

# Methylcyclopentane Conversion Catalysis by Zeolite Encaged Palladium Clusters and Palladium-Proton Adducts

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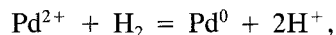
The conversion of methylcyclopentane (MCP) has been studied over the prototype catalysts HY, Pd/HY, Pd/NaHY, and proton-free Pd/NaY. Ring opening (RO) of MCP to hexane isomers is catalyzed by Pd<sub>n</sub> clusters, but ring enlargement (RE) of MCP to cyclohexane and benzene requires metal sites and protons. It is found that catalysts containing Pd and protons, in the same zeolite cavity, are dramatically more active for RE than a physical mixture of HY and proton-free Pd/NaY. As other data indicate that protons and Pd<sub>n</sub> clusters inside supercages of zeolite Y form "electron-deficient" [Pd<sub>n</sub>H]<sup>+</sup> adducts, it is proposed that these adducts expose active sites, where MCP is converted to benzene during one residence of the adsorbed molecule. This novel reaction path compares favorably with the classical "bifunctional" route which requires shuttling of reaction intermediates between metal and acid sites. © 1991 Academic Press, Inc.

## I. INTRODUCTION

Zeolite-supported transition metals display high catalytic activity for various hydrocarbon reactions such as isomerization, hydrogenolysis, aromatization, and (de-)hydrogenation (1–7). Since the pioneering work by Rabo *et al.* (2), noble metals on zeolites have been established as important industrial catalysts (8, 9) and considerable research has focused on these systems (10). Numerous studies have shown that the catalytic characteristics of a zeolite-supported transition metal often differ significantly from those of the same metal on an amorphous support. These differences are attributed either to the metal particle morphology or to some chemical interaction of metal and support. Metal particles in zeolite cavities tend to be more uniform in size and shape than particles on amorphous supports due to geometric constraints of the zeolite lattice (11–13). The special geometry of the encaged particle can lead to stereochemical catalytic consequences which have been discussed for Pt in L and Y zeolites (3–5, 14–17). Chemical interactions of noble met-

als with either the zeolite framework, other metals, or charge-compensating cations have been the subject of much research (18–28). Such interactions are specific for the nature of the zeolite support and often absent for amorphous supports.

In the case of amorphous supports, the metal precursor is often an oxide or halide. Its reduction with hydrogen leads to volatile coproducts which will not form a major constituent of the reduced catalyst. For zeolite supports, however, reduction of ion-exchanged metal cations,



results in a bifunctional catalyst (29) because metal particles and acidic protons are coproduced.

Recent work in this laboratory suggests that these protons will not only be attached to oxygen ions of the zeolite cage walls, but can also interact with metal clusters forming positively charged [Pd<sub>n</sub>H]<sup>+</sup> adducts, in which the positive charge is distributed between metal and hydrogen atoms; i.e., the metal becomes "electron-deficient" (30). From studies of the release of CO from zeo-

lite-occluded Pd carbonyl clusters Sheu *et al.* concluded that zeolite protons interact with palladium clusters, leading to positively charged palladium proton adducts (31, 32). More recent TPR and FTIR results with Pd/MgY and Pd/CaY (33) confirmed that the formation of palladium proton adducts is favored by a high concentration of divalent charge-compensating ions, e.g.,  $Mg^{2+}$  or  $Ca^{2+}$ . This is thought to be due to the preferential population of sodalite cages and hexagonal prisms by divalent ions. If these positions are occupied, e.g., with  $Ca^{2+}$ , the  $Pd^{2+}$  ions will remain inside supercages; during their subsequent reduction,  $Pd_n$  clusters and protons will both be formed in supercages, setting the stage for the formation of the  $[Pd_nH]^+$  adducts.

