

Temperature Programmed Desorption (TPD) of CO from Alkali Doped EUROPT-1 (6.3 % Pt/SiO₂)

MUSHTAQ AHMAD AND G.S. McDOUGALL
NPSL (PCSIR)16-H-9, Islamabad, Pakistan

(Received 12th August, 1995, revised 21st October, 1995)

Summary: The temperature programmed desorption technique was applied to investigate the changed characteristics of Pt/SiO₂ (EUROPT-1) upon alkali doping. CO desorption peak maxima shifted towards higher temperature as the concentration of alkali increased. This indicated strengthening of catalyst-CO bonding. These results are similar to those previously observed in the case of thermal desorption of CO from potassium covered Pt(III) single crystal.

Introduction

The interaction of gases such as hydrogen, nitrogen and carbon monoxide with metal surfaces have shown that process of adsorption, surface reaction and desorption, can be complex in nature [1,2]. Even when the catalyst is a single crystal and the experiments are performed in a well controlled environment applying ultra high vacuum conditions, the interpretation of the mechanism of desorption or adsorption are not clear [2,3].

Carbon monoxide desorption has been studied by TPD from several metals. Komer [4] *et al* first reported CO desorption from supported platinum. The authors observed a flat broad spectrum from 320-870 K. Carbon monoxide desorption has since been studied by several workers. Foger and Anderson [5] reported a broad CO desorption spectrum from room temperature to 850K, for CO desorption from Pt/SiO₂ and Pt/Al₂O₃. Way and Falconer [6] likewise reported CO desorption over a broad temperature range for a series of Pt/SiO₂ catalysts of varying dispersions. Herz *et al.* [7] carried out CO desorption from Pt/Al₂O₃ from 295-770 K, but most of their CO desorbed between 380-550 K, in contrast to the other's studies.

The interaction of alkali metal atoms with the transition metal surface has received considerable attention in the past. Interest in these systems originated from the significant enhancement observed in electron emission upon alkali adsorption [8]. An understanding of the alkali induced phenomenon on transition metal surfaces is also important due to their promoter action in heterogenous catalysis [9]. In particular,

potassium is used in two important catalytic reactions, the hydrogenation of carbon monoxide and synthesis of ammonia. In an attempt to understand the promoter action recent coadsorption experiments have shown that alkali metals change the chemisorptive characteristics of smaller reactive molecules on catalyst surfaces [8, 10,11].

In the present study the adsorption of carbon monoxide on the as-received and alkali doped Pt/SiO₂ (EUROPT-1) Catalyst having 0.25%, 0.50%, and 1.0% (Wt) KOH was investigated. It thus helped to know the effectiveness of the promoter and some fine details about the existence of various binding states.

Results and Discussion

Profiles of CO desorption from 'as-received' and alkali doped EUROPT-1 are shown in Figure 1. The CO desorption (TPD) was carried out over a temperature range 298-900 K. The minimum temperature at which the desorption began was 320K and the maximum temperature of desorption completion was observed to be 900K. This range of desorption temperature is significantly higher compared with the desorption of hydrogen [3].

The CO desorption profiles are broad peaks with shoulders at different temperatures of desorption indicating different unresolved binding states of Carbon monoxide.

The CO desorption from 'as-received' EUROPT-1 gave a broad desorption profile with a distinct shoulder at 480 K, indicating a low

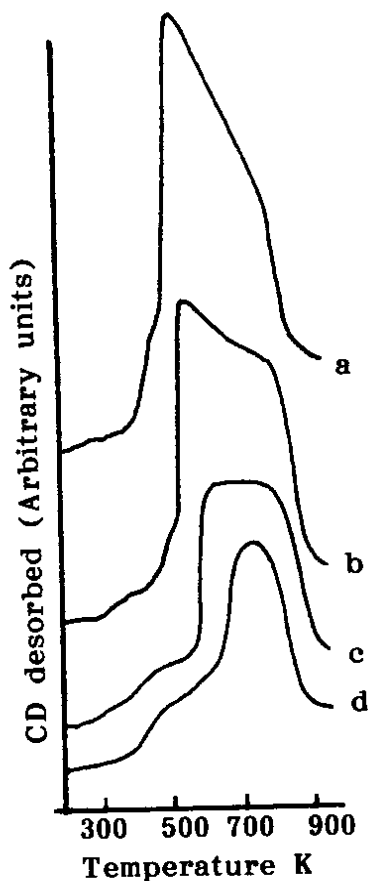


Fig. 1: Temperature programmed desorption of CO preadsorbed at room temperature by pulses: (a) as-received EUROPT-1; (b) 0.25% KOH (wt)/EUROPT-1; (c) 0.50% KOH (wt)/EUROPT-1; (d) 1.0% KOH (wt)/EUROPT-1.

