Catalysis Letters 5 (1990) 257–264

STRUCTURE-FUNCTION RELATIONSHIPS IN Pt-Cr-H-ZSM-5 ALLOY CATALYSTS

Richard W. JOYNER *[1], Khabib M. MINACHEV [2], Paul D.A. PUDNEY [1], Efim S. SHPIRO *[2] and Gulia TULEOUVA [2]

[1] *Leverhulme Centre for Innovative Catalysis, Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, U.K.*

[2] *N.D. Zelinsky Institute of Organic Chemistry, Academy of Sciences USSR, Leninskii Prospect 47, 117334 Moscow, USSR*

Received 15 February 1990; accepted 22 March 1990

Hydrogenolysis, EXAFS, bimetallic, XPS

The activities of 0.5% Pt/H-ZSM-5 and 0.5% Pt/0.75% Cr/H-ZSM-5 catalysts for alkane hydrogenolysis have been compared. The presence of chromium suppresses propane hydrogenolysis by an order of magnitude, but has a much less pronounced effect on ethane hydrogenolysis. Catalyst characterisation by EXAFS and XPS indicates the formation of small alloy particles, typically containing 10 platinum and 3 chromium atoms. The change in catalytic activity is related to electronic structure modification rather than to an ensemble effect.

The efficient use of alloy and bimetallic materials represents one of the most important opportunities for progress in catalysis by metals. To date development has been limited in many cases by difficulties in catalyst characterisation and in particular in demonstrating alloy formation in very small particles. Thus, although many elements, including rhenium, iridium, gallium, chromium and tin, are used with platinum reforming catalysts, the mechanism by which catalyst performance is improved is often unclear. The addition of chromium to reforming catalysts has recently attracted attention [1–6], and here we present a study of the influence of chromium on a Pt/ZSM-5 catalyst, where we have been able to establish a detailed connection between structure and function. An important role of additives to reforming catalysts is to reduce coke formation, so the activity of the catalysts in hydrogenolysis has been measured. This reaction is also an appropriate choice because of its well known 'structure sensitivity'. Engels et al. [6], have very recently reported that addition of chromium to a highly dispersed Pt/Al_2O_3 catalyst suppresses ethane hydrogenolysis. By analogy with the behaviour of unsupported Pt/Cr samples containing much larger particles, they

---

* To whom correspondence may be addressed.

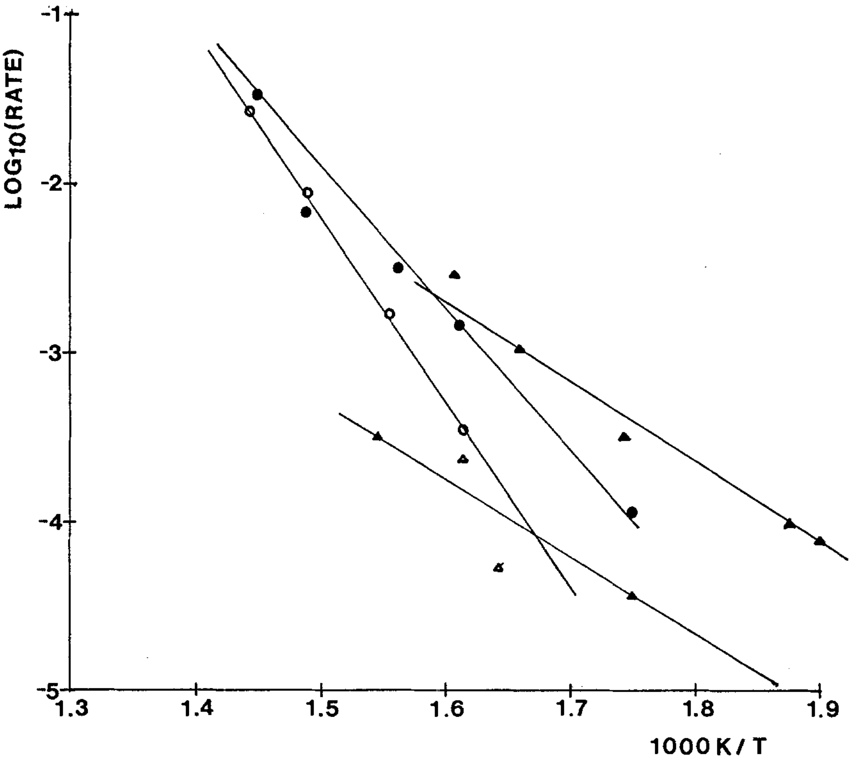

Fig. 1. Arrhenius plots for hydrogenolysis at atmospheric pressure, H_2/hydrocarbon ratio 10/1 and conversions < 10%. Filled symbols refer to the Pt/H-ZSM-5 catalyst and open symbols to the catalyst promoted with chromium. Circles relate to ethane hydrogenolysis and triangles to the propane reaction.

have concluded that alloying between platinum and chromium is implicated.

