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Intermetallic Pt–Cr Clusters in Zeolites as Models of Bimetallic Aromatisation and Reforming Catalysts

II. Structure–Catalytic Function Relationships

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The catalytic properties of a series of Pt–Cr/ZSM-5 zeolites with variable Pt/Cr ratios have been studied in propane and ethane hydrogenolysis. Kinetic results demonstrate a strong effect of the chromium additive both on the reaction rates and activation energies. With propane, the reaction rates drop by an order of magnitude and the activation energies increase from 80 to 120–150 kJ mol^{-1}. The major effect in ethane hydrogenolysis is a dramatic increase of the apparent activation energy from 135 kJ mol^{-1} (Pt/ZSM-5) to 230–330 kJ mol^{-1} (Pt–Cr/ZSM-5). The amount of chromium above 0.75 wt% only slightly affects both the reaction rates and activation energies. The role of chromium in suppressing the hydrogenolysis reaction is explained on the basis of structural analysis of Pt–Cr catalysts and segregation of platinum in the surface monolayer of the alloy particles. The platinum–chromium interaction is assumed to reduce the strength of bonding between the hydrocarbon or its fragments and the metal surface and, consequently to reduce the hydrogenolysis activity. The kinetic compensation observed with ethane may be related to Pt–Cr particle redispersion, noted by EXAFS. The behavior of Pt–Cr catalysts in ethane aromatisation depends on the chromium loading. At lower loading (0.75%) the aromatisation selectivity increases significantly, while at higher loadings the aromatics yield drops dramatically. The promotion is attributed to Pt–Cr alloying, while pore blockage by chromia is probably responsible for deactivation. © 1993 Academic Press, Inc.

INTRODUCTION

The demands placed on technology by environmental concerns and legislation justify the continuing interest in research on bimetallic and multimetallic supported catalysts. The development of appropriate physical techniques also offers real opportunities to study structure–function relationship, both for pure alloys and supported materials which contain very highly dispersed alloy particles. Among bimetallic catalysts, promoted platinum systems are still of most interest due to their tremendous importance in gasoline reforming and other current and prospective industrial processes.

Many different approaches have been proposed to explain catalytic effects induced by alloying, the ensemble effect being most popular and clearly recognised (*1–3*), especially when active and inactive components are mixed. Monte-Carlo simulations (*4–6*) and other theoretical approaches (*7*, *8*) have been used to show selective segregation of the promoter to specific sites, such as corners and edges on the alloy surface and to estimate the probability of forming ensembles with different numbers of atoms. Coq *et al.* (*7*, *8*) applied a site-segregation model to explain the different effects of gallium and germanium on the properties of bimetallic rhodium catalysts. There is nonetheless much experimental data, especially for promoted platinum catalysts, that are

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not well explained by the ensemble model. Recently Joyner and Shpiro (*9*) proposed a quite different segregation model. This model was suggested by surface science studies of various Pt alloys that revealed formation of so-called sandwich structures in the surface layers, with the top layer consisting entirely of platinum and the second layer enriched in the additive (*10–12*). The model explains Pt promotion by additives (Ir, Cr, Ga, Re) as due to an electronic interaction between platinum, which comprises exclusively the outer surface layer, and the second component which is enriched in the immediate subsurface layer.

This paper presents results on the catalytic activity of a relevant bimetallic system, Pt–Cr/H-ZSM-5, using as test reactions propane and ethane hydrogenolysis. Normally these reactions are used as a test of structure sensitivity and the ensemble effect (*1–3, 14–16*), but recent results derived for highly dispersed systems (*17, 18*) show that the reactions are also sensitive to the electronic state of the metal. We seek to establish the relationship between the structure and composition of Pt–Cr alloy particles, characterised in detail in Part I (*13*), and their catalytic properties. We hope to arrive at a general understanding of promotion in bimetallic Pt-supported catalysts. Pt–Cr formulations are not only important as model catalysts, since they have been successfully used for gasoline reforming and lower alkane aromatisation (*19–21*). Despite extensive studies of Pt–Cr/Al_2O_3 catalysts (*19, 20, 22–24*), direct evidence of chromium reduction to the metallic state and possible alloying with Pt was found only quite recently (*20, 23*). The catalysts studied by Engels *et al.* (*23*), however, contain rather large and nonuniform particles. The advantage of the Pt–Cr/zeolite catalyst is that very highly dispersed Pt–Cr clusters are produced (*25*) and size effects can be excluded, because the dispersions of both Pt/H-ZSM-5 and catalysts with different Pt–Cr compositions are very similar (*13, 18, 25*).

