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Skeletal Reactions of Neopentane over Supported Platinum–Gold Catalysts

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Skeletal reactions of neopentane have been studied over a range of supported platinum–gold catalysts. The activation energy and frequency factor for the overall reaction rise with increasing gold content, and these changes are most pronounced in the gold-rich part of the composition range. The selectivity for isomerization passes through a maximum at an intermediate composition. This behavior is interpreted in terms of two different reaction mechanisms which require different types of active sites. The active sites are identified as different ensembles of surface platinum atoms, and ensemble probabilities at various gold contents have been estimated by computer simulation experiments for comparison with reaction data. Reaction selectivity is influenced by both ensemble availability and surface hydrogen concentration.

Skeletal reactions of saturated hydrocarbons have been extensively studied over various platinum catalysts (*1*, *2*), and more recently this type of reaction has been extended to supported platinum–gold catalysts (*3*, *4*). However, this has been confined to the composition range ≤ 15 mol% platinum.

In recent work (*5*), a number of supported platinum–gold catalysts were characterized in terms of surface composition and metallic particle size for overall composition in the range ≥ 15 mol% platinum: we have therefore studied skeletal hydrocarbon reactions over these catalysts with a view toward seeking a correlation between the reaction parameters and catalyst structure. In this work we have used neopentane because this is an archetypal reactant for a bond-shift process and has not been studied previously over this type of catalyst.

EXPERIMENTAL

The preparation, characterization, and surface properties of the supported platinum–gold catalysts have been described elsewhere (*5*). The characterization parameters and the overall compositions in the range $1.0 \geqslant X_{(T)Pt} \geqslant 0.15$ are summarized in Table 1. In all cases the support was Degussa 200 Aerosil (200 $m^2\ g^{-1}$). It should be noted that at the overall composition Pt15, Au85 the value quoted for $X_{(S)Pt} = 0.17$ is a nonequilibrium value. However, as reported previously (*5*), the achievement of surface equilibration at this composition is an extremely difficult and protracted process, and for the present work this catalyst was used in the nonequilibrated condition (referred to as the "standard" condition in the previous description (*5*)).

The reactions were carried out using a gas flow reactor. The apparatus and technique have been described previously (*6*). Neopentane reactant was drawn as a gas directly from a cylinder. The normal reaction mixture contained hydrogen and hydrocarbon in the molar ratio of 20/1 to prevent surface poisoning by carbon residues, and the reaction was carried out at 1 atm pressure.

The analytical technique and the method for evaluating reaction rates have been described previously (*6*).

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TABLE 1

Details of Catalysts

Catalysts[a]	$\bar{d}$[b] (nm)	$X_{(s)Pt}$[c]
Pt100, Au0; 0.9 wt% metal	4.0 ± 0.3	1.0
Pt98, Au2; 1.0 wt% metal	4.0 ± 0.3	0.92
Pt90, Au10; 0.9 wt% metal	4.0 ± 0.3	0.58
Pt67, Au33; 0.9 wt% metal	1.7 ± 0.2	0.43
Pt15, Au85; 1.0 wt% metal	2.0 ± 0.2	0.17

[a] Overall metallic compositions given in mol%.

[b] Average metallic particle diameter by electron microscopy (*5*).

[c] Mole fraction of platinum in the surface atomic layer.

RESULTS

Product distribution data are given in Table 2, and the corresponding Arrhenius plots for the variation of reaction rate (expressed per unit mass of total metal in the catalyst) with temperature are given in Fig. 1. The product distributions and reaction rates were obtained at low conversions, in all cases <10% and in most cases <1%, and at low contact times, ensuring negligible contribution from secondary reactions.

DISCUSSION

The Arrhenius plots in Fig. 1 yield values for the activation energies and frequency factors for the overall reactions. Values for the activation energies are contained in Fig. 2 as a function of surface composition ($X_{(S)Pt}$); (the correspondence between $X_{(S)Pt}$ and overall metallic composition is given in Table 1).

