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Palladium-platinum powder catalysts manufactured by colloid synthesis II. Characterization and catalytic tests after oxidizing and reducing treatment

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Abstract

Unsupported Pd, Pt and PdPt bimetallic catalysts were prepared in different atomic ratios using methods of colloid chemistry. They were characterized by XPS, UPS and TEM. Four subsequent treatments with O_2 and H_2 up to $T = 603$ K were applied in the preparation chamber of the electron spectrometer and before the catalytic runs. Platinum strongly hindered the oxidation of palladium in the bimetallic samples indicating an alloying of the two components. The H_2 treatment after O_2 led to rather clean metals. These treatments up to 603 K decreased the Pt enrichment near to the surface found by XPS, destroying presumably the Pt islands on the surface of a Pd-rich matrix. The particle composition approached thus a homogeneous metal mixture. The catalytic behavior was tested in the hydrogenative ring opening reaction of *cis*- and *trans*-methyl-ethyl-cyclopropane (MECP) at 373 K. The product ratios 2-methylpentane/3-methylpentane (2MP/3MP) and 2-methylpentane/n-hexane (2MP/*n*H) were used to characterize the ring-opening pattern of the samples. The bimetallic catalysts revealed higher activity and completely different selectivities than the monometallic Pt and Pd. Moreover, the 2MP/3MP ratio from *trans*-MECP and 2MP/*n*H ratio from *cis*-MECP increased as the surface Pt enrichment decreased. PdPt catalysts were cleaner than Pd or Pt, their activity higher and selectivity closer to random C–C rupture, due, very likely, to the presence of active Pd-Pt ensembles.
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Keywords: Bimetallic catalyst; Pd; Pt; Cyclopropane ring opening; XPS; UPS

1. Introduction

The opening of small cycles is their main catalytic reaction. Hydrogenative ring opening (HRO) occurs, when the reaction takes place in the presence of hydrogen. The products are open-chain hydrocarbons with unchanged number of carbon atoms [1,2]. Several details were reported on the transition metal catalyzed transformations of alkyl-substituted cyclopropanes and cyclobutanes [3–7]. Flat-lying or edge-wise adsorbed intermediates were also proposed, their importance depends on the catalysts, on the reactant structure and the reaction conditions. According to the literature, the carbon ring opens selectively, that is, the sterically less hindered C–C bond cleavage is favored. Cyclopropane hydrogenolysis can be considered as a structure-sensitive reaction on supported Pt catalysts, since the rate of ring opening increases as the mean Pt particle size decreases [8]. Maire et al. [9] showed that the selectivity in methylcyclobutane hydrogenolysis on supported Pt depended mostly on the platinum content: a high-loaded catalyst is far more selective than that with lower platinum content (more dispersed). The reaction rate was

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slower on supported palladium than on Pt/Al_2O_3 and the "dispersion effect" was smaller.

Rather few studies have been published on hydrocarbon conversions over PdPt bimetallic catalysts. The group of Karpinski investigated "skeletal" hydrocarbon reactions on different PdPt catalysts [10–14]. Synergistic effects were found for isomerization selectivity of neopentane, isomerization and C_5-cyclization of pentane and hexane [10,12]. The appearance of this synergism depended on the presence of hydrogen excess during reaction [13]. A large variety of PdPt catalysts was studied, including evaporated films [10,11], disperse supported particles [12,13,15] and powders [16]. After calcination in oxygen, followed by hydrogen treatment, $PdPt/Al_2O_3$ showed higher activity and better selectivity in hexane dehydrocyclization and isomerization, than monometallic Pt/Al_2O_3 catalysts [17,18]. Another model reaction was the selective hydrogenation of 1,3-butadiene. It was hydrogenated on supported Pd and Pt catalysts under comparable conditions. The butene selectivity was ∼100% on Pd, while Pt resulted in marked fraction of butane. A notable feature in 1,3-butadiene hydrogenation was the *trans*/*cis* ratio for 2-butene. This ratio was 10 to 14 on Pd catalysts, whereas a ratio of 1.5 to 2 was observed on Pt catalysts. Isomerization during 1-butene hydrogenation was much more rapid on Pd than on Pt catalysts. It was assumed that the differences in selectivity depended on the different rates of desorption of reactive surface intermediates, due to their specific modes of adsorption [19].

Part I discussed the preparation of unsupported Pd, Pt and PdPt powder catalysts by colloid synthesis (with nominal Pd:Pt ratios of 4:1, 1:1 and 1:4) and their physical characterization by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) [20]. In spite of what is expected on the basis of pure thermodynamics (differences in the heats of sublimation of Pt and Pd) predicting surface Pd enrichment [21], XPS showed more Pt in the surface region than the nominal composition. This was attributed to the faster rate of reduction of Pd salt during preparation. The customary pretreatment of such metal catalysts before hydrocarbon reactions is reduction in H_2 [22,23]. H_2 treatments at 373 K (Case A) and 473 K (Case B) produced cleaner metallic state, with some residual C and O impurity. The high "surface" Pt excess decreased slightly after treatment B. Pt enrichment is not exceptional. Venezia et al. [24,25] reported surface enrichment of the component present in lower nominal amount in the range of 1–99% Pd in PdPt. By controlled surface redox reactions, selective deposition of platinum was observed on Pd/Al_2O_3. In the presence of preadsorbed hydrogen, Pt was located as a "decoration" on low-coordination sites of Pd. Deposition of Pt by direct redox reactions brought it on to low Miller-index Pd faces, like (1 1 1) [26]. This latter method led ultimately to "more intimately mixed bimetallic system". The importance of oxygen treatment is evident, since these catalysts were also tested in $^{18}O/^{16}O$ exchange reactions at 723 K [26]. O_2–H_2 titration reportedly promoted segregation of Pt and Pd [27].