EXPERIMENTAL

Materials

Details of catalyst preparation methods have been given in Part I (*13*). In addition to the series of Pt–Cr catalysts prepared by co-impregnation of NH_4/ZSM-5 with a mixture of H_2PtCl_6 + CrO_3 solutions, several 0.5% Pt-0.75% Cr/H-ZSM-5 samples prepared by different routes have been investigated. The catalysts are listed in Table 1.

Catalytic Studies

Propane and ethane hydrogenolysis reactions were carried out in a flow microreactor, described in Ref. (*26*). Preliminary experiments were performed to establish the region of differential operation; linearity between conversion and reciprocal space velocity was found for hydrocarbon conversions up to 6%. Normally conversion was restricted to <2%, with a catalyst charge of 0.05 g, a linear velocity of 1.2 l h^{-1}, and a hydrocarbon/H_2 ratio of 1/10. Conversion and reaction rate results are accurate to within 10%. Several samples were checked to ensure reproducibility. The Pt/ZSM-5 samples showed highly reproducible activity over the full range of temperatures studied (from lower temperature to higher temperature and back), with reaction rates reproducible to within 20% and activation energies to within 10 kJ mol^{-1}. For some Pt–Cr samples, activation or deactivation effects observed at higher temperatures caused increased errors. Error bars therefore were estimated individually for each sample, as indicated in Tables 2 and 3. With propane, the selectivity towards ethane formation was calculated as $S(C_2H_6)/\% = 100 \cdot Y(C_2H_6)/[Y(CH_4) + Y(C_2H_6)]$, where Y is the yield of the corresponding hydrocarbon.

Ethane aromatisation was studied using a pulse microreactor described in Ref. (21). After reduction, the samples were exposed to a helium flow and after 20 min an ethane pulse was injected into the flow (V = 0.8 ml).

TABLE 1

Composition of Catalysts and Details of Preparation[a]

No.	%Pt	%Cr	Initial compound	Preparation procedure	SiO_2/Al_2O_3
1	0.5	—	$Pt(NH_3)_4Cl_2$	Ion exchange + impregn.	35;40
2	0.5	0.75	H_2PtCl_6 + CrO_3	Coimpregnation	35;40
3	0.5	0.75	$Pt(NH_3)_4Cl_2$;CrO_3	Ion exchange (Pt), then impregnation (Cr)	35
4	0.5	1.25	H_2PtCl_6 + CrO_3	Coimpregnation	40
5	0.5	1.75	H_2PtCl_6 + CrO_3	Coimpregnation	40
6	0.5	2.25	H_2PtCl_6 + CrO_3	Coimpregnation	40
7	0.5	0.75	$Pt(NH_3)_4Cl_2$, $Cr(NO_3)_3$	Coimpregnation	35
8	—	0.75	CrO_3	Ion exchange and impregnation	35

[a] The NH_4 form of H-ZSM-5 was used as the starting zeolite.

Catalyst Characterisation

In addition to the experiments described in Part I (*13*) EXAFS spectra were recorded for the sample 0.5% Pt–0.75% Cr/H-ZSM-5 after treatment with a 1 : 4 mixture of C_2H_6/Ar, at 823 K. The sample was then decooled in the flowing gas to 300 K, and exposed to the synchrotron beam. XPS spectra for an analogous specimen were also measured. The procedures for analysis of both EXAFS and XPS measurements are given in Part I (*13*).

RESULTS

Propane Hydrogenolysis

The reaction was studied in the temperature range 523–673 K (Table 2, Fig. 1). Two main effects were observed when chromium was added to Pt/H-ZSM-5, namely, a decrease of the reaction rate by an order of magnitude, and an increase of the activation energy. The major changes occurred with the addition of 0.75% Cr by weight. Further increase of the chromium content only slightly influenced the reaction rate or the

TABLE 2

Propane Hydrogenolysis Activities and Selectivities over Catalysts Studied (Conversion Less than 6%, H_2/C_3H_8 = 10/1, Atmospheric Pressure)

Cat. no.	Reaction temperature (K)														E_a (kJ mol^{-1})
	523		548		573		598		623		648		673		
	W^a	S^b	W	S	W	S	W	S	W	S	W	S	W	S	
1	0.76	40			4.6	24	8.6	20	29	7.5					76 ± 10
2			0.08	38	0.35	35	0.69	37	2.9	34	12	38			136 ± 20
			(0.06)	(33)	(0.10)	(42)	(0.39)	(37)	(0.85)	(40)[c]					120 ± 20
3					0.36	27	0.55	28	2.8	34	3.2	20	22.4	26	120 ± 20
4			0.05	42	0.22	37	0.82	42	2.5	23	26	34			150 ± 20
5					0.21	37	0.36	37	1.2	35	10	31			150 ± 20
6					0.22	37	1.2	33	3.9	38	9.8	36			150 ± 20

[a] W—overall reaction rate based on propane conversion, μmol (g Pt)$^{-1}$ s^{-1}.