Since values for the average metallic particle size and surface composition are known, it is possible to express the reaction preexponential factor in rate units per surface platinum atom. The data so obtained are also given in Fig. 2. The parameters used in this conversion were: mean area per surface metal atom, 7.99×10^{-20} m^2; mean volume per metal atom, 1.593×10^{-20} m^3.

There is a large increase in both the activation energy and the preexponential factor when $X_{(S)Pt}$ decreases from 0.43 to 0.17. At $X_{(S)Pt} > 0.43$, the change of these parameters with composition is much slower; in-

TABLE 2

Data for Neopentane Reaction

Catalyst	Reaction temperature (K)	Reaction product[a] (%)[b]						Isomerization selectivity[c]
		M + E	P	i − B	n − B	i − P	n − P	
Pt100, Au0	553	12.1	3.7	29.5	4.3	50.4	—	50.4
	593	16.6	4.4	29.6	4.6	42.0	2.8	44.8
Pt98, Au2	553	8.8	2.0	23.4	1.6	64.2	—	64.2
	593	11.4	5.0	18.6	2.5	56.5	5.9	62.5
Pt90, Au10	573	5.3	2.6	12.1	—	80.0	—	80.0
	613	9.3	3.5	13.6	—	63.9	9.7	73.5
Pt67, Au33	573	10.0	3.1	20.5	—	60.4	6.0	66.4
	613	15.1	7.4	21.4	—	50.7	5.4	56.1
Pt15, Au85	589	16.5	4.6	41.1	—	37.8	—	37.8
	620	24.2	9.8	44.0	—	22.0	—	22.0

[a] Primary products at low conversions (0.5–4%): M, methane; E, ethane; P, propane; i-B, isobutane; n-B, *n*-butane; i-P, isopentane; n-P, *n*-pentane.

[b] Expressed as mol% of parent converted to indicated product.

[c] mol% of parent reacting to C_5 products.

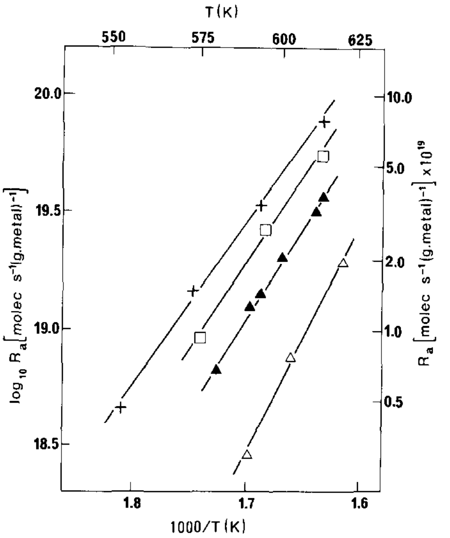


FIG. 1. Arrhenius plot for reaction of neopentane over platinum–gold/Aerosil catalysts. R_a, Total rate of neopentane reaction per unit mass of metal. +, Pt98, Au2; ▲, Pt90, Au10; □ Pt67, Au33; △, Pt15, Au85 (mol%). For catalyst characteristics see Table 1.

deed, the preexponential factor appears to be roughly constant in the range $0.92 \geqslant X_{(s)Pt} \geqslant 0.43$. This behavior of the activation energy and preexponential factor with $X_{(s)Pt}$ suggests that there is a change in the reaction mechanism occurring in the range $0.43 > X_{(s)Pt} > 0.17$.

We begin a qualitative discussion of the origin of this change in mechanism in terms of two factors: they are (i) the way in which the relative concentrations of different sized surface ensembles of platinum atoms are expected to vary with $X_{(s)Pt}$, and (ii) the way in which the neopentane reaction mechanism is known to change with varying platinum structure (*6*).