The ammonium form of a ZSM-5 zeolite, Si/Al ratio 16.5/1, was converted into the hydrogen form by calcination at 820 K for 55 h. Platinum and chromium were simultaneously impregnated from a solution of chloroplatinic acid and chromium (VI) oxide, at 273 K. After 24 h the excess solution was evaporated at 353 K and the sample was dried in air at 393 K. Catalysts were calcined at 620 K for 3 h and subsequently at 790 K for 3 h. Further details of catalyst preparation and characterisation may be found in refs. [4] and [5]. The preparation and characterisation of Pt/ZSM-5 catalysts used for comparison has been described elsewhere [7,8].

Fig. 1 compares the activity of catalysts with and without chromium for the hydrogenolysis of ethane and propane. Reaction conditions are defined in the legend and details of the experimental measurements have been given elsewhere [4]. The chromium loading chosen is that which has been found to be most useful in practical reforming catalysts [1,2]. Addition of chromium reduces the hydro-

Table 1
The methane/ethane ratio observed during hydrogenolysis over the two catalysts. The reaction conditions are given in the legend to fig. 1.

Temperature/K	573	598	623
0.5% Pt/H-ZSM-5	0.32	0.26	0.08
0.5% Pt/0.75% Cr/H-ZSM-5	0.36	0.38	0.52

genolysis activity of the catalyst, however the markedly different effect on ethane and propane reactivity is of the greatest interest. There is a small change in the activation energy for ethane hydrogenolysis and the reduction in activity varies between < 2 and ca 5 over the temperature range studied. Propane hydrogenolysis is much more markedly affected, the rate dropping by an order of magnitude. Table 1 shows how the ratio of methane to ethane formed, which is a measure of the 'depth' of the hydrogenolysis reaction, varies over the two catalysts.

To understand the changes in reactivity, the catalyst has been characterised by extended X-ray absorption fine structure, (EXAFS) and X-ray photoelectron spectroscopy, (XPS). Studies of Pt/ZSM-5 catalysts by these methods and by electron microscopy have been described elsewhere [7,8], as have the experimental techniques and the methods of data analysis used. In the absence of chromium, the platinum exists in the form of small metallic particles of average diameter 7–11 Å, and which are largely located within the zeolite framework. The particle size observed depends on the calcination temperature, but not markedly on the reduction temperature. The Pt-Pt nearest neighbour distance is contracted 1–4% with respect to the bulk and there is clear evidence of bonding to the oxygen of the zeolite framework. XPS measurements have been interpreted as indicating charge transfer from metal to zeolite.

XPS analysis of the Pt/Cr/ZSM-5 catalyst has been performed after in-situ reduction in 1 bar of static hydrogen at 873 K, in a specially developed cell attached directly to a Kratos XSAM spectrometer and using Mg Kα radiation. As noted previously for Pt/Cr/Al_2O_3 catalysts, platinum promotes reduction to metallic chromium [4–6]. The chromium 2p peaks are shown in fig. 2, which also indicates the resolution into component oxidation states. The fresh catalyst shows the presence of Cr(VI) and Cr(III); on reduction at 820 K, Cr(VI) disappears and there is evidence of reduction of about 15% of the chromium to the metallic state. This fraction was reoxidized to Cr(III) on exposure to oxygen at 298 K. Quantitative details of the spectra are given in table 2.