[b] S—selectivity of ethane formation, mol%.

[c] Figures in parentheses were obtained in a run from higher to lower temperatures.

TABLE 3

Ethane Hydrogenolysis Reaction Rates and Activation Energies over Catalysts Studied (Conversion Less than 6%, H_2/C_2H_6 = 10/1, Atmospheric Pressure)

Cat. no.	%Pt	%Cr	Reaction temperature (K) 623	648	673	698	723	748	E_a (kJ mol^{-1})
			Reaction rate (μmol (g Pt)$^{-1}$ s^{-1})						
1	0.5	0	1.2	2.7	7.2	15.8	39.0	—	134 ± 10
2	0.5	0.75	[a]	[a]	7.3	36	120	2100	260 ± 20
3	0.5	0.75	0.36	1.83	9.8 (12.3)[b]	38	—	—	215 ± 20
4	0.5	1.25		0.56	3.2	18	126	651	270 ± 20
5	0.5	1.75	[a]	[a]	2.0	25	60	990	300 ± 30
6	0.5	2.25	[a]	[a]	[a]	1.2	5.4	140	320 ± 30

Note. All samples were air calcined and reduced at 793 K.

[a] No measurable activity.

[b] Back from higher temperature.

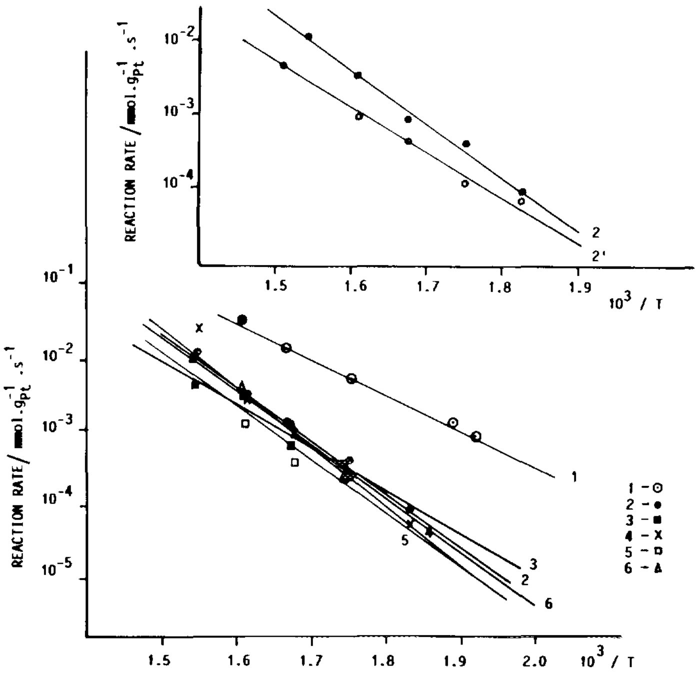

FIG. 1. Arrhenius plots for propane hydrogenolysis over platinum–chromium/zeolite catalysts. The numbers for the curves correspond to the catalysts listed in Table 1. The insert shows the changes in temperature dependence between the first (from lower to higher temperature) and second (from higher to lower temperature) run.

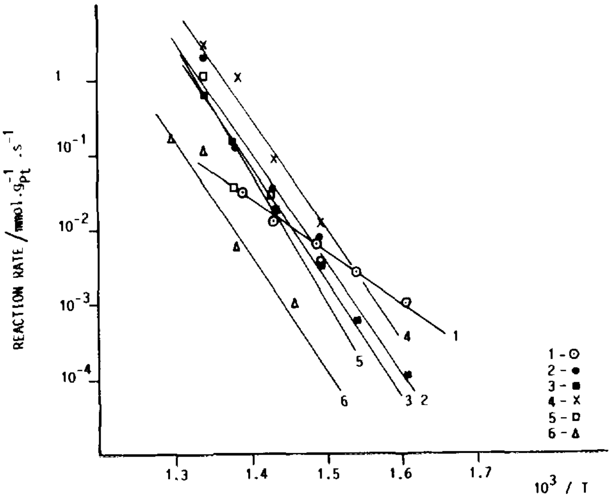

FIG. 2. Arrhenius plots of ethane hydrogenolysis over platinum-chromium zeolite catalysts. The numbers for the curves correspond to the catalysts listed in Table 1.

activation energy. During one set of experiments a slight deactivation was observed, but the activation energy remained the same within experimental error (see inset in Fig. 1).