Surface Ensemble Probabilities

It is clear that as $X_{(s)Pt}$ decreases, the surface will contain an increasing proportion of small surface ensembles of platinum atoms. A quantitative estimate of the distribution frequency for surface platinum ensembles of various sizes has been made by computer simulation (*5*, *7*), assuming a value for the interchange energy parameter in the platinum–gold system of 15 kJ mol^{-1}. For the present purpose we confine ourselves to a (111) surface, since this contains the triangular atomic arrangement required for the triadsorption of neopentane in the manner discussed by Anderson and Avery (*8*) and Boudart and Ptak (*9*). It is convenient to express these data in terms of the way the ratio P_0/P_n varies with $X_{(s)Pt}$. Here P_0 is the average chance that, if a given surface site is occupied by a platinum atom, all surface nearest-neighbor atoms will be gold

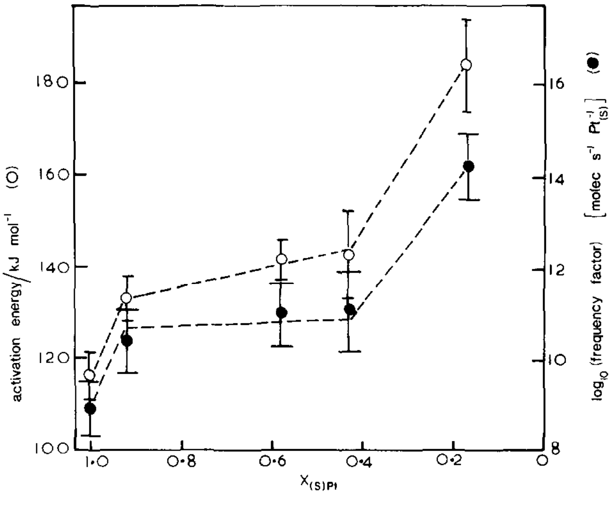
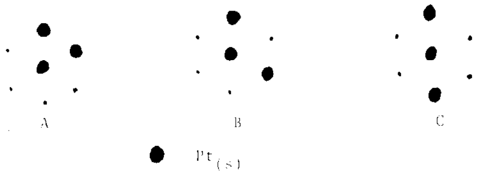


FIG. 2. Activation energies (○) and frequency factors (●) for total neopentane reaction as a function of mole fraction of surface platinum ($X_{(s)Pt}$) of Pt–Au/Aerosil catalysts.

(we shall refer to this as an "isolated surface platinum atom"), and P_n is the average chance that, if a given site is occupied by a platinum atom, *n contiguous* nearest-neighbor sites will be occupied by platinum atoms.

The meaning of P_n will be made clear by noting that the term "contiguous" specifies, for instance, the inclusion of configuration A in P_2, but excludes configurations B and C, below.



This is an arbitrary selection of ensemble configurations, and all others are readily obtained from the simulation experiments. This selection was made on the grounds that the ensembles so defined are sterically the most appropriate for the triadsorption of neopentane. The computed results are shown in Fig. 3 for temperatures of 600 and 400 K, and this also includes, for comparison, data obtained for a random mixing model. The data for 600 K are considered to be the best a priori estimate for the actual catalysts, since 600 K is close to the temperature of catalyst pretreatment, and at temperatures appreciably below this the rate of equilibration is likely to be too slow (cf. interdiffusion data for the platinum–gold system (*10*)).

