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The Structure and Activity of Silica-Supported Palladium–Cobalt Alloys

II. Skeletal Reactions of *n*-Hexane and Methylcyclopentane over Pd–Co/SiO_2 Catalysts

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n-Hexane and methylcyclopentane conversions appeared to be very useful tools for probing surfaces of bimetallic Pd–Co composites supported on silica. Very large changes in activity and selectivity constitute a good basis for diagnosing the extent of interaction between two metal components. The overall activity of cobalt is much higher than that of palladium; in particular, Co predominantly promotes hydrogenolysis of hydrocarbons, whereas other, nondestructive reactions are preferred over Pd and the Pd-richest alloy. A variety of information offers several "fingerprint-like" parameters which enable one to characterize additional properties of these composition regions (i.e., the range of 25–75 at% Co) as compared to neopentane conversion [Part I (W. Juszczyk, Z. Karpinski, D. Łomot, J. Pielaszek, Z. Paál, and A. Yu. Stakheev, *J. Catal.* **142,** 617 (1993)] This work confirms our earlier conclusions that the employed preparation method (incipient wetness coimpregnation technique) produces well-mixed Pd–Co alloy catalysts. Individual Pd-like properties promoting C_5-cyclic skeletal reactions (ring closure, isomerization) are observed up to 25% Co content only. © 1993 Academic Press, Inc.

INTRODUCTION

In Part I of this series (*1*), we reported results on the characterization of silica-supported Pd–Co alloys by using various physical (XRD, XPS) and chemical (TPR, chemisorption, neopentane conversion) methods. It was shown that coimpregnation of silica by the incipient wetness technique with higher amounts of metal salts (to give 10 wt% metal loading) followed by reduction at 380°C resulted in well-homogenized bimetallic catalysts. In addition, some surface enrichment in palladium was seen (*1*). Neopentane conversion used as a catalytic probe exhibited a maximum of isomerization selectivity for Pd-rich alloys. Such a catalytic behavior, very far from that characteristic of a physical mixture of Pd/SiO_2 + Co/SiO_2, strongly suggests the existence of interactions between two metals.

Alloy catalysts have been the subject of a large number of studies [see, e.g., Ref. (*2*)]. The basic question arising with multicomponent system(s) is whether any catalytic property absent with pure components is created, and if so, whether the effect is purely geometric or (also) electronic. An electronic interaction has not been excluded, either, when inactive metals are added to an active one (*3*). The electronic effect has been emphasized as being of primary importance in determining catalytic reactivity (*4*). As opposed to Pd–Au, both components of the Pd–Co binary system are catalytically active in alkane reactions. The Pd–Co system has not been the subject of detailed studies; we demonstrated in Part I (*1*) that an intimate interaction produced

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active sites possessing properties different from both pure Pd and Co. The aim of the present paper is to characterize these mixed catalysts with different model reactants.

Usually in the search for suitable catalytic probes one tries to employ reactions which are regarded as structure-sensitive, such as conversion of saturated hydrocarbons in the presence of hydrogen. The reactant structure exerts a great influence on the reactions expected (*4*). "Iso-units" and "C_2-units" have been proposed as main "archetypes" for various structures (*5*). The "C_5-unit" (containing five C atoms in a chain) has been proposed as a third archetype for alkane reactions (*6*). This unit can split off in hydrogenolytic reactions as a separate entity and may undergo C_5-cyclization and C_5-cyclic isomerization. There are essentially two opinions as regards the geometry of the C_5-cyclic surface intermediate: the Gault school proposes that it is standing almost prependicularly to the catalyst surface (*7*), while others (*8–10*) propose that it is lying flat as a nondehydrogenated intermediate (*8*), in a form something like cyclopentadiene (*9*) or as a unit losing a few hydrogen atoms by 1,3-interaction with the metal surface (*10*).

Reactions of alkanes with a longer carbon-chain provide more detail than shorter ones since more reaction paths are possible. For this reason we decided to employ reactions other than neopentane conversion for probing the surfaces of Pd–Co/SiO_2 catalysts. Our hope was that the information obtained from studies with *n*-hexane and methylcyclopentane (MCP) as model reactants, hopefully richer in details, would reveal additional characteristics of Pd–Co alloys. We observed rather moderate changes in the catalytic behavior (activity and selectivity) of Pd–Co/SiO_2 samples in the composition range between 25 and 75 at% Co for the reaction of neopentane in the presence of H_2. To the best of our knowledge, *n*-hexane and MCP reactions on Pd–Co alloys have not been studied earlier. The present work, therefore, is not only devoted to search for convenient probe reactions but also to collect new data on the catalytic chemistry of hydrocarbon reactions over the Pd–Co alloy system. Literature data are available on the product distribution obtained from hexanes over Pd black (*11*), Pd/Al_2O_3 (*12*), and also Pd–Au/Al_2O_3 (*13*) catalysts. Isomerization and hydrogenolysis characteristics of several metals, including Pd and Co, have been summarized (*10*).