The selectivity of ethane formation by Pt and Pt–Cr catalysts is rather similar at lower temperatures (26–35%) and is independent of temperature for Pt–Cr catalysts. By comparison, Pt catalysts produced significantly more methane at higher temperatures.

Ethane Hydrogenolysis

The behavior of Pt–Cr catalysts and Pt catalysts is different in ethane hydrogenolysis. For temperatures at which both Pt and Pt–Cr catalysts are operative (for instance, 623 K), their activity is very similar. At lower temperatures (573 K) the Pt–Cr catalysts have no activity under the chosen conditions, while at higher temperatures they become more active than Pt/H-ZSM-5 (Table 3). Chromium introduction thus results in a substantial increase of the apparent activation energy. As for propane, the major effect was found when changing from 0.5% Pt/ZSM-5 to 0.5% Pt–0.75% Cr/ZSM-5 catalysts. Further increases of the chromium loading caused less pronounced effects. An exception was the 0.5% Pt–2.25% Cr/ZSM-5 catalyst, which was less active over the whole temperature range with respect to other catalysts (see Fig. 2).

We have examined the influence of preparation and pretreatment on catalytic activity (Table 4). The chromium effect is more pronounced for 0.5% Pt-0.75% Cr catalysts reduced at 823 K than at 673 K (catalyst no. 3), the most important change being in the activation energy for the latter sample, which approached that of Pt/ZSM-5. Changes in preparation method have less important effects. It should be noted that subjecting both preparations to subsequent high-temperature reduction resulted in the observation of metallic chromium and Pt–Cr alloy formation (*13*).

Ethane Aromatisation

The experiments performed in the pulse mode (Fig. 3) demonstrate the effect of chromium on catalytic activity and selectivity in ethane aromatisation at 823 K. The catalyst containing 0.5% Pt–0.75% Cr yields more aromatics than Pt/H-ZSM-5 and less of the hydrogenolysis/cracking product, methane. Cr/H-ZSM-5 is essentially inactive. On go-

TABLE 4

The effect of preparation and pretreatment of 0.5% Pt–0.75% Cr/HZSM-5 on the activity in ethane hydrogenolysis

Preparation	Reduction temperature (K)	Cat. no.	Reaction rate, (μmol (g Pt)$^{-1}$ s^{-1}		E_a (kJ mol^{-1}) (623–748 K)
			623 K	673 K	
H_2PtCl_6 + CrO_3	823	2	0.056[a]	7.3	260 ± 20
$Pt(NH_3)_4Cl_2,CrO_3$	823	3	0.36	9.8	215 ± 20
$Pt(NH_3)_4Cl_2,CrO_3$	673	3	1.84	12.3	154 ± 20
$Pt(NH_3)_4Cl_2$[b]	823	1	1.2	7.2	134 ± 10

[a] Determined by extrapolation of the Arrenius plot.
[b] 0.5% Pt/H-ZSM5.

ing to higher chromium contents the aromatisation activity sharply declined, and the catalysts produced mainly methane.

Ethane Interaction with Pt–Cr/H-ZSM-5 Catalysts

The results reported earlier (*27*) indicate a distinct effect of ethane treatment on the activity of prereduced Pt–Cr catalysts, both in hydrogenolysis and aromatisation. To look for possible changes in the structure and dispersion of metallic particles in the course of the reactions, we have studied the ethane interaction with several Pt–Cr catalysts at high temperature, 823 K, by *in situ* EXAFS. A preliminary account of these experiments was reported earlier (*28*).