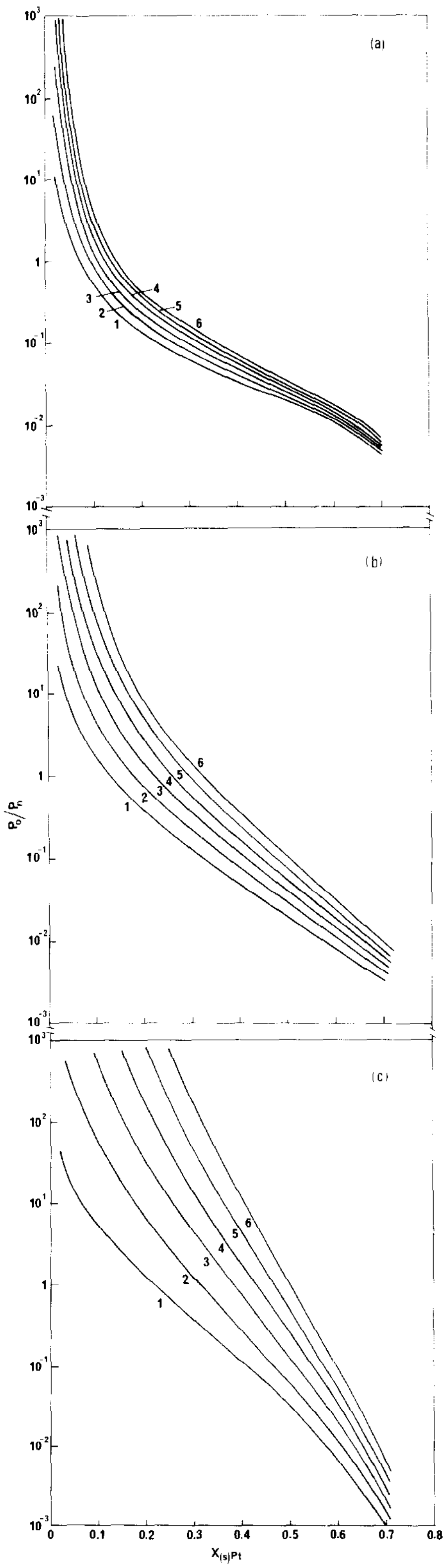


FIG. 3. Variation of P_0/P_n with $X_{(s)Pt}$, for (111) platinum-gold surface. P_0 is the average chance that, if a given surface site is occupied by a platinum atom, all surface nearest-neighbor atoms will be gold; P_n is the average chance that, if a given site is occupied by a platinum atom, n contiguous nearest-neighbor sites will be occupied by platinum atoms. The number on each curve defines n; that is, for example, curve 3 represents P_0/P_3. (a) Regular solution interchange energy 15 kJ mol^{-1}, 400 K; (b) regular solution interchange energy 15 kJ mol^{-1}, 600 K; (c) regular solution interchange energy zero (random mixing).

Neopentane Reaction Mechanism

There are two alternative pathways for the reaction of neopentane on platinum. This conclusion has been reached from a study of the way in which the reaction depends on $\bar{d}_{\mathrm{Pt}}$ (*6*). The activation energy increases from about 104 kJ mol^{-1} at $\bar{d}_{\mathrm{Pt}} \approx 7$ nm to about 150 kJ mol^{-1} at $\bar{d}_{\mathrm{Pt}} \approx 1$–$1.5$ nm, while the fraction of reaction proceeding by isomerization decreases substantially. The two reaction pathways are differentiated by the number of surface platinum atoms involved in the active site (*6*).

One mechanism, which is dominant with large platinum particles (or massive metal), requires a surface site consisting of more than one platinum atom, at which the adsorbed intermediate consists of diadsorbed or triadsorbed neopentane, and a (111) platinum surface appears to be particularly favorable for this process to lead to isomerization (cf. (*1*)). The second mechanism, which is dominant on very small platinum particles and for which hydrogenolysis is particularly favored, requires a surface site which contains a smaller number of platinum atoms than the first, probably a single platinum atom of lower than average coordination number, and proceeds with a substantially higher activation energy (and preexponential factor).

We turn now to the reaction of neopentane on platinum–gold catalysts. We propose that the mechanism which operates on platinum via a diadsorbed or triadsorbed intermediate also operates over platinum–gold but at large ensembles of platinum atoms, while the mechanism which predominates over very highly dispersed platinum also operates over platinum–gold but at very small platinum ensembles—possibly at isolated surface platinum atoms. When the surface is relatively dilute in platinum, very small platinum ensembles predominate, and this favors the reaction mechanism with a high activation energy and a relatively high selectivity to hydrogenolysis. When the surface is relatively rich in platinum, large platinum ensembles predominate, and this favors the reaction mechanism with a lower activation energy and a higher selectivity to isomerization.