In this part of the study, we investigated how the pretreatments applied affected the catalytic performance of the samples in the transformation of two methyl-ethyl-cyclopropane isomers. Two additional pretreatments were applied, with O_2 and H_2 at higher temperatures, representing typical "regenerations" before catalytic runs [22].

2. Experimental

2.1. Catalysts

Nanosized Pd, Pt and PdPt bimetallic particles were prepared by a method of colloid chemistry [28,29]. Aqueous solutions of K_2PdCl_4 and K_2PdCl_4 were reduced with $NaBH_4$ in the presence of a cationic tenside at 323 K. Adding 2-propanol dissolved the stabilizing tenside layer and caused precipitation of the metal, as described in our previous paper [20]. The nominal composition of the catalysts were 100% Pt, 100% Pd and PdPt in the atomic ratio 4:1, 1:1 and 1:4.

2.2. Photoelectron spectroscopy

The surface composition was determined by X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy (UPS). These measurements used a Leybold LHS 12 MCD instrument as described earlier [22,23,30]. UPS used He II excitation (40.8 eV), pass energy (PE) = 12 eV. A Mg Kα anode was used for XPS (PE = 48 eV). Atomic compositions were determined from peak areas using literature sensitivity factors [31] and the homogeneous composition model.

Three pretreatments were applied to the catalysts, in the preparation chamber of the electron spectrometer, as follows:

A: as prepared.
B: pretreatment with H_2 (100 mbar) at 473 K for 20 min.
C: pretreatment with O_2 (40 mbar) at 573 K for 10 min.
D: pretreatment with H_2 (200 mbar) at 603 K for 20 min.

These treatments were carried out in the preparation chamber after each other, i.e., A → B → C → D, with XPS and UPS in-between. Evacuation of the system was carried out while the sample was cooled. It is obvious that the measurements in UHV may not reproduce exactly the surface state before evacuation [32].

2.3. Electron microscopy

The size distribution of the particles in the state after D plus reaction was determined by transmission electron microscopy in a Philips CM20 analytical microscope. No EM pictures were taken between treatments. High-resolution EM used a JEOL 3010 TEM with a resolving power of 0.17 nm.

2.4. Catalytic measurements

The reactions were carried out in a conventional pulse microreactor system [4]. Treatments with H_2 and O_2 similar to those in XPS measurements were carried out before catalytic runs, which took place at 373 K. A H_2 treatment at 373 K preceded the first catalytic run on the "as received" catalysts (denoted as A here, too). Pulses of 5 μl were injected into a hydrogen flow (10 mL min^{-1}). The amount of catalysts were 5–6 mg. A gas chromatograph with a thermal conductivity detector was attached to the system. A 2 m long 17% squalane/Chromosorb PAW column was used for analysis at 313 K. The reactants, *cis*- and *trans*-methyl-ethyl-cyclopropane (*c*-MECP and *t*-MECP, respectively) were synthesized in Moscow and were gas chromatographically pure.

3. Results and discussion

3.1. XPS and UPS

Table 1 shows the surface composition of the samples after each treatment (data for A and B were taken from Ref. [20]). Experience of several years confirmed that a homogeneous composition model may be an acceptable approximation for dispersed samples like in this case. Our metal powders exposed small surfaces in all directions towards the X-ray source thus the XPS signal is a large average of electrons arriving from different angles, as discussed in an earlier paper of ours [33]. This is obvious when one looks at the EM pictures. The surface enrichment of Pt continued to decrease. Contact with O_2 (Case C) had more marked effect in the Pd-rich or the 1:1 sample: their composition approached or even reached (with Pd:Pt = 4:1) the nominal values. A subsequent H_2 treatment (Case D) reversed this process in the case of the latter sample: the surface Pt enrichment increased again in Pd:Pt = 4:1. The surface Pt concentration of Pd:Pt = 1:4 decreased continuously and approached the nominal value after the final H_2 treatment (Case D) (agreeing with the bulk concentration measured by EDS [20]). Pd and Pt retained more than twice as much carbon as the bimetallic samples in the "as received state" and after H_2 treatment (case A and B) [20]. This situation continued after treatments C and D, too. Oxygen treatment (C) was rather effective in removing the carbon impurity: the residual C content was between 0 (PdPt 1:4) and 7% (Pd). Close values were measured after treatment D, too.