EXAFS measurements were performed at the Daresbury synchrotron radiation source and reduction of the catalyst sample was carried out in-situ at 1 bar, in flowing hydrogen at 673 K. Data were collected for the Pt L_{III} edge and analysed by standard methods [9]; no facilities for fluorescence detection were available, so study of the chromium K edge was not possible. Figure 3 shows the experiment-

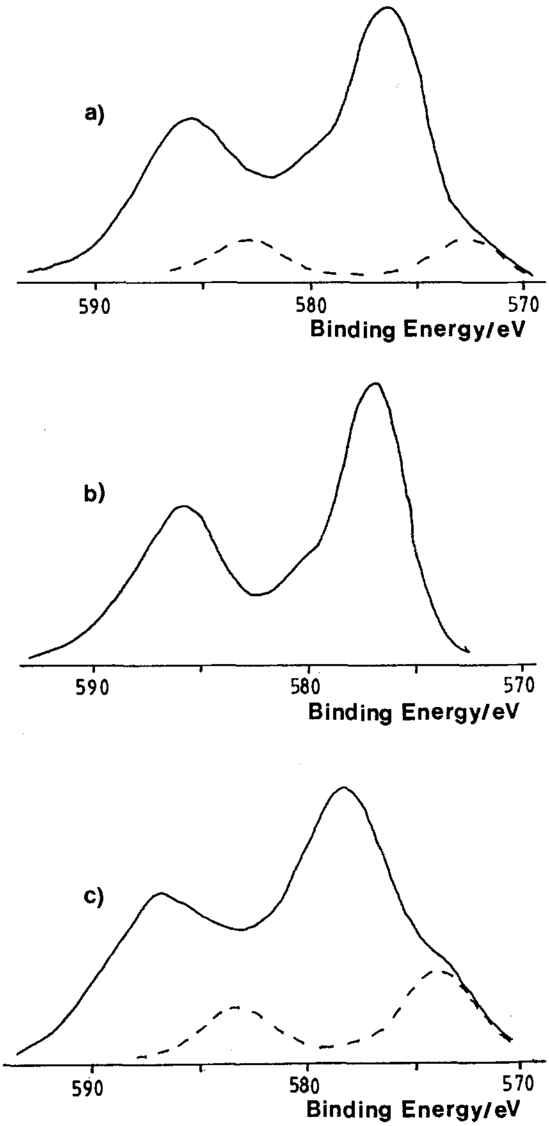

Fig. 2. Chromium 2p XPS spectra; quantitative details are given in table 2. Curve a), After in situ reduction in hydrogen at 820 K. The dashed line shows the contribution from Cr(0), the remainder of the spectrum being due to Cr(III); Curve b), As a, after exposure to oxygen at 298 K; the spectrum is now wholly due to Cr(III); Curve c), As b, after reduction in hydrogen at 873 K. The dashed line again shows the contribution from Cr(0).

theory comparison and the parameters used in the calculation are listed in table 3. Agreement between theory and experiment was tested using a fitting index discussed in detail elsewhere [10]. The Pt-Pt and Pt-O shells of neighbours are similar to those noted for a Pt/ZSM-5 catalyst. It was found that including a Pt-Cr interatomic distance into the analysis decreased the fitting index by 51%,

Table 2
Results of XPS analysis

Treatment	Pt (0)	Pt (II)	Cr (0)	Cr(III)	Cr (VI)
Fresh catalyst					
BE/eV *	72.4	74.0	–	577.5	579.5
Amount observed	44.3%	35.7%	–	78.8%	21.2%
Reduced in H_2, 820 K					
Be/eV *	72.3	–	573.4	577.2	–
Amount observed	100%	–	12.3%	87.7%	–
Exposed to O_2, 298 K					
BE/eV *	72.8	–	–	577.2	–
Amount observed	100%	–	–	100%	–
Rereduced at 870 K					
BE/eV *	72.2	–	573.0	577.4	–
Amount observed	100%	–	16.2%	83.8%	–

* Binding energies refer to Pt $4f_{7/2}$ and Cr $2p_{3/2}$ peaks, and are referenced to the Si 2p peak of the zeolite framework, BE 103.8 eV.

and this is significant at the excellent statistical level of 0.5%. (A significance level of < 5% is considered sufficient if a new shell of neighbours is to be accepted; see ref. [10] for a fuller discussion.) The existence of platinum-chromium coordination in the catalyst is thus well established and the observed distance is in the range expected for metallic bonding. Several groups have demonstrated that