This model may be compared with the surface platinum ensemble probability data contained in Fig. 3. To accord with the model, we would expect $P_0/P_{n'} \ll 1$ at $X_{(s)\mathrm{Pt}} \geqslant 0.43$, and $P_0/P_{n'} \gg 1$ at $X_{(s)\mathrm{Pt}} = 0.17$, where $n' + 1$ is the size of the surface platinum ensemble required for neopentane reaction by the low activation energy pathway. As indicated above, if this ensemble is defined solely in terms of the number of platinum atoms required to bind the adsorbed hydrocarbon intermediate (that is, ignoring the possible need for the ensemble also to provide adsorption sites for hydrogen), we expect $n' + 1$ to be in the region of 2 or 3 (cf. (8)).

The data in Fig. 3 show that for all three cases given there, the criterion $P_0/P_{n'} \ll 1$ at $X_{(s)\mathrm{Pt}} \geqslant 0.43$ is obeyed for $n' \geqslant 1$. However, for the regular solution model at 400 K, (Fig. 3a), the criterion $P_0/P_{n'} \gg 1$ at $X_{(s)\mathrm{Pt}} = 0.17$ cannot be met at any value of n': this latter criterion is met by the regular solution model at 600 K (Fig. 3b) for $n' \geqslant 4$, and by the random mixing model (Fig. 3c) for $n' \geqslant 2$. Under the present conditions one cannot expect to be able to establish more than a qualitative and indicative relationship between computed ensemble probability and reaction pathway because there are present too many factors which are unknown or subject to gross approximation: chief among these are ensemble size, and the crudity of the model used for ensemble probability calculation. Nevertheless it is clear that the ensemble probabilities required to accord with the reaction model occur within the limits of the 600 K regular solution model of Fig. 3b and the random mixing model of Fig. 3c.

The selectivity for the neopentane reaction varies with catalyst composition, and this is shown in Fig. 4 as the fraction of neopentane reacting by isomerization at 593 K as a function of $X_{(s)\mathrm{Pt}}$. Although the

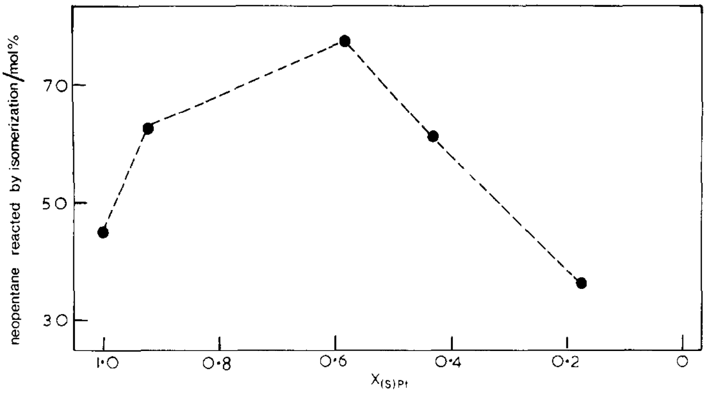


FIG. 4. Fraction of neopentane reacting by isomerization as a function of mole fraction of surface platinum ($X_{(s)Pt}$) in Pt–Au/Aerosil catalyst. Reaction temperature 593 K.

isomerization selectivity at $X_{(s)Pt} = 0.17$ is smaller than at $X_{(s)Pt} = 1.0$, in accordance with the reaction model given above, the isomerization selectivity passes through a maximum at an intermediate surface composition. This behavior probably arises by the operation of two factors.

In the platinum-rich range, large platinum surface ensembles are dominant, and the reaction is dominated by the pathway requiring diadsorbed or triadsorbed neopentane. However, in this composition range, as the gold content increases, the concentration of adsorbed hydrogen falls and the effect is to divert an increasing proportion of the reaction to isomerization, even though the nature of the dominant adsorbed reaction intermediate is unchanged. The effect of the influence of the concentration of adsorbed hydrogen on the reaction selectivity has been demonstrated previously for platinum catalysts (*6*). However, when the gold content becomes sufficiently high, the alternative reaction pathway which has a high intrinsic hydrogenolysis selectivity becomes increasingly important: this becomes dominant at $X_{(s)Pt} = 0.17$. Clearly, at an intermediate value of the surface composition, the hydrogenolysis selectivity will be a minimum, and the isomerization selectivity a maximum, in agreement with Fig. 4.

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