Treatment of the prereduced catalyst with ethane led to a decrease of the nearest neighbour Pt–Pt coordination number (CN)

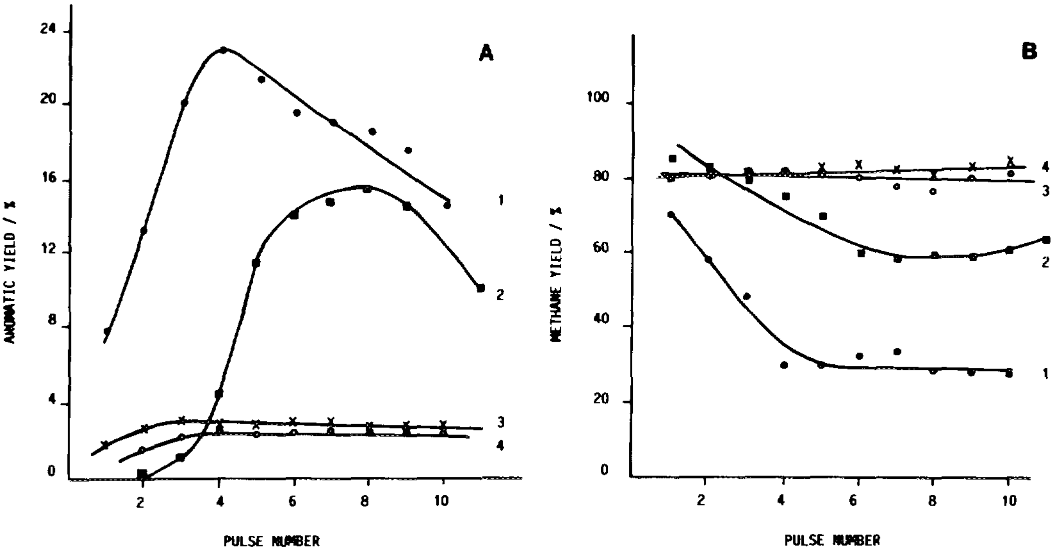

FIG. 3. The yields of aromatics (A) and methane (B) obtained in ethane aromatisation at 823 K in pulse mode experiments, with Pt and Pt–Cr loaded H-ZSM-5 catalysts. Curve (1) 0.75% Pt–0.75% Cr/H-ZSM-5, (2) 0.5% Pt/H-ZSM-5, (3) 0.5% Pt–1.75% Cr/H-ZSM-5, and (4) 0.5% Pt–2.25% Cr/H-ZSM-5. All catalysts were prereduced in hydrogen at 823 K.

which is outside experimental error (Table 5). The absolute error in N1 (Pt–Pt) does not exceed ± 0.8, including correlation between the CN and the Debye–Waller factor, while relative errors are expected to be significantly smaller, probably ± 0.5 (*29*). The results obtained show metallic particle redispersion during high-temperature ethane treatment. The average particle size decreased from 12 ± 2 Å to 8 ± 1 Å and the number of atoms in the average cluster decreased from 60 ± 20 to 15–20 (±5), assuming spherical particles (*18*). The observed changes are not due to increasing static disorder within the metal particles since the Debye–Waller factors did not increase on exposure to ethane.

Reaction with ethane is the most probable explanation for the disruption of metal particles. To probe whether metal-carbon bonds were formed during ethane treatment, a platinum-carbon shell was included in EXAFS analysis, replacing the Pt–O shell. This led to a slight improvement in the fit and a further reduction of the Pt–Pt coordination number. The changes in fitting indexes are too small to allow definite conclusions, since phase shifts for carbon and oxygen are very similar. The redispersion or disruption was not observed with 1% Pt–0.75% Cr/H-ZSM-5 catalyst, which contained larger particles, 20–25 Å in diameter.

DISCUSSION

It is first interesting to compare the hydrogenolysis results for metal in zeolite catalysts with those observed for catalysts of platinum on amorphous supports. The reference catalyst EUROPT-1, containing 6.3% Pt at ca 60% dispersion on silica, is a particularly appropriate comparison since reproducible results, including turnover numbers and activation energies, are available from several laboratories, and are said to be generally representative of platinum catalysts (*30*). Measurements on the reference catalyst were performed under similar conditions to those used here, in particular the hydrogen and hydrocarbon pressures were similar. Table 6 gives comparative data for both ethane and propane hydrogenolysis and for catalysts with and without chromium. It can be seen that at 573 K the turnover numbers for platinum-only catalysts on the H-ZSM-5 and the silica support are similar, although the close agreement for ethane hydrogenolysis is probably fortuitous. The activation energies obtained on the zeolite supported materials are lower than noted on the silica support. In view of the marked compensation effects observed both in our studies and for EUROPT-1 (*30*), the significance of these differences is unclear. Diffusion limitations, which might be expected to be more severe in the zeolite catalyst, seem unlikely to be responsible. The turnover numbers are similar at 573 K, which is the lowest temperature reported in our studies. The lower activation energy for the Pt/H-ZSM-5 catalyst therefore means that, at temperatures higher than 573 K, the reaction is faster for this material than it is over the silica-supported catalyst.