EXPERIMENTAL METHODS

Catalysts

The preparation and pretreatment were described in Part I of this series (*1*). Briefly, silica gel (Serva, puriss, 80–100 mesh, acid washed) was coimpregnated with an aqueous solution of the metal chlorides via the incipient wetness technique to prepare monometallic Pd and Co and three bimetallic Pd–Co catalysts (atomic ratio of Pd-to-Co: 75 : 25, 50 : 50 and 25 : 75). The overall metal loading was 10 wt%.

Apparatus and Procedure

We used a pulse-microcatalytic reactor described elsewhere (*14*). The catalysts (0.025 g) were placed in a glass tube (I.D., 4 mm) attached directly to a Packard 427 gas chromatograph (3.2-m column packed with 18% squalane on Chromosorb P, 45-60 mesh).

The sample was pretreated in air at 300°C for 30 min before each experiment. After cooling to room temperature in helium the catalyst was reduced in a H_2 flow (30 ml/min) by heating at 8°C/min to 380°C, maintaining that temperature for 2 h, or, alternatively, 15 h. After reduction the catalyst was purged with helium (30 ml/min) at 500°C for 1 h. After cooling in helium to the lowest temperature of reaction (usually 260°C), three consecutive 1 μl pulses of *n*-hexane were injected onto the catalyst bed in the hydrogen stream (30 ml/min) and analyzed with the gas chromatograph. The temperature was gradually raised within one run from the lowest to the highest value (320°C)

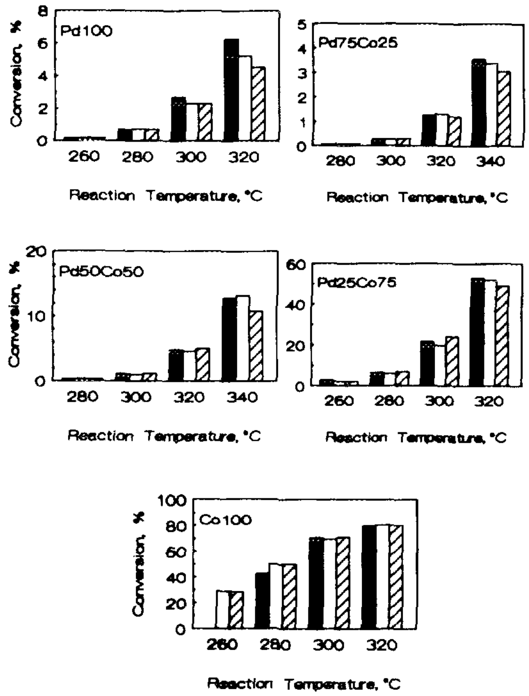

FIG. 1. Extent of conversion of *n*-hexane as a function of pulse number at various temperatures for different Pd–Co/SiO$_2$ catalysts: first pulse (solid bar), second pulse (open bar), and third pulse (lined bar).

with no intervening regeneration. Experiments with methylcyclopentane were carried out in the same way.

Turnover frequencies were calculated from extents of conversion in the manner described in Ref. (*14*), i.e., assuming a nearly square shape of pulses of *n*-hexane (methylcyclopentane) and the contact time = 1 s, a 1-μl pulse contained 5.3 × 10^{18} molecules of methylcyclopentane or 6.0 × 10^{18} molecules of *n*-hexane. Metal dispersions were taken from Part I of this series (*1*).

RESULTS

Catalytic Activity

Figures 1 and 2 show conversion changes with pulse number in the reactions of *n*-hexane and methylcyclopentane, respectively. As can be seen, the levels of activity are fairly stable. In order to avoid excessive data accumulation, we decided to use for presentation only kinetic results obtained for second pulses, without further reference to this fact.

Turnover frequencies, product distributions, and apparent energies of activation are presented in Table 1 (for *n*-hexane conversion) and Table 2 (for the MCP reaction). In addition, catalytic activities for *n*-hexane reaction at three temperatures are displayed as a function of Pd–Co alloy composition in Fig. 3. It is seen that the reaction rate changes with the alloy composition within a quite substantial range, with a minimum for Pd-richer alloys.

