt-Na/SiO_2 an acetyl intermediate is stabilized by the promoter. Investigations of these points are still underway in our laboratory to control the application of these findings to other catalytic systems.

References

[1] E.K. Poels and V. Ponec, Catalysis-Specialist Periodical Report vol. 6, p. 196, Royal Society of Chemistry, London, 1983.
[2] M. Ichikawa, Bull. Chem. Soc. Jpn. 51 (1978) 2268; ibid, 2273.
[3] M.L. Poutsma, L.F. Elek, D.A. Ibarbia, A.P. Risch and J.A. Rabo, J. Catal. 52 (1978) 157.
[4] M. Ichikawa, Shokubai 21 (1979) 253.
[5] Y.A. Ryndin, R.F. Hicks, A.T. Bell and Y.I. Yermakov, J. Catal. 70 (1981) 287.
[6] E.K. Poels, E.H. van Broekhoven, W.A.A. van Barneveld and V. Ponec, React. Kinet. Catal. Lett. 18 (1981) 221.
[7] J.M. Driessen, E.K. Poels, J.P. Hindermann and V. Ponec, J. Catal. 82 (1983) 26.
[8] Y. Kikuzono, S. Kagami, S. Naito, T. Onushi and K. Tamaru, Chem. Lett. (1981) 1249.
[9] Y. Kikuzono, S. Kagami, S. Naito, T. Onushi and K. Tamaru, J. Chem. Soc., Faraday. Disc. 72 (1981) 135.
[10] R.P. Underwood and A.T. Bell, Appl. Catal. 34 (1987) 289.
[11] G.D. Van der Lee and V. Ponec, Catal. Rev. Sci. Eng. 29 (1987) 189.
[12] W.M.H. Sachtler and M. Ichikawa, J. Phys. Chem. 90 (1986) 4752.
[13] T. Fukushima, H. Arakawa and M. Ichikawa, J. Phys. Chem. 89 (1988) 4440.
[14] R.P. Underwood and A.T. Bell, J. Catal. 111 (1988) 325.
[15] M.N. Bredhikin, Yu. Lokhov and V.L. Kuznetzov, Kinet. Katal. 28 (1987) 671.
[16] M.N. Bredhikin and Y. Lokhov, Kinet. Catal. 28 (1987) 671.
[17] J.C. Lavalley, J. Saussey, J. Lamotte, R. Breault, J.P. Hindermann and A. Kiennemann, J. Phys. Chem. 94 (1990) 5941.
[18] S.A. Stevenson, A. Lisitsyn and H. Knözinger, J. Phys. Chem. 94 (1990) 1576.
[19] C. Diagne, H. Idriss, J.P. Hindermann and A. Kiennemann, Appl. Catal. 51 (1989) 165.
[20] J.S. Rieck and A.T. Bell, J. Catal. 99 (1986) 262.
[21] A. Palazov, G. Kadinov, Ch. Bonev and D. Shopov, J. Catal. 74 (1982) 44.