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Characterization of Platinum–Zirconium Alloys by Competitive Hydrogenation of Toluene and Benzene

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The catalytic activities of Pt and $Pt_{1-x}Zr_x$ catalysts ($0 \leq x \leq 0.25$) supported on C or ZrO_2 have been studied in the hydrogenation of benzene either pure or in competition with toluene. The turnover frequencies of C_6H_6 hydrogenation are not sensitive to the alloy composition. In constrast, the ratio $K_{T/B}$ of the adsorption coefficients of toluene and benzene, derived from kinetic analysis of the competitive hydrogenation of these hydrocarbons, increases linearly with the alloy composition x. Since toluene is more of an electron donor than benzene, the higher the values of $K_{T/B}$, the higher the number of unoccupied states in the Pt *d* band. This is consistent with an electron transfer from Pt to Zr in agreement with the Engel–Brewer theory (L. Brewer, *Acta Metall.* **15**, 553 (1968)). The catalytic activity of $Pt_{0.75}Zr_{0.25}$ poisoned with sulfur is more easily regenerated because the electron-deficient platinum is less strongly bonded with electrophilic sulfur. © 1986 Academic Press, Inc.

INTRODUCTION

Benzene hydrogenation is a useful reaction to characterize the activity of metal-supported catalysts because its rate depends essentially upon the number of active sites, and these involve very few contiguous metal atoms (*1, 2*). However, since this reaction is only slightly sensitive to the structure of the catalysts it can hardly be used to probe the modifications of the electronic or geometric structure of the active sites. On the other hand, the relative reactivities of unsaturated hydrocarbons in competitive hydrogenation reactions depend essentially upon their relative adsorption coefficients (*3*). For a pair of hydrocarbons of different electronic structure, any change in the structure of the surface sites should result in a modification of the ratio of the adsorption coefficients. Conversely, the determination of the relative adsorption coefficients should provide information on the electronic structure of the surface atoms. Indeed, in previous papers (*4, 5*), the ratios $K_{T/B}$ of the adsorption coefficients of toluene and benzene on Pt catalysts have been determined from a kinetic analysis of the competitive hydrogenation of these hydrocarbons. For 1-nm Pt aggregates supported in a zeolite, the modifications of the electronic structure due to environment effects (support acidity, electric field of cation adsorbates) were clearly evidenced from the $K_{T/B}$ values. Since the toluene molecule is more of an electron donor than the benzene molecule, the larger the electron acceptor properties of platinum surface atoms, the larger the $K_{T/B}$ values.

It has been shown (*6–8*) that Pt–ZrO_2 catalysts supported on carbon or ZrO_2 and reduced between 623 and 1273 K under hydrogen give $Pt_{1-x}Zr_x$ alloys with $x = 0.25$ at 1273 K. According to the Engel–Brewer theory (*9*) the formation of alloys between platinum and zirconium involves an electron transfer of paired Pt *d* electrons to empty Zr orbitals which should decrease the population of the *d* shell of platinum.

In the present work the formation of the Pt–Zr alloys and the expected change in the electronic structure of platinum have been

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monitored with the $K_{T/B}$ values deduced from the study of the competitive hydrogenation of benzene and toluene. The sulfur resistance of platinum before and after alloying with zirconium was also studied by poisoning and regeneration experiments.

EXPERIMENTAL

Materials. The carbon-supported catalysts were prepared by impregnating the support (carbon black C Vulcan 6 from Cabot, $S_{BET} = 115\ m^2\ g^{-1}$) with a 50/50 water/ethanol solution of $H_2PtCl_6 \cdot 3H_2O$ (Caplain St André) and of $Zr(NO_3)_4 \cdot 5H_2O$ (Touzart et Matignon) under ultrasonic agitation. The atomic ratio was Pt : Zr = 3 : 1. The solution was freeze-dried under 1 to 10 Pa residual pressure from 210 to 298 K and then heated to 623 K. The $Pt-ZrO_2/C$ catalysts were obtained by heating under vacuum (10^{-3} Pa) at different temperatures between 673 and 1273 K (heating rate (4°C min^{-1}), the carbon support acting as reducing agent. The concentrations of Pt and Zr in the final catalysts were 20.6 and 3.1 wt%, respectively. A Pt/C catalyst (15.3 wt% Pt) was also prepared by heat treatment at 1273 K.