Figures 4 and 5 show Arrhenius plots for *n*-hexane and MCP reactions, respectively. The E_a values are rather close to each other, except for *n*-hexane over Co/SiO$_2$ and somewhat different from those reported in

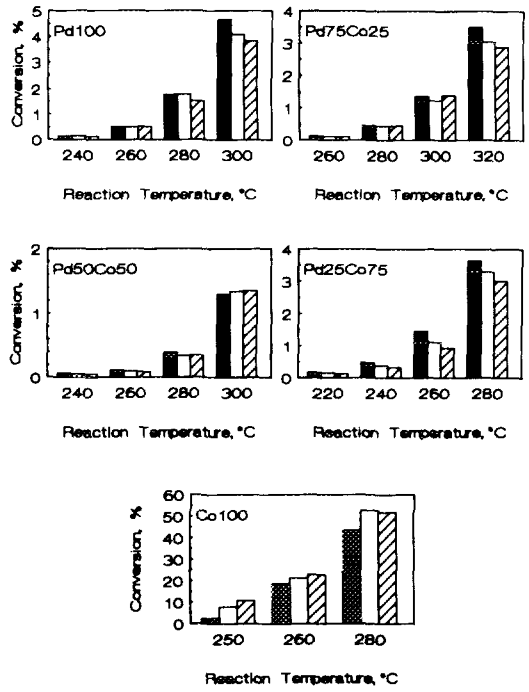

FIG. 2. Extents of conversion of methylcyclopentane as a function of pulse number at various temperatures for different Pd–Co/SiO$_2$ catalysts: first pulse (solid bar), second pulse (open bar), and third pulse (lined bar).

TABLE I

n-Hexane Conversion over 10 wt% Pd–Co/SiO$_2$ Catalysts: Turnover Frequencies, Selectivities, and Apparent Energies of Activation

Catalyst[a] (H/M[b])	*t* (°C)	TOF (1/s)	Selectivity (%)[c]				E_A (kcal/mol)
			$<C_6$	iC_6	MCP	Others	
Pd100 (0.50)	262	1.35×10^{-3}	64.6	14.0	21.4	—	7.6 ± 3.6
	281	6.07×10^{-3}	56.2	20.8	23.0	—	
	299	1.93×10^{-2}	51.8	28.4	19.8	—	
	321	4.40×10^{-2}	48.5	32.0	18.9	0.6	
Pd75Co25 (0.44)	280	5.11×10^{-4}	62.7	18.5	18.9	—	45.4 ± 2.3
	300	2.21×10^{-3}	45.9	18.9	35.2	—	
	321	1.11×10^{-2}	44.1	24.0	32.0	—	
	341	2.86×10^{-2}	45.9	25.6	26.6	1.9	
Pd50Co50 (0.27)	282	3.04×10^{-3}	98.8	1.2	—	—	43.9 ± 2.4
	299	9.62×10^{-3}	97.6	1.7	0.7	—	
	319	4.51×10^{-2}	96.1	2.0	1.9	—	
	341	1.29×10^{-1}	94.5	2.8	2.5	0.2	
Pd25Co75 (0.11)	260	5.21×10^{-2}	99.3	0.7	—	—	33.9 ± 1.1
	279	1.50×10^{-1}	99.0	0.9	—	0.1	
	299	5.04×10^{-1}	98.6	1.1	0.1	0.2	
	321	1.33	98.6	1.1	0.1	0.2	
Co100 (0.10)	262	6.71×10^{-1}	99.98	0.02	—	—	11.0 ± 2.1
	279	1.17	99.98	0.02	—	—	
	300	1.62	99.98	0.01	—	0.01	
	320	1.88	99.98	0.002	—	0.01	

[a] For catalyst designation, see text.

[b] Metal dispersion (D_H)—Ref. (*1*).

[c] Expressed as mol % in products: $<C_6$ = hydrogenolysis to shorter alkanes; iC_6 = isomers of *n*-hexane; MCP = methylcyclopentane; others = benzene and higher boiling hydrocarbons.

the literature: Co black gave an E_a value of ca. 22 kcal mol^{-1} for hydrogenolysis *n*-butane (*10*), while the values for *n*-butane and *n*-heptane over Pd were reported to be around 38 kcal mol^{-1}. Isomerization of butanes exhibited somewhat lower values (*10*).