Table 1
Distribution of the metal components measured by XPS (normalized to Pd + Pt ≡ 100%)

	Composition (at.%)							
	Pd	Pd:Pt 4:1		Pd:Pt 1:1		Pd:Pt 1:4		Pt
A	100	70.5	29.5	30	70	6	94	100
B		74	26	33	68	13	87	
C		79	21	44	56	15	85	
D		76	24	43	57	20.5	79.5	

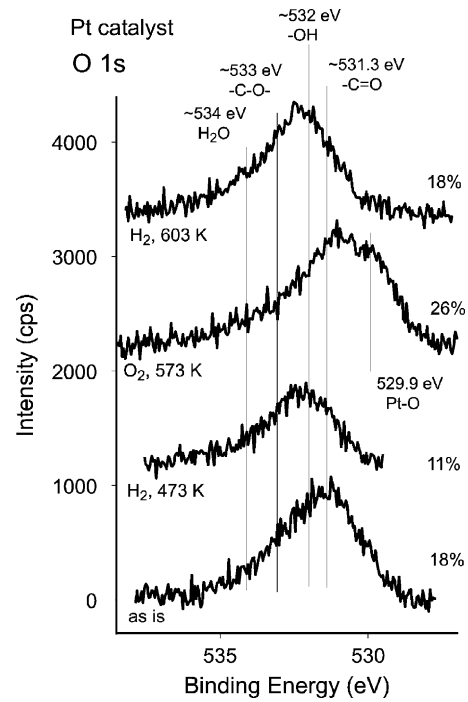


Fig. 1. XPS spectrum of pure Pt, the O 1s spectrum measured after the four pretreatments.

Fig. 1 shows the O 1s spectrum of Pt measured after these four treatments. The amount of surface O was between 26 and 11%. The untreated sample contained oxidized carbon impurity (as >C=O, with some –C–O–entities). After contact with H_2, oxygen was mainly present as surface OH or H_2O, possibly attached to surface carbon impurity. Treatment C resulted in the appearance of a component corresponding to surface metal oxide (BE ≈ 530 eV). More oxygen was present after the second reduction (treatment D), but the shape of the O 1s line showed that it was in similar chemical state as observed after treatment B. With Pt black [34], transformation of the surface Pt–O into Pt–OH and/or Pt/H_2O was observed, while keeping it overnight in vacuum at ∼600 K. Direct monitoring of the O 1s line was not possible in the presence of palladium, since the Pt 3p 3/2 peak overlaps with O 1s. The Pd 3d line can indicate reliably whether PdO is present.

Fig. 2 shows changes in the Pt 4f line after treatments C and D (O_2 and H_2). In view of the appearance of some oxidized metal component in the O 1s line, one would expect a rather intensive change in Pt 4f, too. The difference of (C–D) shows, however, a rather small excess of oxygenated Pt after C. Its chemical state points mainly to the presence of PtO_{ads} [35]. This difference can be explained by the higher inelastic mean free path, therefore larger information depth of the electrons originating from the Pt 4f core level. The Pt 4f difference spectra in Pt and Pd:Pt = 1:1 (but the other bimetallic sample as well) are rather similar.

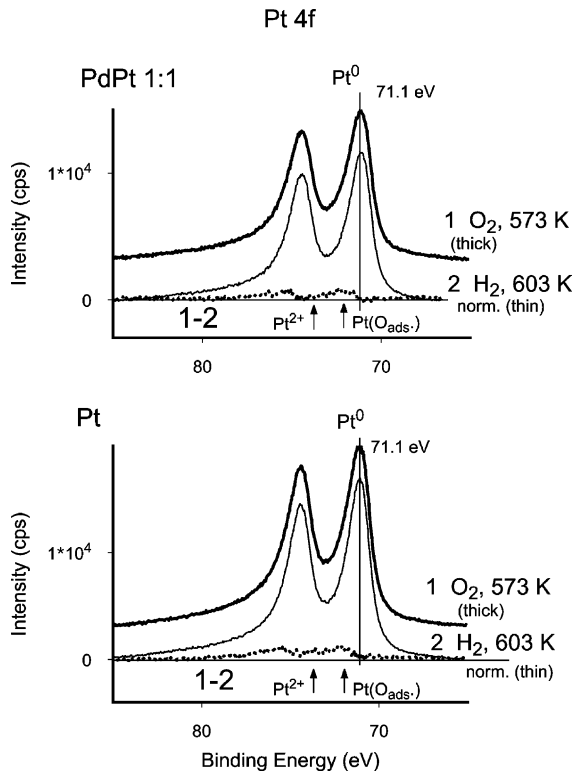


Fig. 2. Changes in the Pt 4f line after treatments C (thick line) and D (thin line) (O_2 at 573 K and H_2 at 603 K).