Table 6 shows that the extent of "deep" hydrogenolysis of propane to give solely methane as the product, is greater for the zeolite-supported materials than for EUROPT-1. This may reflect sequential reaction of ethane in the zeolite pores, although the turnover number for ethane hydrogenolysis is much smaller than that for propane.

The results show that inclusion of chromium in the catalysts markedly changes their behaviour in hydrogenolysis. For propane the rate and extent of hydrogenolysis is decreased and the activation energy increased, while for ethane the rate is broadly similar although the activation energy is dramatically increased. Since neither H-ZSM-5 or Cr/H-ZSM-5 is active in hydrogenolysis under the conditions used, the changes observed are attributed to a direct interaction between chromium and platinum. Variations in dispersion can be ruled out, since both EXAFS and TEM indicate that addition of chromium has little influence on particle size. Moreover, varying the particle size for Pt/H-ZSM-5 catalysts in the range

TABLE 5

EXAFS Results for Pt-Cr Catalyst

	Pt–Pt						Pt–O (Pt–C)[a]		Pt–Cr	
	N	*R* (Å)	*N*	*R* (Å)	*N*	*R* (Å)	*N*	*R* (Å)	*N*	*R* (Å)
Heating at 820 K in hydrogen	7.3 ± 0.5	2.75 ± 0.01	3.8 ± 1	3.88 ± 0.02	2.3 ± 0.7	4.86 ± 0.04	1.9 ± 0.4	1.95 ± 0.03	0.7 ± 0.2	2.68 ± 0.02
After reduction and heating ethane/Ar at 820 K	5.6 ± 0.5	2.75 ± 0.01	2.7 ± 1	3.90 ± 0.02	2.2 ± 0.7	4.82 ± 0.4	1.2 ± 0.4	1.97 ± 0.03	0.6 ± 0.2	2.65 ± 0.02
	5.0 ± 0.5[a]	2.76 ± 0.01	2.8 ± 1	3.91 ± 0.02	2.8 ± 0.07	4.88 ± 0.04	0.7 ± 0.3[a]	1.92 ± 0.03	0.6 ± 0.2	2.67 ± 0.02
Similar, but measured *in vacuo*	6.0 ± 0.5	2.76 ± 0.1	3.0 ± 1	3.88 ± 0.02	1.9 ± 0.6	4.82 ± 0.06	1.1 ± 0.2	1.97 ± 0.03	0.5 ± 0.2	2.68 ± 0.02
	5.2 ± 0.5[a]	2.75 ± 0.01	3.3 ± 1	3.88 ± 0.02	2.1 ± 0.6	4.88 ± 0.06	0.8 ± 0.3[a]	1.96 ± 0.03	0.6 ± 0.2	2.70 ± 0.02

Note. All spectra were taken after cooling to 298 K.

[a] Fits including a Pt–C distance instead of a Pt–O distance.

TABLE 6

Comparison of Hydrogenolysis Results with Those of the Reference Catalyst, EUROPT-1

Hydrogenolysis reaction result	EUROPT-1[a]	Pt/H-ZSM-5	Pt–Cr/H-ZSM-5 (average values)
Ethane hydrogenolysis			
Turnover number at 573 K (h^{-1})	0.2	0.23[b]	<0.01[b]
Activation energy (kJ mol^{-1})	205 ± 15	134 ± 10	240 ± 40
Propane hydrogenolysis			
Turnover number at 573 K (h^{-1})	1.5	5.4	0.25–0.4
Activation energy (kJ mol^{-1})	185 ± 5	76 ± 10	130 ± 20
Selectivity to ethane (%) at 573 K[c]	43[d]	24	33 ± 4
Selectivity to ethane (%) at 623 K	—	7.5	35 ± 3

[a] From Ref. (*30*): P_{H_2} = 0.83–0.94 bar, $P_{Hydrocarbon}$ = 0.04–0.08 bar.

[b] Extrapolated from Fig. 2.

[c] For method of calculation, see text.

[d] Recalculated from Ref. (*30*), assuming 90% selectivity to ethane + methane; temperature not specified.

8–500 Å has been shown to change only the reaction rate, and not the activation energy (*18, 30*), in contrast to the results reported here.