Selectivity

Selectivities for hydrogenolysis, isomerization, and C_5-cyclization in the reaction of *n*-hexane over Pd–Co/SiO$_2$ catalysts are shown in Fig. 6. As expected from literature data (*10, 15*), cobalt exhibits almost pure hydrogenolysis characteristics. The hydrogenolysis selectivity remains almost unchanged up to 50% Pd content, but with more Pd present, it decreases abruptly. The ratio of hydrogenolysis-to-C_6 product formation changes even more strongly with the Pd bulk content (Fig. 7). This means that the minor loss in overall activity from Pd to Pd75Co25 is not accompanied with marked selectivity changes, but the subsequent gain in activity with increasing the Co content further is due entirely to the enormous enhancement of fragmentation. Figure 7 also contains data points calculated from the literature for Pd/Al$_2$O$_3$ (*12*); these are fairly close to the present values.

Selectivity aspects for hydrogenolysis are presented in Fig. 8. This figure presents details of the "depth" of hydrogenolysis over Pd–Co/SiO$_2$ catalysts, using the values of the "fragmentation factor," ζ (*15*), and the "fission parameter," M_f (*16*). By definition, ζ characterizes the depth of hydrogenolysis as the number of fragment molecules per

TABLE 2

Methylcyclopentane Conversion over 10 wt% Pd–Co/SiO$_2$ Catalysts: Turnover Frequencies, Selectivities, and Apparent Energies of Activation

Catalyst[a] (H/M[b])	t (°C)	TOF (1/s)	Selectivity (%)[c]				E_A (kcal/mol)
			$<C_6$	R.O.P.	Bz	Others	
Pd100	261	3.82×10^{-3}	1.4	98.6	—	—	33.3 ± 1.2
(0.50)	281	1.34×10^{-2}	1.5	97.7	0.8	—	
	300	3.06×10^{-2}	2.7	95.8	1.5	—	
Pd75Co25	280	3.39×10^{-3}	3.6	92.2	4.2	—	34.7 ± 2.0
(0.44)	299	9.33×10^{-3}	3.0	90.7	6.3	—	
	320	2.29×10^{-2}	5.3	89.1	5.3	0.3	
Pd50Co50	280	3.65×10^{-3}	73.0	22.0	5.0	—	32.9 ± 4.1
(0.27)	300	1.44×10^{-2}	75.1	18.4	5.0	1.5	
Pd25Co75	240	8.82×10^{-3}	74.5	25.5	—	—	27.2 ± 1.7
(0.11)	260	2.51×10^{-2}	76.4	23.0	—	0.7	
	280	7.46×10^{-2}	79.1	19.6	0.5	0.8	
Co100	249	1.63×10^{-1}	98.0	1.9	—	0.1	33.1 ± 6.4
(0.10)	260	4.40×10^{-1}	98.8	1.1	—	0.1	
	281	1.09	99.7	0.3	—	—	

[a] As in Table 1.

[b] Metal dispersion (D_H)—Ref. (1).

[c] Expressed as mol% in products. $<C_6$ = hydrogenolysis to shorter alkanes; R.O.P. = ring opening products; Bz = benzene.

molecule of feed split up:

$$\zeta = \frac{\Sigma C_i}{\Sigma (i/n) C_i}.$$

M_f, in turn, relates the higher fragments to the amount of methane,

$$M_f = \frac{\sum_{i=2}^{n-1} (n-i) C_i}{C_1},$$

and, by doing so, permits one to distinguish between "terminal" ($M_f \approx 1$), multiple ($M_f > 1$) and random or internal ($M_f < 1$) splitting.

Figure 8a shows the variation of ζ as a

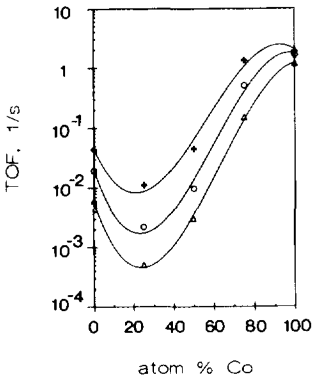

FIG. 3. Turnover frequency vs the Co bulk content in n-hexane conversion at 280°C (triangles), 300°C (circles), and 320°C (crosses).