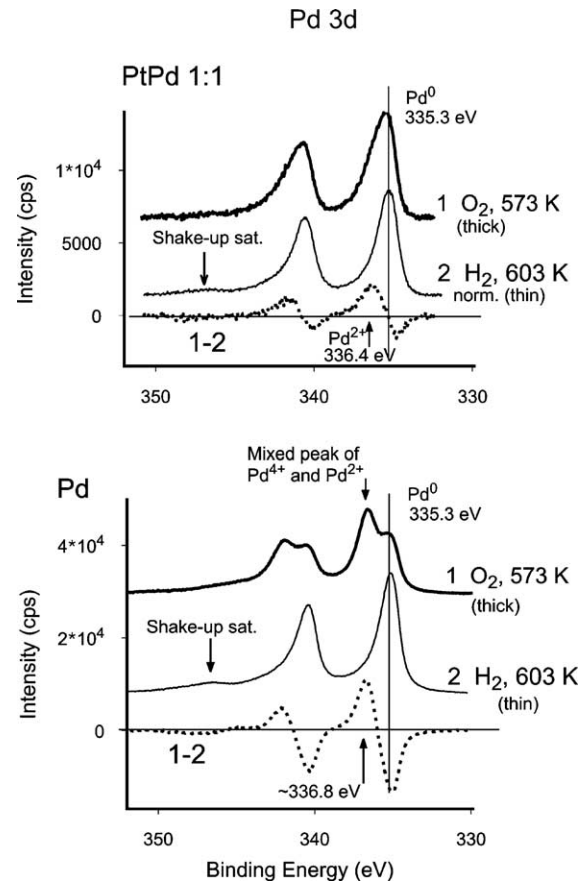


Fig. 3. Changes in the Pd 3d line after treatments C (thick line) and D (thin line) (O_2 at 573 K and H_2 at 603 K).

The Pd 3d lines show a completely different picture (Fig. 3). The BE of PdO and Pd silicides were reported to be between 336.3 and 336.8 eV [36,37]. The Pd sample was profoundly oxidized after C, the amount of Pd^{n+} exceeding that of Pd^0. The qualitative picture was similar in the PdPt = 1:1 sample, too, but the relative amount of Pd^{n+} was much lower here. Its valence state was closer to Pd^{2+} (BE ≈ 336.3 eV). Pd in the PdPt = 4:1 sample was also much less oxidized. An approximate quantitative fitting of its Pd 3d doublet after O_2 treatment showed about the same amount of Pd^{n+} and Pd^0. Pt obviously "protects" palladium from oxidation and it is logical to expect that the higher is the Pt concentration, the more difficult is to form a PdO phase, considering also that atomically mixed domains of the two metals can be present.

Thus, the concentration changes (i.e., increasing of the relative abundance of surface Pd) must have been partly caused by surface chemical reaction: oxidation of surface Pd promoted its accumulation on the surface. The present data are not sufficient to decide if there is a thin PdO layer covering the particles in state C or if the enrichment involved also pulling out metallic Pd. The difference between Fig. 3a and b, however, indicate that the presence of Pt hindered the oxidation of the palladium component. This is an argument for the presence of rather intimately mixed areas of the two metals rather than well-separated Pd and Pd domains. Electron microscopy of $PdPt/SiO_2$ after oxidation at 623 or 673 K showed the coexistence of PdO with Pt, although at that temperatures, some PtO was also observed [38]. A subsequent reduction with H_2 (treatment D) slowed down the change of surface Pd towards nominal composition (PdPt 1:1 and 1:4) or even reversed it (PdPt 4:1).

Heat treatment of a similar system (Pd-Pt foils) at 770–800 K in hydrogen caused surface Pd enrichment, as determined by soft X-ray emission spectroscopy (SXES) [39]. This was relatively more marked with 15% Pd (15% → 35–40%) than with a sample containing 30% Pd (30% → 35–40%). Heating in helium caused less surface enrichment. A layer-by-layer model calculation of the metal concentration showed Pt-rich even layers (2 and 4) with Pd-rich odd layers (3 and 5). Photoemission studies with synchrotron radiation pointed also to Pt enrichment in the first subsurface layer [40]. Szabo et al. [39] pointed out also the possible role of subsurface hydrogen [41] in promoting this separation. Heat treatment contributed to leveling off these differences. XPS results of the same foils (not published that time) show Pd enrichment in foils heated in vacuum (Table 2). It was more pronounced after heating at 773 K and with the Pd-richer foil. This confirms again (a) the inherent character of inhomogeneous distribution of Pd and Pt in our disperse samples, arising from the method of preparation and (b) the role of oxidation–reduction processes (mainly of Pd) as one of the causes of their concentration changes, in addition to mere temperature effects.

Table 2
Pd and Pt concentrations in differently treated Pd-Pt foils

Sample	Treatment	Pd	Pt[a]
15%	None	16	84
Pd + 85%	Flashed, 623 K	18	82
Pt	1 h 773 K	25	75
30%	None	45	55
Pd + 70%	Sputter[b]	48	52
Pt	Sputter, 1 h 773 K	62	38

[a] Measured with Mg Kα excitation. The samples [39] contained 30–60% C; the compositions were normalized to Pd + Pt ≡ 100%.
[b] Sputtering removed about half of carbon impurity.