ZrO_2-supported catalysts were prepared in two steps. First $Zr(OH)_4$ was precipitated by ammonia from aqueous solutions of $ZrCl_4$ (Merck), washed, dried and calcined in air at 673 K. Then a 12.8 wt% Pt/ZrO_2 catalyst was obtained by impregnating the ZrO_2 support with $H_2PtCl_6 \cdot 3H_2O$ as described above and by reducing under hydrogen in the temperature range 623–1273 K.

Characterization of the catalysts. A detailed report on the characterization of the catalysts is given elsewhere (*6–8, 11, 12*). The main points are the following. The formation of $Pt_{1-x}Zr_x$ alloys was detected by X-ray diffraction. A solid solution of zirconium in the fcc platinum lattice was observed, and its composition was determined from Végard's law for Pt–Zr alloys previously established by Ott and Raub (*10*). The atomic fraction of Zr increases from $x = 0$ at 673 K to $x = 0.25$ at 1273 K. This bulk composition was checked in many single particles by high spatial resolution analytical electron microscopy with the Vacuum Generators STEM HB5. However, the surface composition of $Pt_{0.75}Zr_{0.25}/C$ determined by Auger spectroscopy was found to be twice as rich in zirconium as the bulk composition (*8, 11*). This was corroborated by H_2 and O_2 chemisorption measurements, and details of this study are given elsewhere (*8, 12*). The composition and the metal dispersion of alloys (percentage of surface Pt and Zr atoms over the total number of atoms) are given in Table 1. The oxidation state of the Zr surface atoms has not been determined unambiguously; ZrO surface species can be postulated from calorimetric measurements of the heat of O_2 chemisorption on $Pt_{0.75}Zr_{0.25}/ZrO_2$.

Catalytic reactions and poisoning experiments. Benzene hydrogenation and benzene–toluene competitive hydrogenation were carried out in a conventional flow reactor at atmospheric pressure. The reactants C_6H_6 and C_7H_8 (from Merck) were further purified by distillation and then kept in the presence of Na wires. Their partial pressures were set by two temperature-controlled saturators and by dilution with

TABLE 1

Percentage Dispersion of Pt/C, Pt + ZrO_2/C, and Pt/ZrO_2 Catalysts Reduced at Different Temperatures

Catalyst	Temperature of reduction (K)	Value of x in $Pt_{1-x}Zr_x$[a]	% Metal Dispersion[b] $= 100 \times \frac{Pt_s + Zr_s}{Pt + Zr}$
Pt/C	1273	0	2
Pt + ZrO_2/C	1273	0.25	4.5
Pt/ZrO_2	673	n.m.[c]	12.5
	773	n.m.	11.5
	873	0.05	9.5
	1023	0.14	6.5
	1273	0.25	5

[a] Measured by X-ray diffraction and using Végard's law.

[b] The $Zr_s/(Pt_s + Zr_s)$ atomic ratio is about twice as large as the x value in $Pt_{1-x}Zr_x$.

[c] Not measurable.

helium. The analysis of the reactants and products was performed by gas chromatography (flame ionisation detector Intersmat IGC-15). Compounds were separated with a Carbowax 20M on Chromosorb P column.

The reactions were performed at 298 K on 20–40 mg of catalyst. The benzene and hydrogen pressures were maintained constant ($P_{C_6H_6} = 0.5$ kPa; $P_{H_2} = 39.5$ kPa) and the toluene pressure was varied between 0 and 0.25 kPa. The total gas flow was 9 l h^{-1} and the conversion of hydrocarbon was less than 10%. Before reaction the samples were reactivated under hydrogen flow for 3 h at their temperature of reduction. Cyclohexane and methylcyclohexane were the only products detected.