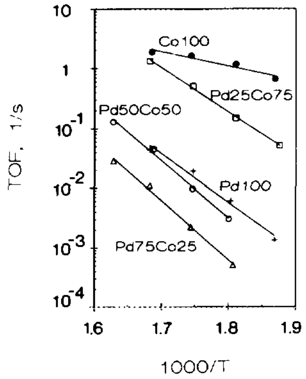

FIG. 4. Arrhenius plots for n-hexane conversion over Pd–Co/SiO$_2$ catalysts.

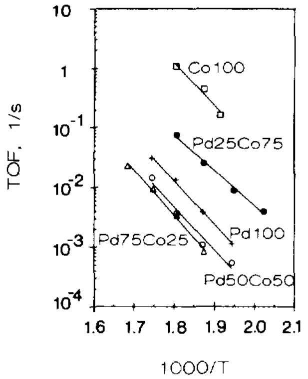

FIG. 5. Arrhenius plots for methylcyclopentane conversion over Pd–Co/SiO_2 catalysts.

function of the alloy composition, whereas Fig. 8b displays analogous changes for M_f.

Selectivities for hydrogenolysis (producing $<C_6$ fragments), ring opening, and aromatization in the reaction of methylcyclopentane over Pd–Co/SiO_2 catalysts are shown in Fig. 9. Again, cobalt shows remarkably high selectivity for fragmentation.

Figure 10 presents changes in the ratio of 2-methylpentane-to-3-methylpentane (2MP/3MP) formation in the reactions of *n*-hexane (a) and MCP (b). This ratio was used to point out the relationship of C_5-cyclization and (predominantly C_5-cyclic) isomerization over various Pt catalysts (*17*). Again, data points obtained over Pd/Al_2O_3 (*12*) are in a remarkable agreement with the present results.

DISCUSSION

Catalytic Activity

Figure 3 shows pronounced changes in overall activity of Pd–Co catalysts in *n*-hexane conversion. The catalytic activity of Co/SiO_2 is higher by two orders of magnitude at 260°C than that of Pd/SiO_2. Because Pd75Co25 is even less active than Pd100, these major changes in activity with the alloy composition constitute a promising basis for future probing of bimetallic Pd–Co surfaces. Again, as in the case of neopentane conversion (*1*), the fact of obtaining a very pronounced minimum (or maximum) in the relation of a catalytic parameter with alloy composition is very fortunate because it immediately shows that the interactions between two alloy components bring about changes in catalytic properties basically different from those observed in the case of a physical mixture (*1*).

At higher temperature, 320°C, the relation between activity and alloy composition is not so suggestive as at 280°C. This is caused by the much lower apparent energy of activation (E_a) for the *n*-hexane reaction over Co100 than in the case of other catalysts

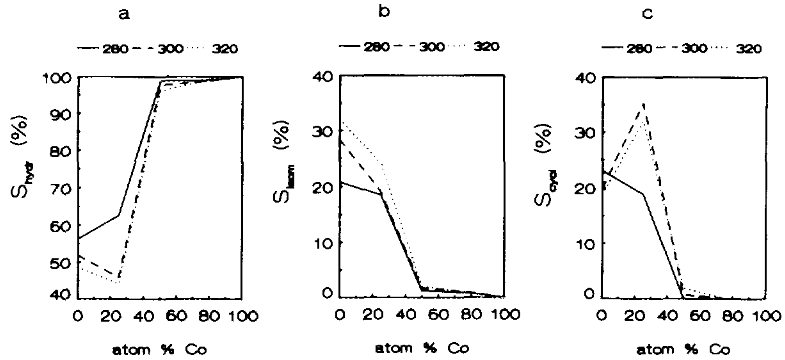

FIG. 6. Selectivities for various reactions in *n*-hexane conversion over Pd–Co/SiO_2 catalysts: (a) hydrogenolysis, (b) isomerization, and (c) cyclization, at 280°C (solid line), 300°C (broken line), and 320°C (dotted line).

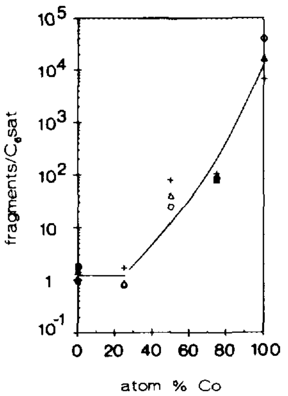

FIG. 7. The hydrogenolysis-to-C_6-saturated hydrocarbon formation in *n*-hexane conversion as a function of the Co bulk content: at 280°C (crosses), 300°C (triangles), and 320°C (circles). The points (just above 1 with pure Pd) denoted with an X (270°C) and a filled circle (350°C) have been taken from the literature (*12*).