UPS was used in Part I to characterize the electronic state of the sample after treatments A and B [20]. Fig. 4 shows He II spectra for all PdPt samples after C (O_2 at 573 K). After C (Fig. 4), the Fermi-edge intensity was higher in Pt than in the other samples. The Pt He II spectra in states A [20] and C were similar. As the palladium concentration increased, the intensity of a peak at ca. 3 eV corresponding to oxidized Pd increased enormously, with minor Fermi-edge intensities.

A marked Fermi-edge appeared in each case after treatment D (H_2 at 603 K). It was more intense with Pd and bimetallic samples (Fig. 5). The He II spectrum of 100% Pt was characteristic of a not very clean Pt, showing a "double peak system" (∼2.5 and ∼4.5 eV, typical of a Pt black reduced by hydrazine and treated with H_2 only [22]. The increased peak at ca. 5–6 eV pointed to some chemisorbed oxygenate [34], in agreement with XPS (Fig. 1). The spectra of Pd:Pt = 1:4 and 1:1 were similar to the UPS of clean Pt

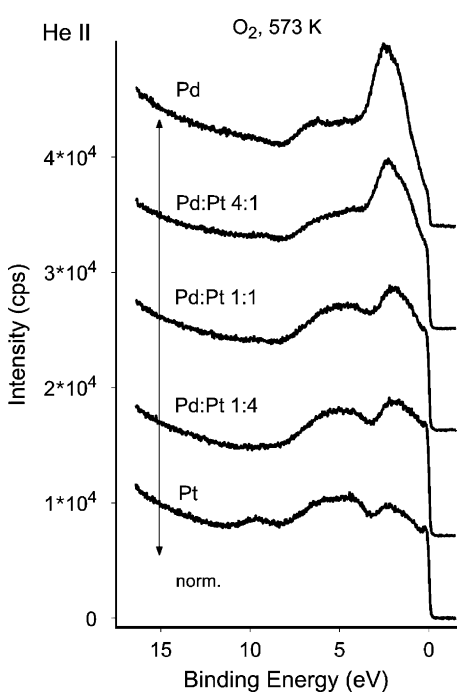


Fig. 4. He II spectra for pure Pt, pure Pd and all PdPt samples after treatment C (O_2 at 573 K).

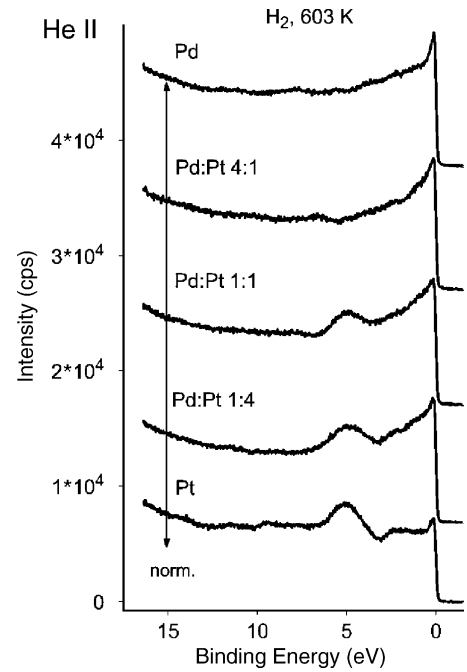


Fig. 5. He II spectra for pure Pt, pure Pd and all PdPt samples after treatment D (H_2 at 603 K).

confirming its surface enrichment [30]. Those of Pd:Pt = 4:1 and 100% Pd were characteristic of palladium spectra.

Fig. 6 compares the He II spectrum of Pd:Pt = 1:1 in states B and D with the average of the He II spectra of Pd and Pt. State B is close to the model spectrum taken by averaging the present Pd and Pt samples. PdPt = 1:1 in state D showed a much cleaner material, better approximated by another model spectrum obtained from averaging the cleanest Pt [22] and Pd blacks of different preparation.

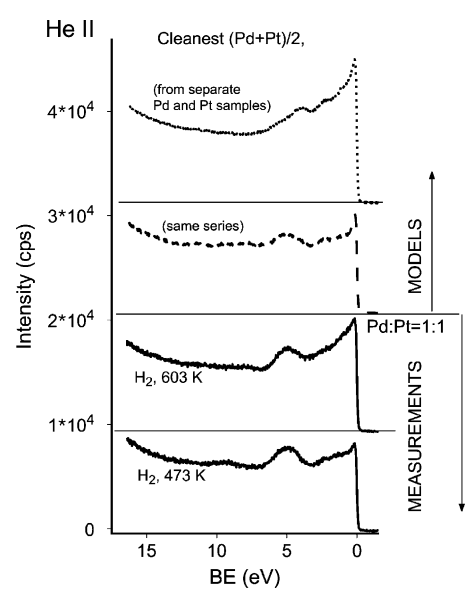


Fig. 6. UPS spectrum of Pd:Pt = 1:1 in states B (473 K) and D (603 K) compared with models, which is average of the He II spectra of Pd and Pt from the same series in state B and from different Pd and Pt samples in state D.

