On the Intrinsic and Carbon-induced Selectivity of Platinum Catalysts

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The exceptional selectivity of Pt catalysts in the reactions of methylcyclopentane and neohexane has been shown using a pulse technique to be an intrinsic property of the catalysts and not purely carbon induced.

The selectivity of Pt catalysts in the skeletal reactions of hydrocarbons is substantially different from that of other group 8 metals,[1,2] varying with particle size and (self) poisoning, whereby the selfpoisoning by carbonaceous layers is itself a particle size sensitive factor.[1,2] Platinum differs from other group 8 metals in that it shows a high selectivity in the isomerization of 2,2-dimethylbutane (neohexane) and in the non-destructive reactions of methylcyclopentane. The latter reactions are interesting since ring-opening (highly prevalent on Pt) can take place in two ways: in the so-called 'non-selective' manner, leading to ratios of hexane : 2-methylpentane : 3-methylpentane of *ca.* 1 : 1 : 0.5 (which are near to the probabilities in random ring-opening and corresponding with thermodynamic stabilities), and in a 'selective' manner, leading to much lower hexane : 2-methylpentane ratios with values sometimes near to zero.[3] Diminishing particle size, diminishing size of Pt ensembles by alloying, and carbon deposition all cause a shift from the 'selective' to the 'non-selective' mode.[4—6] Since the shift to non-selective ring-opening caused by carbonaceous layer deposition is significant and other shifts in selectivities are also observed with other hydrocarbons such as hexane and neohexane, the question arises of whether the exceptional Pt selectivities are not due to carbonaceous layers, since under comparable conditions, the carbonaceous layers built up from adsorption of hydrocarbons are more extensive on Pt than on *e.g.* Rh or Ni.[7] The answer to this question can be found by applying the technique of reactions in pulses, which, in contrast with continuous flow experiments, allows us to determine the fractions S_i of pulses which are converted into the groups of

Table 1. Selectivities in methylcyclopentane reactions on Pt/SiO_2 (EuPtI) at 563 K.[a]

Pulse no.	$S_{hydrogenol.}$		$S_{ring\text{-}opening}$		$S_{arom.}$		$S_{retained\ C}$		Surface coverage[b]	
	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2
1	0.029	0.014	0.940	0.455	0	0.056	0.031	0.474	0.02	0.58
2	0.029	0.015	0.943	0.425	0	0.193	0.028	0.366	0.03	0.89
5	0.029	0.015	0.94	0.375	0	0.233	0.031	0.377	0.08	1.56
9	0.030	0.017	0.943	0.325	0	0.184	0.028	0.477	0.15	2.37

[a] H_2, N_2 indicates in which carrier the pulse is injected. [b] Surface coverage by carbon retained from the pulse; in equivalent monolayers at 563 K, on Pt/SiO_2(EuPtI).

Table 2. Selectivity ratios at 563 K showing variation with particle size, gas phase composition, and catalyst used.

	Carrier gas	EuPtI, $\bar{d}$ = 1.8 nm	10% Pt/SiO$_2$, $\bar{d}$ = 20.0 nm
Hexane: 2-MP[a]	H_2	1.03	0.24—0.33
Hexane: 2-MP	N_2	0.44—0.55	—
2-MP: 3-MP	H_2	2.7	2.84—3.06
2-MP: 3-MP	N_2	2.76—3.1	—

[a] MP = methylpentane.

gaseous products (hydrogenolysis, ring-opening, isomerization, aromatization reactions) and the fraction retained on the surface. A part of the retained hydrocarbons can be removed undetected in the period between pulses and a part always stays irreversibly adsorbed. 'Carbon' left on the surface determined as below is thus the maximum possible coverage of the surface by 'carbon.'

In the experiments performed, 5—10 mg of the catalyst stands under a steady state flow of a carrier gas, H_2 or N_2. A g.l.c., 6-way dosing valve is used and two openings form a loop through which a steady state reaction mixture flows: with methylcyclopentane, H_2/methylcyclopentane = 59; with neohexane, H_2/neohexane = 24. The pulse is created by flushing the content of the loop with the carrier gas (3 s). Using experimentally determined calibration factors, the g.l.c. response is converted into the fractions S_i of the total number of C atoms of the pulse converted into the various products. The surface area of the EuPtI was determined in ref. 8: its mean particle size is about 1.8 nm; the surface of the 10% Pt/SiO$_2$ has been determined by CO adsorption in this study: we found a mean particle size of about 20.0 nm. An equivalent monolayer of the carbonaceous layer is defined as the ratio of retained carbon atoms and metal surface atoms.

The results obtained are presented in Tables 1 and 2. Table 1 shows the analysis obtained with one of the samples of EuPtI ($\bar{d}$ = 1.8 nm) in several sequential pulses. The behaviour in the hydrogen rich and hydrogen lean atmosphere is compared. The corresponding surface coverage by the carbon retained (or rather the maximum possible values) is also given in Table 1. Table 2 shows hexane : 2-methylpentane ratios and 2-methyl- : 3-methyl-pentane ratios, as a function of particle size. These ratios did not vary too much with successive pulses.

The conclusions are straightforward. (i) In the continuous presence of hydrogen the destructive reactions and dehydrogenation (aromatization) are suppressed when compared with methylcyclopentane–H_2 pulses in N_2 as a carrier. (ii) Also with virtually free surfaces (for surface coverage by carbonaceous layer see Table 1) the selectivity in non-destructive reactions is high (Table 1) and the ratio hexane : 2-MP is also rather high (Table 2). None of these characteristic selectivities is thus 'carbon induced,' both are intrinsic properties of small Pt particles. Large particles show a lower hexane : 2-MP ratio, a fact which is already known from the literature.[3]

These conclusions are corroborated by the results obtained in the same T-range with neohexane. An extensive isomerization occurs with EuPtI even when the carbonaceous layer is still only of the order of 0.02 of an equivalent monolayer. Thus also in this case the high and exceptional selectivity of Pt is due to its intrinsic (and not carbon induced) property.

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