We relate the changes in catalytic behaviour to the formation of Pt–Cr alloy particles, which has clearly been demonstrated by EXAFS. Where catalysts have been subjected only to low temperature reduction (623 K), which does not cause alloy formation, the behaviour of Pt–Cr catalysts is similar to that of Pt/H-ZSM-5 materials. Specifically, and as shown in Table 4, the activation energy is the same. EXAFS measurements show that the chromium content of the Pt–Cr alloys is little affected by the chromia loading of the catalyst. This indicates clearly why the activity changes observed are independent of chromium content. The only exception is the highest chromium-containing catalyst in the ethane hydrogenolysis reaction, where pore blocking may render sites unavailable.

The results can be understood within our general structural proposal for bimetallic platinum reforming catalysts (*9*), and the specific structural model for these catalysts that has been developed in Part I (*13*). We have suggested that additives to platinum catalyst, such as gallium, iridium, and chromium, form a unique structure in which the surface monolayer is wholly platinum, while the immediate subsurface layer is enriched in the additive. Observations of decreased hydrogenolysis activity as a result of alloy formation are commonly interpreted within the ensemble hypothesis, in which the added atom is argued to break up the ensemble of contiguous platinum atoms necessary to carry out the reaction. There are, however, strong arguments why the ensemble model is not applicable to Pt–Cr catalysts, since it is normally invoked for additive atoms such as copper and tin that are inert in hydrogenolysis. The most important objection is that chromium should have a much higher activity in hydrogenolysis than platinum. Because chromia is difficult to reduce and maintain in the zerovalent state, there are no measurements of its hydrogenolysis activity. However, the comprehensive studies of Sinfelt's group show that its neighbours, iron, cobalt and nickel, all have similar activities for alkane hydrogenolysis, and that these are ca. 10^3 times that of platinum *(14)*. In the absence of experimental measurements on chromium catalysts we must assume that it is also a much more active catalyst for hydrogenolysis than platinum. Thus, if chromium were present in the surface layer of the alloy particle we would expect an increase in hydrogenolysis activity rather than the decrease that is noted. For chromium-containing catalysts, this argument also invalidates the decoration model for the role of additives that has been proposed by Coq *et al.* (*7*, *8*) and by Strohl and King (*5*).

A possible role of the additive in promoting structural change should also be considered. Somorjai *et al.* have shown that hydrogenolysis of a range of hydrocarbons occurs at a more rapid rate on stepped and kinked planes than our flat surfaces (*31*), although there are no data for ethane or propane hydrogenolysis. Engstrom *et al.* have performed extensive studies of these molecules on nickel and iridium single crystals (*32–34*). Ethane hydrogenolysis is structure dependent, and slow on the close-packed (111) plane, where it is thought to occur only at defects. Reaction is more rapid on the more open (100) plane and accompanied by a significant decrease of the activation energy. For the platinum catalysts both EXAFS and electron microscopy suggest that the particles are spherical in the absence of chromium, and will therefore expose predominantly (111) surface planes. In the chromium-doped materials both techniques provide some evidence for the existence of rafts, which EXAFS suggests expose the (100) plane preferentially. Within the framework of structure sensitivity adopted by Engstrom *et al.*, this would be expected to cause an increase rather than a decrease in the hydrogenolysis activity.

The structural model for the doped platinum catalysts which we have proposed previously (*9*), and which is considered in detail in Part I (*13*), requires that the surface monolayer of the catalysts is entirely composed of platinum and that the chromium is present only in the subsurface layers. The evidence for the model comes from XPS and EXAFS measurements, from our LEISS studies of a bulk Pt–Cr alloy, from metallurgical considerations and from relevant surface science studies (*10–12*, *35*, *36*). From this model, it is clear that the role of the chromium additive is to modify the electronic properties of the active surface of the catalyst. Adsorption studies on platinum–cobalt and platinum–titanium alloy surfaces (*10–12*), provide an important clue to understanding our kinetic results. Alloying has been shown to reduce the strength of chemisorption of carbon monoxide on these surfaces below that found on pure platinum. The reason for this is not clear, but Rodrigez *et al.* have reported similar observations resulting from electronic interactions in Pd–Ti and Pd–Mo monolayer alloys (*37*). Bonding between platinum and the additive element appears to be stronger than that between platinum and platinum, and this is an important driving force in the "sandwich" surface segregation model (*35*). The chemisorption results suggest that an approximate sum rule may apply between the (Pt–Additive) and the (Pt–Adsorbate) bond strengths. The reduction of adsorption strength that is observed for carbon monoxide is equally expected to occur for other adsorbates such as alkanes.