3.2. Electron microscopy

Part I [20] reported EM of these catalysts in the "as received" state, where most of the particles exhibited a more or less hexagonal shape projection although some quadratic and triangular shapes were occasionally observed, too. The bimetallic nanoparticles seemed to have aggregated and exhibited a more irregular, rounded shape than the pure Pt and Pd particles. Typical TEM images of the bimetallic particles, after treatments plus catalytic measurement are shown in Fig. 7. We observed aggregates consisting of larger crystallites (approximately 20–30 nm in diameter) indicating sintering upon the four treatments mentioned. The particle size increased and most of the particles were fully aggregated. Similar (maybe even stronger) aggregation has been observed with the monometallic samples which were, therefore, not investigated in detail by EM. Nevertheless, we could also distinguish individual particles (in contact with other ones) in a HRTEM picture (Fig. 8).

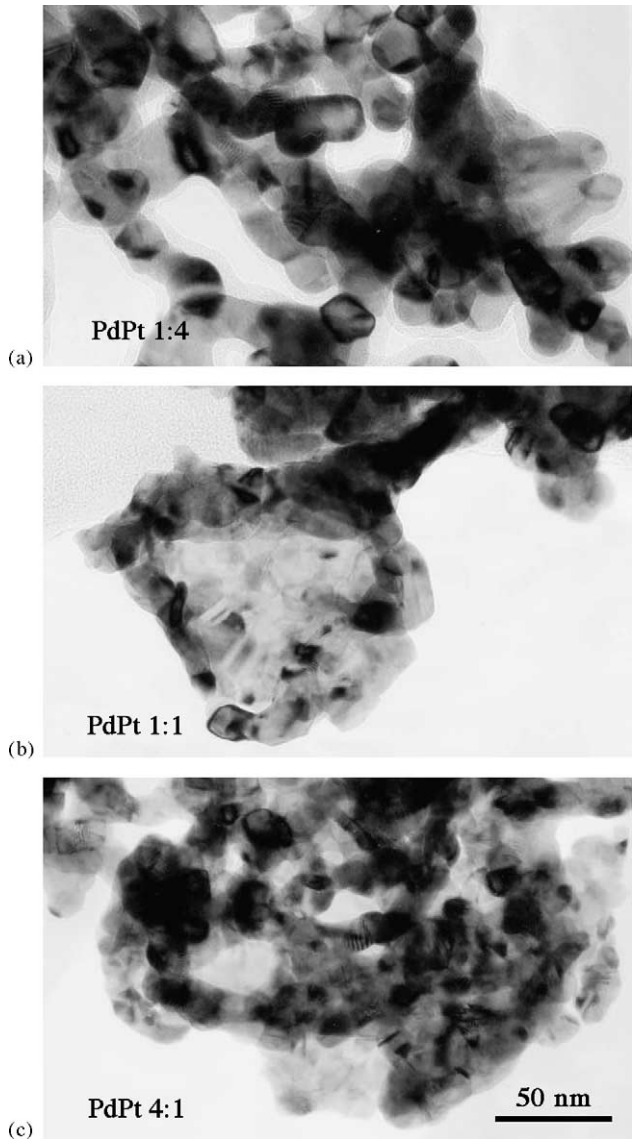


Fig. 7. Bright-field electron micrographs of aggregated particles of PdPt 1:4 (a); PdPt 1:1 (b) and PdPt 4:1 (c) bimetallic catalysts after treatments A, B, C, D and catalytic reactions.

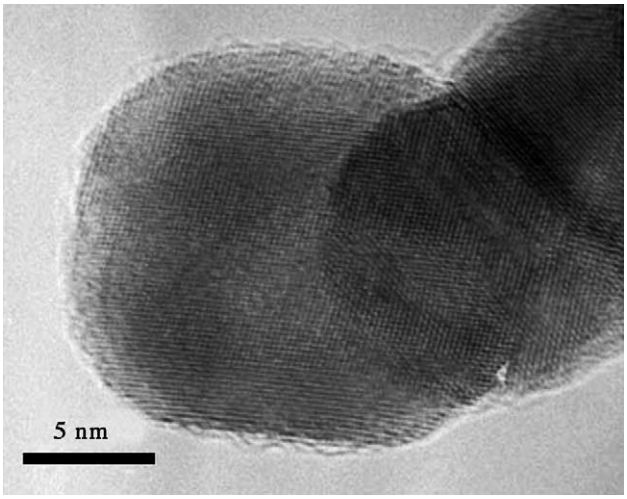


Fig. 8. High resolution electron micrograph of a single PdPt 1:4 particle of about 15 nm diameter after various treatments and catalytic reactions.