(Table 1 and Fig. 4). This fact is indicative of self-poisoning of cobalt by carbonaceous residues (*18*). Another explanation could be that, in the case of the *n*-hexane reaction over Co100, we worked at a very high level of conversion (up to ca. 80% at 320°C). However, in the case of MCP conversion, the apparent E_a is comparable to the corresponding values for Pd and Pd–Co alloy catalysts, the E_a for pure metals being, indeed, higher with MCP (Table 2 and Fig. 5). It should be said that the MCP reaction was investigated at lower temperature than *n*-hexane conversion, at somewhat lower conversion, and, consequently, with lesser self-poisoning (Fig. 2 vs Fig. 1 and Table 2 vs Table 1).

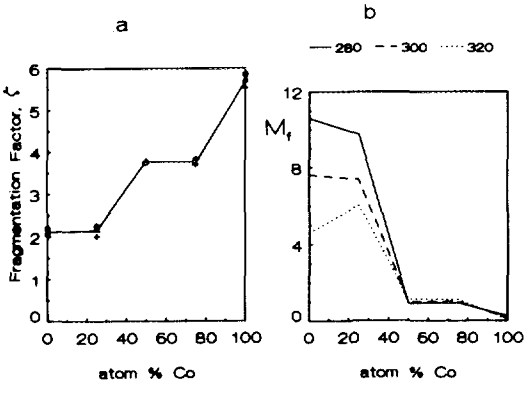

FIG. 8. *n*-Hexane hydrogenolysis over Pd–Co/SiO_2 catalysts: (a) fragmentation factor, ζ, at 280°C (crosses), 300°C (triangles), and 320°C (circles); and (b) fission parameter, M_f at 280°C (solid line), 300°C (broken line), and 320°C (dotted line).

Selectivity

It is seen (Fig. 6) that the selectivity for hydrogenolysis of *n*-hexane is almost 100% for Co100, in agreement with earlier data (*10, 18, 19*). The level of hydrogenolysis selectivity remains high for the two Co-rich alloys and drops by factor of 2 from Pd50Co50 to Pd75Co25. Some separated Co species may be responsible for increased fragmentation over Pd25Co75. The high level of hydrogenolysis selectivity for Pd50Co50/SiO_2 is rather surprising if one recalls the results obtained in neopentane conversion on the same series of catalysts (*1*). For neopentane, although Co100 gave almost 100% hydrogenolysis, its alloying with Pd resulted in an exceptional increase of isomerization selectivity (>60%), at the expense of hydrogenolysis ability. This difference between reactivity of neopentane and *n*-hexane over Pd–Co alloy surfaces must result from different modes of activation of the two molecules. Neopentane is the "archetype molecule" for 1,3-interaction (*5*); its hydrogenolysis was attributed to triadsorbed intermediates on sites consisting of three atoms (*20*). This type of hydrogenolysis has been claimed to have a higher activation barrier than that where 1,2,3 interaction is possible, such as in the case of *n*-hexane (*10*). The 1,2,3 type of interaction is possible on two-atom sites, too (*10*). It is clear from the basic principles of alloy catalysts (*2*) that the population of contiguous sites containing three Co atoms decreases more steeply when Co is alloyed with Pd than does the population of two-atom Co sites. One can surmise that the effect in the case of neopentane is mostly geometric.

Figure 7 shows that the ratio of hydrogenolysis-to-C_6(sat) formation strongly

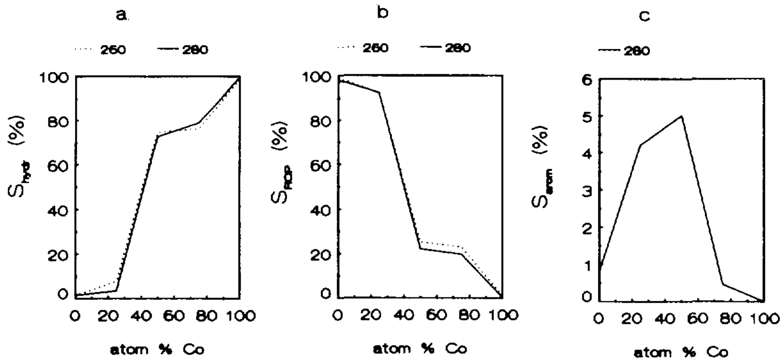

FIG. 9. Selectivities for various reactions in methylcyclopentane conversion over Pd–Co/SiO_2 catalysts: (a) hydrogenolysis to <C_6-alkanes, (b) ring opening, and (c) aromatization, at 260°C (dotted line) and 280°C (solid line).

changes with the alloy composition, but now the relation is more uniform than in the case of the hydrogenolysis selectivity vs Pd–Co alloy composition relation (Fig. 6a). The surface active intermediates with *n*-hexane may possess a π-complex structure and this was claimed to be rather favoured with Pd catalysts as opposed to other metals (*12*).