The resistance to sulfur poisoning was examined on the Pt/ZrO_2 catalysts reduced at 673 K (Pt nonalloyed) and 1273 K ($Pt_{0.75}Zr_{0.25}$). Two kinds of experiment have been performed: (1) The rate of benzene hydrogenation was measured following the introduction in the reactant flow of successive doses of 5 cm^3 of H_2S diluted in H_2 (1100 ppm); (2) the activities after total poisoning were measured after regeneration by heating the catalysts in H_2 flow for 2 h at 673 K (Pt and Pt–Zr alloy) and at 1023 K (Pt–Zr alloy).

RESULTS AND DISCUSSION

Benzene Hydrogenation

The rate of benzene hydrogenation has been measured on Pt/C, $Pt_{0.75}Zr_{0.25}$/C, and Pt/ZrO_2 catalysts reduced at different temperatures. The turnover frequencies (TOF/s^{-1}) were calculated per surface platinum atoms determined from chemisorption measurements (Table 1). They are given in Fig. 1 as a function of the alloy composition determined from the X-ray diffraction pattern.

The TOF on Pt/ZrO_2 catalyst reduced at 673 K, i.e., before alloying, is 20×10^{-3} s^{-1} and is similar to that found previously on Pt/SiO_2 catalyst. Thus, the ZrO_2 support does not modify the activity of platinum in benzene hydrogenation, unlike the CO + H_2 reaction (*13*). At higher reduction temperatures, i.e., as the $Pt_{1-x}Zr_x$ alloy composition increases from $x = 0$ to $x = 0.25$, the TOF does not change significantly (Fig. 1). Thus, the Zr atoms or ZrO_x species on the surface are inactive in the reaction and do not perturb the activity of Pt surface atoms by ligand effects or by ensemble effects. This is not surprising since benzene hydrogenation requires very few contiguous sites. In contrast, it has been shown that alloying Pt with Zr results in a marked decrease of the rate of ethane hydrogenolysis because this reaction requires a large ensemble of adsorption sites (*7*, *8*).

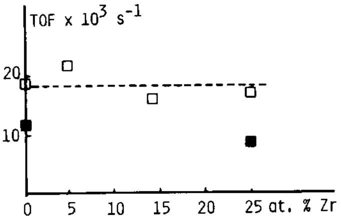

FIG. 1. Hydrogenation of benzene at 298 K. Turnover frequency per exposed Pt_s atom, as a function of alloy composition (at.% Zr). Dashed line: Pt/ZrO_2 reduced between 673 and 1273 K. Filled symbols: Pt/C and $Pt_{0.75}Zr_{0.25}$/C.

The activity of the Pt/C catalyst is about half that of Pt/ZrO_2 (Fig. 1). Diffusional limitation cannot account for the lower activity since the C Vulcan 6 support is not microporous and the activation energy of the reaction (46 kJ mol^{-1}) is similar to that measured on other supports. The lower activity could be due to a partial contamination of the metal surface by impurities from the carbon support but so far no information on the nature of these impurities is available. The TOF of $Pt_{0.75}Zr_{0.25}$/C is similar to that found on Pt/C; thus alloying with Zr does not change the activity of platinum in benzene hydrogenation on both supports (C or ZrO_2).

Competitive Hydrogenation

The analysis of the kinetic data of the competitive hydrogenation of benzene and toluene used to derive the ratio $K_{T/B} = b_T/b_B$ of the adsorption coefficients of toluene (b_T) and benzene (b_B) has been described in a previous paper (*4*, *5*). It is also given in the Appendix.

The competitive hydrogenation reactions were carried out on the Pt–ZrO_2/C and Pt/ZrO_2 catalysts reduced at different temperatures. It was checked that there is a zero reaction order with respect to the hydrocarbon pressure and that the final results do not depend upon the hydrogen pressure. The ratios V_B°/V_B (V_B° and V_B are the rates of C_6H_6 hydrogenation in the absence and in the presence of toluene, respectively) are given as a function of the ratios of the partial pressures P_T/P_B in Figs. 2 and 3 for the different catalysts. In all cases, the data points give a straight line intersecting the ordinate axis at $V_B^\circ/V_B = 1$ as expected from the linear transform $V_B^\circ/V_B = 1 + K_{T/B}$ (P_T/P_B) (Eq. (1) in the Appendix). The curves corresponding to Pt–ZrO_2/C and Pt/ZrO_2 catalysts reduced at different temperatures are collected in Figs. 4 and 5, respectively. The linear transforms obtained previously (*5*) with Pt/SiO_2 and PtHY catalysts are also given in Fig. 5. The values of $K_{T/B}$ are plotted as a function of the alloy composition determined from the X-ray diffraction pattern in Fig. 6.