- (a) as received EUROIT-1:-
 (b) 0.25% KOH (wt)/EUROIT-1:
 (c) 1.0% KOH (wt)/EUROIT-1

temperature CO binding state. Following this shoulder there is an immediate rise in the peak height having a maximum at 530K, indicating that most of the CO is desorbed at this stage. Finally there is a high temperature shoulder at 700K, which might be an indication of a third CO binding state.

The desorption of CO from 0.25% KOH (wt)/EUROPT-1 and 0.5% KOH(Wt) EUROPT-1 shown in Figure 1. The profiles show a continuing

shift of desorption maxima a higher temperature as a function of alkali. These trends are listed in Table-1.

Table: Temperature programmed desorption of CO preadsorbed by pulses at room temperature.

Catalyst	Amount of CO $\mu\text{mol g}^{-1}$		CO/M	T_{max}/K		
	Adsor- bed	Desor- bed				
As-received EUROPT-1	218	214	0.66	450	430	700
0.25% KOH (wt)/EUROPT-1	186	184	0.57	520	439	780
0.50% KOH (wt)/EUROPT-1	148	148	0.46	570	635	820
1.0% KOH (wt)/EUROPT-1	136	128	0.39	630	752	-

The TPD profile of CO from 1% KOH(Wt)/EUROPT-1 shown in Figure 1 is slightly different from the others of the series. The shape of the profile indicates that the previous broad desorption profile collapsed into a single sharp high temperature desorption feature.

The desorption profile of CO from 'as-received' EUROPT-1 indicates a shoulder at 450K, a distinct peak centered at 530K, and another shoulder at 700K, a total of three different adspecies of carbon monoxide seem to exist on EUROPT-1.

This is similar to that observed by Kärner *et al.* [12]. Some differences in temperature (peak maxima) and peak intensities could be attributable to the different experimental parameters and conditions. In the extensive literature on the CO adsorption on Pt single crystal model catalysts only two CO species are reported with desorption maxima corresponding approximately to the first two peaks observed in the present study. Of these two species the lower temperature one is ascribed to adsorption on flat, low index planes, and the higher temperature one to adsorption on more open, high index planes or on steps edges and corners. The third high temperature peak observed in the present study at 740K can be assigned to the CO sites existing on metal support interface which is in agreement to that observed by Kramer [12]. This state has not been obviously reported in the case of single crystal model catalyst.

Komer *et al* [4] reported CO desorption from Pt/SiO₂ catalyst. They observed a flat broad spectrum extending over a range of temperature

from 323 - 873 K (same range has been noted in the present study). They described the unusual behaviour of CO, perhaps related to surface interconversion of the two forms (linear and bridge) of adsorbed CO.

The CO desorption behaviour from alkali EUROPT-1 proved to have some interesting features. First, the area of desorption profile decreased with increasing alkali concentration initiating suggesting that alkali doping is either inhibiting the CO adsorption or reducing the accessible sites for CO adsorption.

In addition to the reduction in area, the desorption peak maxima shifted towards higher temperatures as the alkali concentration increased suggesting the thermal stability of adsorbed CO being increased upon potassium doping.

The catalysts 0.25% and 0.50% KOH(Wt)/EUROPT-1 exhibited three distinct states of adsorbed CO similar to that previously observed for clean EUROPT-1. It is interesting that the CO desorption profile of 1% KOH(Wt)/EUROPT-1 is somewhat different from others of the series. There is one clear T max. intermediate in temperature between the original higher miller index peak and desorption assigned to single metal atom site/metal support sites. Although, the later is shifted to lower temperature, this still has appearances of single metal atom peak.

The alkali effects have been discussed in details some where else. In the present work, alkali, might have destroyed support structure or support structure porosity, which could have encapsulated the metal as no longer accessible, causing reduction in the uptake of CO. This could be the cause of the disappearance of the third binding state of CO sites exhibiting such dependence could be either atoms of lower coordination such as edges and corner or platinum atoms adjacent to support [13]. Thus the higher temperature peaks at 700, 800, 820 K on the as received, 0.25%, 0.50% KOH(Wt)/EUROPT-1 has to be assigned to the sites at Pt/support phase boundary [14,15].