Figure 8a shows the relation between the fragmentation factor, ζ, and Pd–Co alloy composition. Very extensive hydrogenolysis leads to almost complete breakdown of *n*-hexane to methane over Co100, as opposed to stepwise (single) bond-breaking over Pd100. This is attributed to inherent differences in the hydrogenolysis properties of palladium and cobalt (*10, 15*). Palladium belongs to single hydrogenolysing metals (which split hydrocarbon molecules into two fragments). This fragmentation pattern was found to be independent of the conversion of 3-methylpentane (*21*) up to about 30%. The ζ value for Co was, in turn, around 3 even at the lowest conversions and this value increased rapidly to ca. 5.5 over 10% conversion (*21*). This behaviour was attributed to a multiple rupture of the parent molecule during its one sojourn on the surface rather than readsorption and repeated bond breaking. Thus, higher absolute conversions of *n*-hexane as compared with MCP may not affect pronouncedly the value of splitting multiplicity.

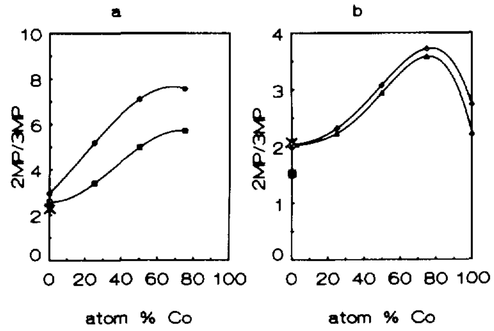

FIG. 10. 2MP/3MP ratio vs Co bulk content: (a) from *n*-hexane at 300°C (circles) and 320°C (squares); and (b) from methylcyclopentane at 260°C (crosses) and 280°C (triangles). The points denoted by a filled square (246°C) and an X (270°C) represent literature values (*12*).

Pd75Co25/SiO_2 behaves, in this respect, as Pd, whereas the two remaining alloy catalysts demonstrate an intermediate behavior. Taking into account that cobalt is two orders of magnitude more active than palladium, one could argue that the π-complex forming ability is still preserved at a composition of 75% Pd. The variations in ζ with even higher Co content point to an appreciable interaction between Co and Pd but the intermediates no longer have π-complex character. Otherwise, a dominating role of Co (higher values of ζ) would be seen over a wide range of composition for bimetallic samples.

Figure 8b presents changes of M_f, another parameter reflecting the hydrogenolysis characteristics. As a rule, the conclusions drawn from this parameter agree well with those suggested by ζ. For pure cobalt, values of $M_f < 1$ indicate multiple fission, in good agreement with earlier data (*15, 18*). However, for pure Pd, $M_f \gg 1$, indicates consecutive hydrogenolysis of a more random (or internal) fission. So far, palladium was regarded as a selective demethylation catalyst (*19, 22–26*). This contradiction can be resolved by considering that the results presented here have been obtained at relatively low temperatures (280–320°C) for the *n*-hexane reaction. Under these conditions, a *single rupture* of the alkane molecule predominates (*10, 15, 21*). Even if this rupture occurs preferentially in the terminal position (*23, 25*), the amount of the other fragments is comparable to that of methane and the value of M_f reflects a situation where repeated demethylation is still negligible. This is valid also for Pd25Co75. The situation changes abruptly at compositions Pd50Co50 and Pd25Co75 where an M_f around 1 indicates mainly terminal rupture, with the number of fragments per fragmented *n*-hexane molecule being higher than 1 (cf. Fig. 8b).

In the single hydrogenolysis range (Pd and Pd75Co25), M_f drops from 10.5 down to 4.5 from 280 to 320°C upon increasing the reaction temperature (Fig. 8b). An even lower M_f value, namely 2.95, has been observed in a single experiment at 340°C (not mentioned in the Results). Such changes in M_f with temperature indicate different activation energies for hydrogenolysis of various C–C bonds in the molecule of *n*-hexane (the state of terminal splitting at higher temperature being approached gradually). An opposite trend (higher E_a for *internal* splitting) has been reported for Pt catalysts (*26*) where, however, the position of preferred rupture is also different. We believe that both ζ as well as M_f play a role of convenient "fingerprint-like" parameters for probing Pd-Co alloy surfaces.