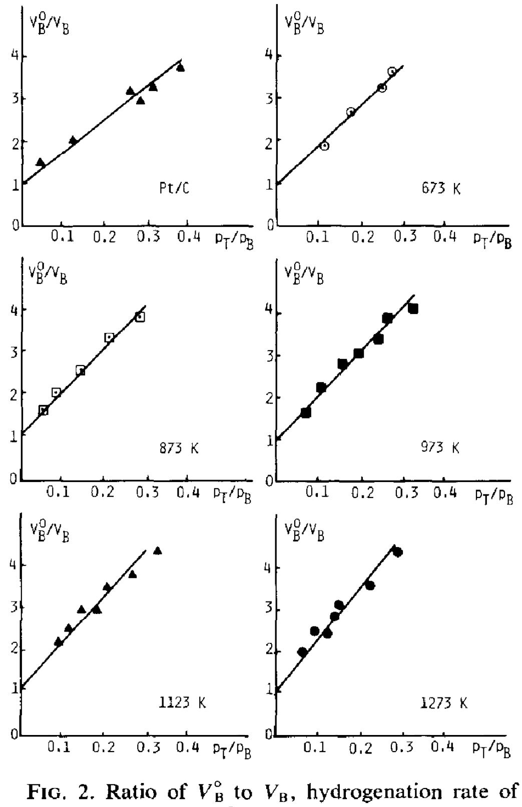

FIG. 2. Ratio of V_B° to V_B, hydrogenation rate of benzene in absence (V_B°) or in presence (V_B) of toluene, as a function of p_T/p_B. Pt/C and Pt + ZrO_2/C heat treated *in vacuo* at 1273 K (Pt/C) or between 673 and 1273 K (Pt + ZrO_2/C).

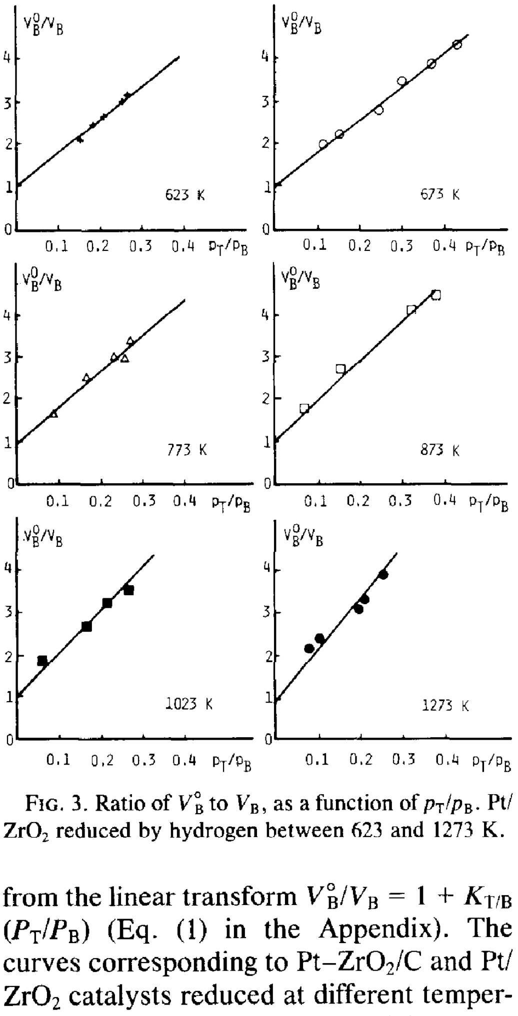

FIG. 3. Ratio of V_B° to V_B, as a function of p_T/p_B. Pt/ZrO_2 reduced by hydrogen between 623 and 1273 K.