The effect of the decrease in the strength of the chemisorption bond on catalytic performance can be deduced from the comprehensive set of kinetic information on hydrogenolysis provided by Sinfelt (*1*, *14*). Volcano relationships exist for the Group VIII metals, and platinum lies far towards the weak adsorption extreme. Also, the activation energies observed for platinum and the other relatively inactive metals are much higher than found for the highly active metals at the centre of the volcano plot. We therefore conclude that weak adsorption is correlated with a high activation energy for hydrogenolysis, and that decreasing the adsorption strength further will cause the activation energy to increase. This is exactly what is observed. Alloying with chromium causes a doubling of the activation energy for ethane hydrogenolysis, from 135 kJ mol^{-1} to 280–320 kJ mol − 1. For propane the increase is equally significant, from 76 kJ mol^{-1} to 120–150 kJ mol^{-1}. Evidence that alloying weakens chemisorption is also provided by the changes observed in the depth or extent of the hydrogenolysis of propane, as a result of alloying. In the temperature range where the results overlap, the Pt/H-ZSM-5 catalyst promotes more extensive deep hydrogenolysis, resulting in a higher methane/ethane ratio than is observed for the chromium-doped material.

For propane hydrogenolysis the increase in the activation energy leads to a marked decrease in the reaction rate over the whole temperature range of interest. For ethane, the activation energy also increases, suppressing the reaction completely at the lowest temperatures studied. However, inspection of Fig. 2 indicates that marked compensation between the activation energy and the preexponential terms is occurring, since the rate of hydrogenolysis becomes similar to that for the platinum-only catalysts at intermediate temperatures, and is significantly greater at the higher temperatures studied.

Although alloying increases the activation energy more for ethane than for propane, the extent of the compensation effect is also greater. Our EXAFS observations may provide a partial explanation of this larger compensation for ethane, since they show that some redispersion of the alloy particles occurs at the higher temperatures used for ethane hydrogenolysis. The change in dispersion is modest, from ca. 70% to ca. 90%, and thus insufficient to explain the magnitude of the increase in the preexponent for ethane, but the decrease in particle size that it represents will have associated electronic and structural consequences that may be important. Further structural and kinetic measurements will be necessary to explore this point.

Two final remarks should be made concerning aromatisation activity and the possible nature of the platinum–chromium interaction. From experiments reported here and results published earlier, it is evident that aromatisation of lower alkanes, including methane, proceeds more effectively on some Pt–Cr compositions than on Pt/H-ZSM-5. This is a consequence of the suppression of hydrogenolysis of certain hydrocarbons. Because aromatisation conditions are quite different from our experiments with hydrogenolysis (low partial hydrogen pressure in aromatisation, hydrogen excess in hydrogenolysis), we suggest that the compensation effect may not be operative in the aromatisation reaction, so conclusions drawn from the low-temperature hydrogenolysis studies will be valid for the aromatisation reaction. At higher chromium loadings, detrimental effects such as pore blockage by chromia may be enhanced and aromatics formation suppressed.

Platinum–chromium electronic interactions are very probable in small particles, either within the sandwich bilayer model or for randomly distributed chromium (*38*). Earlier studies postulated that charge transfer from chromium to platinum increased the platinum electron density (*22*). Similar conclusions have been derived from XPS observations for platinum alloyed with other electron-positive elements (Ti, Co) (*10–12*). We found no significant chemical shifts for Pt and Cr in the unsupported alloy (*13*). For platinum–chromium particles in zeolites positive shifts were observed in Pt 4f levels; these have been discussed extensively earlier (*13, 27*). The preliminary conclusion from Pt 4f peak analysis of 0.5–0.75 Cr/H-ZSM-5 is that the fraction of Pt($\delta+$) state decreases with respect to 0.5 Pt/H-ZSM-5.

CONCLUSIONS

The marked effects of chromium on the catalytic properties of Pt/H-ZSM-5 are unambiguously related to the formation of small (10–15 Å) alloy particles within the zeolite matrix. We postulate that segregation in such particles parallels that in platinum alloys diluted with chromium or ordered intermetallics, with the formation of a sandwich bilayer. This model explains the kinetic results, since the activation energy increases, suppressing the activity in the temperature range where the Pt catalysts are active. This implies that a platinum–chromium electronic interaction rather than simple dilution of platinum with chromium is responsible for the strong catalytic effects found both for hydrogenolysis and aromatisation of lower alkanes. The improvement of selectivity and stability of Pt–Cr containing catalysts for gasoline reforming, noted in the literature, can also be explained by this approach. EXAFS measurements on particle redispersion in the reaction mixture revealed that active site reconstruction can also influence the kinetic results.

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