Figure 9 shows selectivity aspects for the MCP reaction over Pd–Co/SiO_2 catalysts. The relation between fragmentation selectivity and alloy composition (Fig. 9a) is similar to that obtained in the case of the *n*-hexane reaction (Fig. 6a). One important difference is that hardly any $<C_6$ fragments are formed from MCP over Pd100/SiO_2 as opposed to *n*-hexane. Also similar in character are the reactions for *n*-hexane isomerization (Fig. 6b) and ring opening of MCP (Fig. 9b). One may conclude that *n*-hexane isomerization proceeds via a cyclic mechanism. The relation between the ratio of 2MP/3MP and Co content substantiates this conclusion (Fig. 10). Although *n*-hexane conversion yields somewhat higher 2MP/3MP values than the reaction of MCP, one should remember the temperature dependence of the position of the C_5 ring opening (*14, 17*); here the two reactions were run at different temperatures. However, the presence of a maximum at 75 at% Co in both cases is noteworthy. In the case of *n*-hexane conversion, a corresponding point for pure Co is missing (Fig. 10a), since the formation of C_6 isomers was too low to calculate a realistic value of this ratio. One has to remember that Co has no special "ring opening activity" to produce mainly C_6 alkanes without pronounced fragmentation (*15*).

Our previous work on characterization of silica-supported Pd–Co alloys revealed a synergistic effect in neopentane conversion; three PdCo alloys (with 25, 50, and 75% Co) were more selective towards isomerization than pure Pd (*1*). That finding is indicative of appreciable interactions between the two metal components. However, after a closer inspection, one has to admit that those three Pd alloys did not differ considerably in isomerization selectivity. One must also remember that Pd has been claimed to be inactive in isomerization of neopentane (*26*). Therefore, a more in-depth probing with *n*-hexane and methylcyclopentane were thought to be necessary. There are several fingerprint-like parameters which permit the probing of various PdCo surfaces: hydrogenolysis selectivity (Figs. 6a and 9a); isomerization selectivity (Fig. 6b); fragmentation factor, ζ (Figure 8a), fission parameter, M_f (Figure 8b) and the 2MP/3MP ratio (Fig. 10). All these show an interaction between the two metal components beyond pure physical mixing.

The different reaction mechanisms involved with different probe molecules are reflected in the results observed. As pointed out above, neopentane probably probes geometric effects of alloying. Isomerization of a quaternary C atom is obviously the most favourable reaction for mixed metal sites (*1*). With a well-mixed catalyst (10% metal loading) the enhanced isomerization ability of the alloy is observed with all compositions. If hydrogenolysis proceeds on triads of Co sites, their population drops drastically on alloying Co with Pd.

Another type of composition dependence is seen with the present results using C_6 molecules where C_5-cyclic reactions are possible or even prevail (*26*). The C_5-cyclic pathway is restricted (*15*) to a few metals (Pt, Pd, Ir, Rh); Pd75Co25 is the only alloy composition where Pd-like selectivities, and probably Pd-type reactant–surface interactions, prevail (Figs. 6 and 7), although the decrease of overall activity (Fig. 3) indicates that the abundance of necessary sites is lower. Dramatic jumps seen from 50% Co content indicate that the higher hydrogenolysis activity of cobalt (and cobalt-type alkane–metal interactions) take over from this composition onwards, although the multiplicity of hydrogenolysis reaches the value characteristic of Co only gradually. While neopentane probes, probably, three-atom sites, the reactions requiring C_5-cyclic intermediates [claimed to proceed over two active atoms (*10*, *14*)] are more sensitive to the composition. One reason may be that these reactions reveal electronic effects as suggested by such features as *maxima* in C_5-cyclic and aromatic selectivities. The catalytic behavior of mixed Pd–Pd–Co or Pd–Co–Co ensembles different from triads of pure metals are interpreted here as electronic effects, as they represent, indeed, atoms in different electronic surroundings (*3*, *4*). Another possible reason, however, may be the different response of these mixed ensembles to carbonization, metal–carbon ensembles exhibiting, probably, individual catalytic features (*2*, *18*, *27*, *28*).[2]

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[2] We thank one of the referees for drawing our attention to this point.

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