The slope $K_{T/B}$ of the linear transform gives a measure of the relative affinity of the toluene and benzene molecules for the surface platinum atoms. Since toluene is more of an electron donor than benzene, the higher the electron acceptor properties of the platinum atoms, the higher the value of $K_{T/B}$. Accordingly Tri *et al.* (*5*) have attributed the increase of $K_{T/B}$ in the series Pt/SiO_2 < Pt/SiO_2 + H_2S < PtHY zeolite < PtCeY < PtHY + H_2S to the increasingly

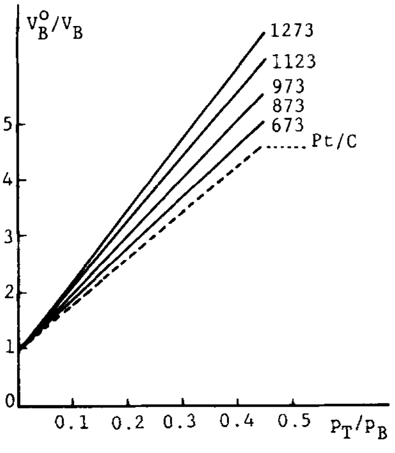

FIG. 4. Ratio of V_B° to V_B as a function of p_T/p_B. Catalysts: Pt/C heat treated *in vacuo* at 1273 K, and Pt + ZrO_2/C (atomic ratio of Pt/Zr = 3/1) heat treated *in vacuo* between 673 and 1273 K.

higher electrophilic or electron-deficient character of platinum in these catalysts.

From Figs. 4, 5, and 6 it is noteworthy that the $K_{T/B}$ values corresponding to Pt/ZrO_2 reduced at 673 K and to Pt/C are similar (ca. 8) to that found previously on platinum supported on SiO_2 which is generally considered as an inert support. The electronic state of platinum supported on ZrO_2 or C is not modified but this does not mean that these supports are inert; rather, because of the low dispersion of platinum, any possible electron transfer cannot be detected.

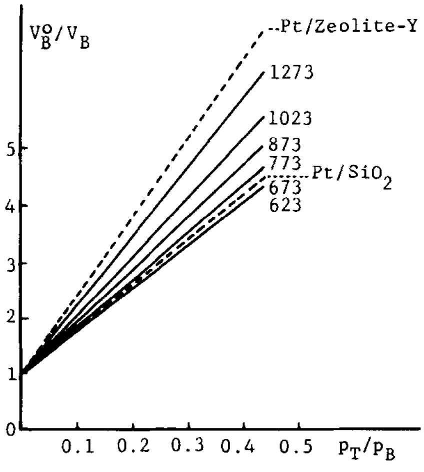

FIG. 5. Ratio of V_B° to V_B as a function of p_T/p_B. Catalysts: Pt/ZrO_2 reduced by hydrogen between 623 and 1273 K (solid lines), 6.3 wt% Pt/SiO_2 and 4.4 wt% Pt/zeolite-Y catalysts (dashed lines).

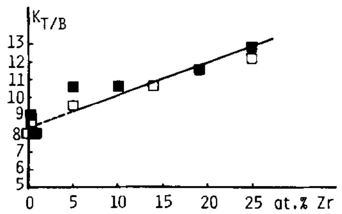

FIG. 6. Variation of $K_{T/B}$, ratio of the toluene and benzene adsorption coefficients, as a function of alloy composition (at.% Zr) determined by XRD measurements. ■, Pt/C and $Pt_{1-x}Zr_x$/C; □, Pt/ZrO_2 and $Pt_{1-x}Zr_x$/ZrO_2.

The data points on Fig. 6 at 0% Zr correspond to the Pt/ZrO_2 catalysts reduced at 623, 673, and 773 K (Fig. 5) and to Pt/C and Pt–Zr/C reduced at 673 K (Fig. 4). In this temperature range X-ray diffraction analysis was not sensitive enough to detect the alloy formation (no significant variation of the Pt lattice parameter); however, the increasing values of $K_{T/B}$ reflect the onset of alloy formation. Although there are only small variations in $K_{T/B}$ values, the chemisorptive properties are deeply modified in this temperature range (*8*, *12*) especially with a marked decrease of the hydrogen over oxygen chemisorption ratio. Similar effects were found when platinum was alloyed with small amount of ruthenium (*14*).