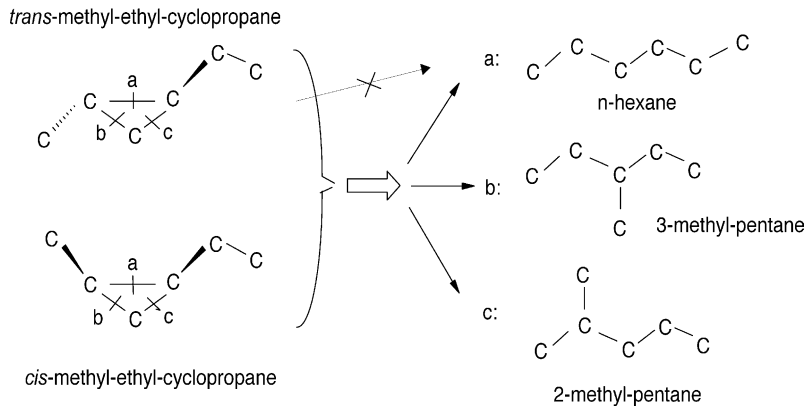
3.3. Catalytic measurement

All catalysts were active in hydrogenative ring opening (HRO) reaction [1,2] of *cis*- and *trans*-methyl-ethyl-cyclopropane. Only HRO occurred, no fragments were formed. All catalysts, including the monometallic ones were studied in state A. The conversion data are shown in Table 3. Pd and especially Pt were conspicuously less active than the three PdPt samples.

Three types of ring opening can take place on the catalyst surface (Scheme 1). The reactivity of various C–C bond in the ring is characterized by the 2MP/*n*H and 2MP/3MP product ratios. The *cis* isomer produced hexane (*n*H), 2-methylpentane (2MP) and 3-methylpentane (3MP), while the *trans* isomer produced 2MP and 3MP only. Earlier results on supported Pt, Pd, Rh or Ni catalysts showed that the ring opening of cyclopropanes occurs dominantly in the sterically less hindered position or in a random manner [2,4,5]. On pure Pt, *n*H was the major product from the *cis* isomer, formed by the rupture of the sterically *more* hindered C–C bond. In the

Table 3
Conversion and product ratios from *cis*- and *trans*-MECP on various catalysts after treatment A

	Pd	PdPt 4:1	PdPt 1:1	PdPt 1:4	Pt
cis-Methyl-ethyl-cyclopropane					
Conversion (%)	48	72	67	78	11
2MP/*n*H	0.68	1.02	0.87	0.96	0.10
2MP/3MP	0.43	0.60	0.59	0.58	0.35
trans-Methyl-ethyl-cyclopropane					
Conversion (%)	30	78	79	86	9
2MP/3MP	0.52	0.81	0.74	0.72	0.46



Scheme 1.

case of pure palladium, hexane formation was also not significantly hindered. We suspect that the deviation from earlier results originates from the presence or absence of supporting material. In fact, a significant effect of supporting materials was found in the ring opening of methylcyclopentane, as reported in numerous studies [42–44]. On the bimetallic catalysts, the 2MP/*n*H ratio was significantly higher (close to 1) than on the monometallic samples, indicating that PdPt samples do not show an intermediate selectivity pattern between palladium and platinum. The absence of *n*H in the case of *trans*-methyl-ethyl-cyclopropane can be explained by the difficulty of both flat-lying and edgewise adsorption of the reactant due to the steric hindrance by the methyl and ethyl groups. We have to remember that two flat-lying chemisorption possibilities are hidden behind the stereochemical projection of the *trans*-isomer. They can be visualized by imagining the active site *below* or *above* the plane of the ring shown in Scheme 1. The ethyl group exerts a stronger hindrance if it points "downwards", i.e., in the direction of the catalytically active site.

Only one flat-lying chemisorption geometry is possible for the *cis* isomer. The geometry of ring adsorption must have been the main factor determining the ring opening selectivities. Any side-chain adsorption would not result its C–C bond splitting, since cyclopropanes are highly strained compounds and the rate of ring opening (selectivity toward the cleavage of sterically less hindered C–C bond) is faster than side-chain hydrogenolysis.

The bimetallic catalysts were examined after the other pretreatments. Fig. 9 depicts the changes of the selectivity ratios after treatments A, B, C, D. The ratio 2-methylpentane/3-methylpentane (2MP/3MP) from *cis*-MECP was close to 0.5 after all treatments. These ratios are substantially higher from trans isomer at similar conversion level and this trend is maintained during the further treatments (see Fig. 9). The "surface" Pt concentration (XPS) is also shown in the figure, including the nominal (=bulk, determined by EDS) concentration in the "as prepared" sample. The Pd surface concentration increased in the sequence A, B, C, D. Note that this change reversed with PdPt 4:1 after H_2 treatment at 603 K (D). The catalytic properties changed simultaneously: the 2MP/*n*H selectivity ratio went up, diverge further from the values of monometallic samples. Note that the 2MP/*n*H and 2MP/3MP ratio turned also back with PdPt = 4:1 after