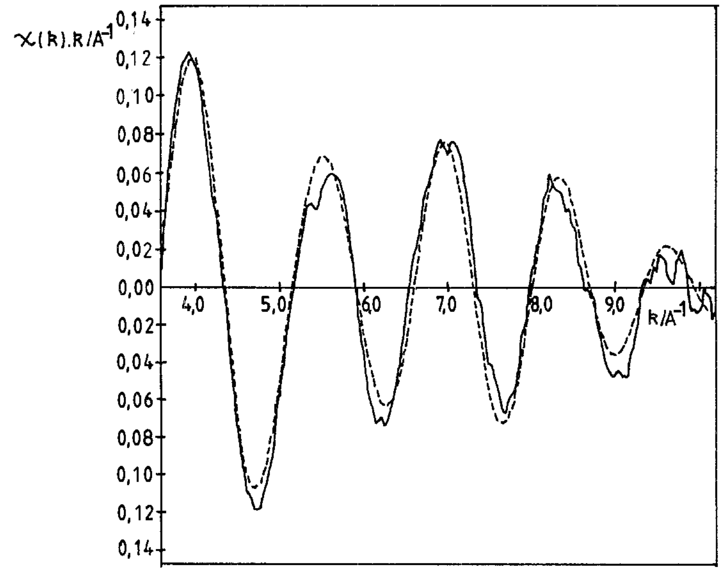

Fig. 3. Pt L_{III} EXAFS for the Pt/Cr/H-ZSM-5 catalyst, solid line, experiment; dashed line calculated using the parameters given in table 3, and including at Pt/Cr distance of 2.65 Å.

Table 3
Parameters used to describe the Pt III shell EXAFS data shown in fig. 3.

Neighbour	Interatomic distance/Å	Coordination number	Debye-Waller factor/Å^2
Chromium	2.65 ± 0.02	1.7 ± 0.5	0.015 ± 0.003
Platinum	2.71 ± 0.01	4.5 ± 1.0	0.016 ± 0.003
Oxygen	1.97 ± 0.03	1.8 ± 0.05	0.015 ± 0.005

alloying of chromium with platinum decreases the lattice parameter [6,11,12]. The coordination numbers suggest a Pt/Cr molar ratio of 3/1 in the platinum particles, provided the chromium is homogeneously distributed.

Taken together, the EXAFS and XPS results allow us to develop a detailed picture of the metallic species present in the catalyst. The XPS results suggest that the molar ratio of Pt(0)/1Cr(0) in the reduced catalyst is ca 2/1, compared to the value deduced, by EXAFS, for the alloy particles, of ca 3/1. This suggests that most of the metallic chromium is to be found in the alloy particles, although some pure chromium could also be present. The average size and composition of the alloy particles may be deduced from the EXAFS results. The sum of Pt-Pt and Pt-Cr nearest neighbour coordination number is 6.3, very close to that found in 13 atom particles, which is 6.5. Thirteen atoms is a 'magic' number, yielding quasi-spherical particles in both cubic close parking and icosahedral schemes. The relative magnitude of Pt-Pt and Pt-Cr coordination numbers allow us to suggest that the average particle has ca 10 Pt and 3 chromium atoms. We cannot, of course, deduce the distribution of chromium within the particles. Chromium is completely soluble in platinum up to a molar limit of 71% [13]. This might imply that the chromium here is dispersed, rather than aggregated, within the small clusters. For a homogeneous distribution the calculated coordination numbers are Pt-Pt 4.9, and Pt-Cr 1.7, which compare well with those observed. We are unable to identify the nature of the packing in these small clusters. The general shape of the near edge structure ($0 < k < 3$ Å) is similar to that in platinum foil, suggesting that cubic close packing is retained [14]. Our picture differs from that developed by Tzou et al., who, in a study of rhodium-chromium in the zeolite sodium–Y [15], concluded that zerovalent rhodium was 'anchored' to the zeolite framework by chromium ions. In the present case the observation of zerovalent chromium and the measured Pt-Cr interatomic distance are much more consistent with the presence of a Pt-Cr alloy.

We now have a clear indication of the effect of chromium addition on both the function and structure of the platinum catalyst and may consider how they are correlated. In the absence of chromium, the platinum particles are the seat of activity, since H-ZSM-5 is on its own inactive in hydrogenolysis [16]. In agreement with Engels et al. [6], we ascribe the suppression of hydrogenolysis activity to alloying of the platinum with chromium. Conventionally, data of the type presented here would be explained by invoking the ensemble concept, in which it is assumed that a certain number of contiguous platinum atoms are required to carry out the reaction of interest [17]. It would be argued that propane, as the bigger molecule, requires a larger ensemble than ethane. The chromium atom dilutes and decreases the size of the available ensembles.