The incorporation of zirconium in the platinum lattice leads to higher $K_{T/B}$ values (Fig. 6); thus for $Pt_{0.75}Zr_{0.25}$, $K_{T/B}$ = 13, a value similar to that found for electron-deficient, 1-nm Pt aggregates in Y zeolites (*5*).

Following the same line of argument as previously (*5*), the higher $K_{T/B}$ values observed upon alloying can be attributed to an electron transfer from platinum to zirconium which depletes the density of charge on Pt. This is in agreement with the theory of Engel and Brewer for alloys of this type (*9*). However, the interpretation in terms of electron transfer is a crude approximation.

Rather, a change in the local density of states on platinum atoms in the alloy should be considered, the lower the density of states, the higher the $K_{T/B}$ values. Similarly in a recent study of Group VIII metals supported on silica we have shown that the $K_{T/B}$ values are inversely proportional to the density of states at the Fermi level (*15*).

If the density of charge on platinum is lower in the Pt–Zr alloy, one should expect a positive shift of the XPS binding energies. Indeed a +0.7-eV shift was observed between Pt/SiO_2 and PtNaHY (*16*) but none was detected between Pt/C and $Pt_{0.75}Zr_{0.25}$/C although both pairs of catalysts give a similar shift of $K_{T/B}$. This is probably because the Pt–Zr alloys have not been reactivated under hydrogen before XPS measurement. In fact, the very first layers of the $Pt_{0.75}Zr_{0.25}$ alloy surface have been shown to segregate in Pt and ZrO_2 after air exposure, and a subsequent reactivation under hydrogen at 973 K at least is necessary to restore the alloy to its initial state (*8*).

Figure 6 shows that the $K_{T/B}$ values increase linearly with bulk alloy composition. Since $K_{T/B}$ is sensitive to surface composition it can be concluded that either the surface and bulk composition are similar or that there is a constant ratio between surface and bulk compositions. The latter hypothesis is confirmed by chemisorption measurements on the alloys of different composition and by low-energy Auger spectroscopy on $Pt_{0.75}Zr_{0.25}$/C (*8, 12*). These techniques indicate that the surface composition is twice as rich in zirconium as the bulk composition. Interestingly, this ratio is constant over the whole range of alloy composition.

Resistance to Sulfur Poisoning

The effect of H_2S adsorption on the rate of benzene hydrogenation is illustrated in Fig. 7 where the ratios V_B/V°_B (activity after poisoning over initial activity) have been plotted as a function of the number of H_2S molecules adsorbed per surface platinum atom. It is assumed that all the H_2S increments were adsorbed on the metal particles.

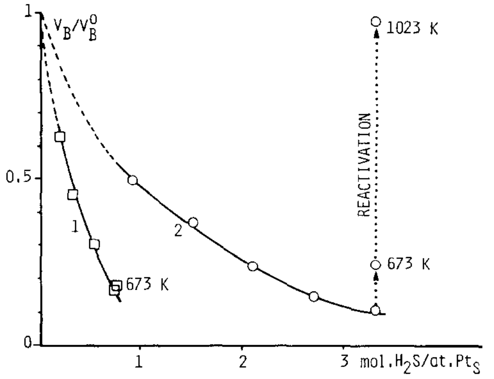

FIG. 7. Relative rate of benzene hydrogenation (V_B/V°_B, activity after poisoning over initial activity) as a function of the number of H_2S molecules introduced per exposed Pt atom. Curve 1: Pt/ZrO_2; curve 2: $Pt_{0.75}Zr_{0.25}/ZrO_2$. Effects of retreatment by hydrogen of the poisoned catalysts at 673 K (Pt and Pt–Zr alloy) or 1023 K (Pt–Zr alloy).