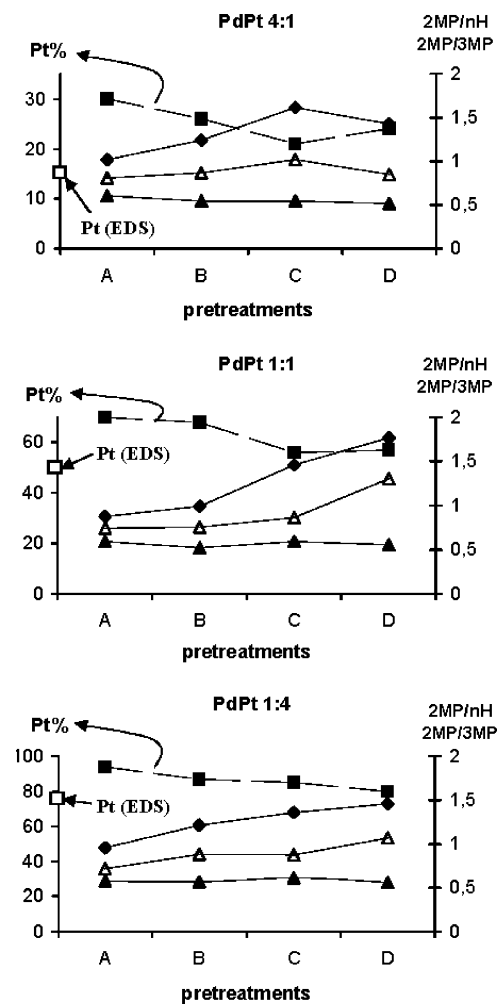


Fig. 9. Selectivity and surface composition changes following different pretreatment conditions on bimetallic samples: (■) Pt on the surface (XPS); (♦) 2MP/*n*H from *cis* isomer; (▲) 2MP/3MP from *cis* isomer; (△) 2MP/3MP from *trans* isomer.

treatment D. This confirms that the selectivity depends on the surface composition. Less surface Pt or more homogenous distribution of the two components seems to favor the cleavage of the sterically less hindered bond, resulting more 2MP than *n*H from *cis* isomer.

The conspicuous changes of conversion and selectivity values in mono- and bimetallic catalysts indicate a marked difference in their catalytic properties. Both the abrupt increase of the activity and the marked selectivity changes indicate that Pd-Pt bimetallic ensembles can represent a special type of active site, different from monometallic ones [10,12,13]. One factor, however, may be catalyst purity. The activity values in Table 3 correlate well with the purity data, indicating that PdPt samples retained much less carbon (down to zero) thus they were much cleaner in similar state than Pd or Pt. This is in agreement also with the UPS results (Figs. 5 and 6). In addition to surface purity (causing increased activity), the peculiar activity of Pd-Pt pairs can be responsible for the selectivity changes. This speaks for Pd and Pt forming a real alloy, exhibiting surface domains where with the two components is atomically dispersed. The very close conversion data with different composition (Table 3) point to the similar absolute number of such Pd-Pt bimetallic surface sites in the three mixed samples. Thus, the catalytic reaction supplied additional, really surface-sensitive information.

The model proposed earlier [15,21], that Pt accumulated as separate islands near to the surface of the particles could partly explain the composition of the "as prepared" catalyst. These "single phases" coexist, however, with a certain number of PdPt metal atom pairs on the surface already after preparation. Subsequent treatments brought the bimetallic particles closer to the nominal composition, increasing, likely also bulk homogeneity. Results of H_2 chemisorption [45,46] provide one possible clue on the changes in the solid state. A preliminary experiment on PdPt 1:1 indicated a H/Pd_{surf} ratio of 2, pointing to hydrogen *absorption*, i.e., the presence of some contiguous palladium phase, with surface Pt present as small islands [15,21]. Repeating this experiment after treatment D, the H/Pd_{surf} ratio decreased to 1, indicating just *adsorption*, due obviously to the replacement of the Pd phase by a PdPt mixed phase.

4. Conclusions

Preparing bimetallic PdPt powders by reduction of their salts to produce colloidal particles resulted in compositions where the surface regions were enriched in Pt. Since this contradicts thermodynamics considerations, it has to be assumed that the reduction of Pd must have been more rapid and the "as prepared" particles were not in equilibrium. The surface Pt excess, as shown by XPS decreased upon treatments with H_2, O_2, and with H_2 again at gradually increasing temperatures. The nominal metal composition values valid in the bulk (as measured by EDS) were approached after H_2 treatment at 603 K. The presence of platinum strongly hindered the oxidation of Pd at 573 K. Bimetallic particles retained less carbon (from the preparation method or as a result of inadvertent adsorption of atmospheric impurity) and showed more metallic character than monometallic ones. A pronounced aggregation of the bimetallic particles was observed after the redox treatments, but some individual crystallites could still be recognized in the TEM picture.

The ring opening of methyl-ethyl-cyclopropanes was a valuable tool to recognise the formation of alloy structure during preparation and its further homogenising in subsequent redox cycles. The product ratios showed marked changes as a function of the surface composition: more homogeneous distribution of Pd and Pt on the surface favored the cleavage of the sterically less hindered bond producing more 3MP and 2MP than *n*H from the *cis* isomer. The PdPt catalysts were (1) more active in HRO of the cyclopropane ring and (2) the selectivity values on them were far different from those observed on the monometallic samples. We attributed these properties to the presence of surface Pd-Pt pairs as peculiar active sites.

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