The ensemble model at its simplest is based on the assumption that a reaction needs a certain number of adsorption sites, and is appropriate where the diluent atom has only weak adsorption activity. It is not appropriate here, where a chromium atom is likely to be an equally effective adsorption site as a platinum atom. Although the activity of chromium in ethane hydrogenolysis has not been reported, extrapolation of Sinfelt's data for other first row transition metals suggests that it would probably be more active than platinum [18]. Also, at the Pt/Cr ratio observed, the alloyed particles still present quite large platinum ensembles. The exact size is to some extent a matter of definition, but is 5 atoms at a minimum and could be as high as 10 if the chromium atoms were to aggregate together.

An alternative explanation to the ensemble idea, based on electronic structure, seems more appropriate. If the chromium atoms are distributed across the cluster, five of the platinum atoms at the surface will be in contact with two chromium atoms, while the remaining four will each touch one chromium atom. Calculations and indeed chemical intuition suggest that this is the range over which electronic interactions can be expected to be important [19], so the whole of the surface electronic structure of the particles will be influenced by alloying. Platinum and chromium lie on opposite sides of their respective volcano curves for alkane hydrogenolysis. Hydrocarbons are insufficiently strongly adsorbed on platinum, while adsorption is too strong on chromium for optimal activity. We therefore conclude that the role of chromium is substantially to increase hydrocarbon adsorption strength on the alloy particles, and that the effect is more pronounced on propane, which is the easier hydrocarbon to activate. Table 1 indicates that there is indeed some change in the 'depth' of hydrogenolysis between the pure platinum and the alloy catalyst. We propose to examine this in more detail in future studies, by systematically varying the platinum/chromium ratio.

References

[1] N.S. Koslov, E.A. Skrigan, G.M. Sen'kov, M.F. Gorbacevic and V.V. Sipikin, Neftekhimija 19 (1979) 370.

[2] K. Anders, R. Feldhaus, H.-G. Vieweg, S. Engels, H. Lausch et al., Chem. Tech. (Leipzig) 37 (1985) 65.

[3] W. Grunert, W. Saffert, R. Feldhaus and K. Anders, J. Catal. 99 (1986) 149.

[4] W. Grunert, E.S. Shpiro, R. Feldhaus, K. Anders, G.V. Antoshin and Kh.M. Minachev, J. Catal. 100 (1986) 138.

[5] E.S. Shpiro, G.J. Tuleuova, V.I. Zaikovskii, O.P. Tkachenko, T.V. Vasina, O.V. Bragin and Kh.M. Minachev, in: *Zeolites as Catalysts, Sorbents and Detergent Builders*, eds. H.G. Karge and J. Weitkamp (Elsevier, Amsterdam, 1989).
[6] S. Engels, H. Lausch, B. Peplinski, M. Wilde, W. Morke and P. Kraak, Appl. Catal. 55 (1989) 93.
[7] O.V. Bragin, E.S. Shpiro, A.V. Preobrazhensky, S.A. Isaev, T.V. Vasina, B.B. Dyusebina, G.V. Antoshin and Kh.M. Minachev, Appl. Catal. 27 (1986) 219.
[8] E.S. Shpiro, R.W. Joyner, Kh.M. Minachev and P.D.A. Pudney, J. Catal., submitted.
[9] S.J. Gurman, N. Binstead and I. Ross, J. Phys. C (Solid State Phys.) 17 (1984) 143.
[10] R.W. Joyner, K.J. Martin and P. Meehan, J. Phys. C (Solid State Phys.) 20 (1987) 4005.
[11] E. Raub and W. Mahler, Z. Metallkd. 46 (1955) 210.
[12] W. Bronger and W. Klemm, Z. Anorg. Allg. Chem. 319 (1962) 58.
[13] M. Hansen, *Constitution of Binary Alloys*, 2nd edn. (McGraw-Hill, New York, 1958).
[14] G.N. Greeves, P.J. Durham, G. Diakun and P. Quinn, Nature 294 (1981) 139.
[15] M.S. Tzou, B.K. Teo and W.M.H. Sachtler, Langmuir 2 (1986) 773.
[16] E.S. Shpiro et al., unpublished results.
[17] G.A. Martin, Catal. Revs. Sci. Eng. 30 (1988) 519.
[18] J.H. Sinfelt, Catal. Revs. Sci. Eng. 3 (1976) 175.
[19] R.W. Joyner, J.B. Pendry, D.K. Saldin and S.R. Tennison, Surf. Sci. 138 (1984) 84;
J.M. MacLaren, R.W. Joyner, J.B. Pendry and P. Meehan, Surface Sci. 175 (1986) 263.