Shift of CO desorption peak maxima towards higher temperatures as the amount of

alkali on EUROPT-1 increases is evident in the present study. These results are similar to those observed previously by Crowell *et al.* [11] from thermal desorption spectra (TDS) of CO adsorbed on clean and K Covered Pt(III) single crystal.

Experimental

Alkali doped 6.3% Pt/SiO₂ catalysts were prepared as detailed somewhere else [16].

The apparatus used in the temperature programmed desorption experiments was similar to that described by Robertson *et al.* [17].

Samples of 'as-received' and alkali doped EUROPT-1 (0.0125 g) were placed in quartz reactor, connected to the conventional TPD apparatus. Pure argon gas was allowed to flush the sample for five minutes and was then replaced by pure hydrogen at room temperature. The sample was heated at the rate of 20 K/minute upto 673K for 90 minutes. At reduction temperature the flow of hydrogen was replaced by flowing argon. The flow of argon was corrected to 10 cm³ per minutes. The sample was flushed for 30 minutes and cooled down in the furnace to room temperature. Carbon monoxide adsorbates brought in contact with the reduced sample by pulses. Five pulses of 0.8 Psig were injected. The uptake of CO was displayed and recorded. The interaction of the peak areas made it possible to estimate the uptake quantitatively.

The thermal conductivity detector was then stabilized, followed by heating the sample from room temperature to 990K.

The uncertainties in H/M ratio based on the accuracy of technique used are estimated to be ± 20 K and 2.0% respectively.

Conclusion

1. The desorption spectra of CO on the EUROPT-1 catalysts are similar to that observed on other supported Pt catalysts. The shift of desorption maxima to higher temperature upon subsequent doping, together with reduction in CO uptake and change in the overall band profile is very similar to that observed on an alkali doped Pt(III) single

crystal, and is consistent with the alkali loading of the catalysts.

2. Strongly held CO dominates on the highest alkali loaded catalyst (1% KOH). This can be attributed to the strongly bonded CO on Pt planes or original CO species thought to exist at the metal/support interface.

References

1. A. Franent, P.B. Wells, *Appl. Catal.*, **18**, 243 (1985).
2. J.L. Falconer and J.A. Shwarz, *Catal. Rev. Sci. Eng.*, **25** (1983).
3. N.W. Hurst, S.J. Gentry, A. Jones and B.D. Macnicol, *Catal. Rev. Sci. Eng.*, **24**, 233 (1983).
4. R. Komer, V. Amenomiya and R.J. Cvetanovice, *J. Catal.*, **15**, 293 (1969).
5. K. Roger and J.R. Anderson, *Appl. Surf. Sci.*, **2**, 335 (1979).
6. J.D. Way and J.L. Falconer, proceedings of the Second Chemical Congress of North America, Las:Vegas; Nevada, Aug. (1980).
7. R.K. Herz, J.B. Kiela and S.P. Marin, *J. Catal.*, **73**, 66 (1982).
8. H.P. Bonzel, *Surf. Sci. Rep.*, **8** (1988).
9. M.R. Dry, T. Shingles and L.J. Boshoff, *J. Catal.*, **15**, 190 (1969).
10. X.L. Zhou and J.M. White, *Surf. Sci.*, **185**, 450 (1987).
11. J.E. Crowel, E.L. Garfunkel and G.A. Somorjai, *Surf. Sci.*, **121**, 303 (1988).
12. R. Kramer, M. Fischbacher and H.L. Gruber, *Appl. Catal.*, **42**, 337 (1988).
13. M. Ahmad, Ph.D Thesis, University Edinburgh, (1990).
14. R.W. McCabe and L.D. Schmidt, *Surf. Sci.*, **66**, 101 (1977).
15. M.R. Mclellan, J.L. Gland and F.R. McFeely, *Surf. Sci.*, **112**, 63 (1981).
16. M. Ahmad and G.S. McDougall, *Physical Chemistry*, **10**, 95 (1991).
17. S.D. Robertson, B.D. Mcnicol and J.H. De bass, *J. Catal.*, **37**, 424 (1975).