The deactivation of Pt/ZrO_2 reduced at 673 K (curve 1, Fig. 7) is much faster than that of $Pt_{0.75}Zr_{0.25}/ZrO_2$ (curve 2, Fig. 7). This is not a definitive proof for a higher sulfur resistance of alloyed platinum with respect to pure platinum because surface zirconium atoms can participate in the H_2S chemisorption. Since the surface concentration of Zr is equal to that of Pt, one might anticipate that the deactivation of $Pt_{0.75}Zr_{0.25}$ would be at least half that of Pt/ZrO_2; actually it is one-third.

A more convincing evidence for the higher sulfur resistance of the Pt–Zr alloy is the easier regeneration of its catalytic activity with respect to that of pure platinum. Indeed, Fig. 7 shows a significant reactivation of the poisoned Pt–Zr alloy following a 673 K hydrogen treatment whereas the activity of the Pt catalyst is not regenerated. Moreover, the activity of the alloyed catalyst is completely regenerated upon treating under hydrogen at 1023 K (Fig. 7). Therefore, it can be concluded that the Pt–S bond strength is weaker when the Pt atoms are alloyed with zirconium. This can be related to the electron deficiency of Pt atoms which lower the binding energy with electrophilic adsorbates like sulfur. A similar interpretation was given earlier (*17*) to account for the easier regeneration of sulfur-poisoned Pt aggregates supported in zeolites.

CONCLUSIONS

1. The turnover frequency of benzene hydrogenation on $Pt_{1-x}Zr_x$ alloy ($0 < x \leq 0.25$) supported on ZrO_2 or on carbon does not change significantly as a function of x. Thus, the dilution of Pt atoms by ZrO_x surface species has no effect because benzene hydrogenation requires few contiguous adsorption sites.

2. The ratio $K_{T/B}$ of the adsorption coefficients of toluene and benzene increase linearly with the alloy composition from $x = 0$ to $x = 0.25$. Since the toluene molecule is more of an electron donor, the higher $K_{T/B}$ values suggest that the platinum atoms in the alloys are more electron acceptor. This is consistent with an electron transfer from Pt to Zr, in agreement with the Engel–Brewer theory. However, the higher $K_{T/B}$ values should rather be interpreted in terms of the modification of the local density of states of surface platinum atoms in the alloy.

3. The catalytic activity of $Pt_{0.75}Zr_{0.25}$ poisoned with sulfur is more easily regenerated because the lower density of charge on alloyed platinum decreases the bond strength with electrophilic sulfur.

4. The ratio $K_{T/B}$ derived from the kinetic analysis of the competitive hydrogenation is a sensitive probe to monitor the change in the electronic structure of the metal upon alloying. This technique would allow the detection of the formation of Pt–Zr alloy in catalytic systems with smaller metal concentration and higher metal dispersion, i.e., when X-ray diffraction is not sensitive enough.

APPENDIX: KINETIC ANALYSIS OF THE COMPETITIVE HYDROGENATION (5)

Let V°_{B} and $V_{B(T)}$ be the rates of benzene hydrogenation at $P_T = 0$ and P_T, variable respectively (P_T = toluene partial pressure). Assuming (i) a competitive adsorption of C_6H_6 and C_7H_8 for the same sites on the metal surface and (ii) a zero reaction order with respect to P_B and P_T results in the Langmuir rate laws

$$V^{\circ}_{B} = k_B b_B P_B/(1 + b_B P_B) \simeq k_B$$

$$V_{B(T)} = k_B b_B P_B/(1 + b_B P_B + b_T P_T) \simeq k_B b_B P_B/(b_B P_B + b_T P_T)$$

where k, b, and P are the rate constant, adsorption coefficient, and partial pressure, respectively, of C_6H_6 (B) and C_7H_8 (T). The hydrogen partial pressure was considered as a constant function in the rate laws and was omitted.

The ratio of these equations becomes

$$V^{\circ}_{B}/V_{B(T)} = 1 + (b_T b_B)(P_T/P_B). \qquad (1)$$

The slope of the linear transform (1) gives the ratio $K_{T/B} = b_T/b_B$ of the adsorption coefficients.

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