It has been shown that the turnover frequency for neopentane conversion over Pd supported in Y-type zeolite can be 150 times higher than over Pd/SiO<sub>2</sub> (34). This superactivity has been attributed to electron-deficient  $[Pd_nH]^+$  adducts. The objective of the present study is to identify the catalysis of the  $[Pd_nH]^+$  adducts in a hydrocarbon reaction which is known to include metal-catalyzed and acid-catalyzed steps. For this purpose, we chose the conversion of methylcyclopentane (MCP) as a probe reaction. In addition, temperature-programmed surface reaction (TPSR) of MCP is used to identify adsorbed intermediates of the MCP ring enlargement reaction.

## II. EXPERIMENTAL

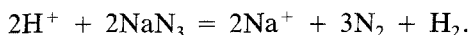
### A. Catalyst Preparation and Pretreatment

Three types of palladium zeolite catalysts were prepared:

(1) Pd/NaY is prepared by reduction of  $Pd^{2+}/NaY$  with H<sub>2</sub>; two protons are generated for each reduced Pd atom. The majority of the charge-compensating cations is still Na<sup>+</sup>.

(2) Proton-free Pd/NaY (Pd/NaY-neutr) is prepared by successive reduction of  $Pd^{2+}/NaY$  with H<sub>2</sub> and NaN<sub>3</sub>. The NaN<sub>3</sub>

eliminates the protons generated in the first step (35–37):



(3) Pd/HY is prepared by introducing palladium cations into HY, followed by calcination in O<sub>2</sub> and reduction with H<sub>2</sub>. After complete reduction, all charge-compensating ions are protons.

Pd/NaY and Pd/HY were prepared by ion exchange; i.e., a dilute solution (0.01 M) of Pd(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Strem Chemical, Lot No. 19167) was added dropwise to NaY or HY at room temperature. The NaY used was Linde LZ-52, with approximate unit cell formula Na<sub>56</sub>(AlO<sub>2</sub>)<sub>56</sub>(SiO<sub>2</sub>)<sub>136</sub>. The HY used for exchange was Linde LZ-72, with approximate unit cell formula H<sub>44.8</sub>Na<sub>9.2</sub>(AlO<sub>2</sub>)<sub>54</sub>(SiO<sub>2</sub>)<sub>138</sub>. The solutions and slurries were prepared using doubly deionized water. This exchange led to a Pd loading of both zeolites of approximately 8 Pd ions per unit cell.

After drying in air at room temperature (RT), samples were calcined under a high flow (180 ml/min) of O<sub>2</sub> in a packed-bed reactor at atmospheric pressure. The calcination temperature was ramped at 0.5°C/min from RT to 500°C and held at 500°C for 2 h. The oxygen was purified by passing over Pt/SiO<sub>2</sub> and a 4A molecular sieve cooled by dry ice. After calcination, samples were cooled to RT in He (UHP, Matheson, USA; 30 ml/min) and reduced in H<sub>2</sub> (UHP, Matheson, USA; 20 ml/min). The reduction temperature was ramped from RT to 350°C at 8°C/min and kept at 350°C for 20 min. The sample was then cooled in flowing H<sub>2</sub> to the reaction temperature, which was 275°C, unless otherwise stated.

The proton-free Pd/NaY catalyst was prepared by mixing reduced Pd/NaY with an aqueous NaN<sub>3</sub> solution under flowing helium. The amount of NaN<sub>3</sub> was dosed exactly equivalent to the protons created in the first reduction step; the volume of the solution was equal to that of the dry sample. After drying at 100°C in flowing helium, the

TABLE 1A

Conversion, Turnover Frequencies, and Product Distributions after 5-Min TOS

Catalyst	Pd/HY	Pd/NaY	Pd/NaY-neutr(I)	HY(II)	Phys. mixt. (I + II)
Total conv. (%)	26.9	9.5	10.3	0.5	9.4
Total TOF ( $s^{-1} \times 10^4$ )	67.0	33.0	37.1	—	25.5
	Product distribution				
Methane	—	1.8	—	—	—
Ethane	—	—	—	—	—
Propane	1.7	—	—	—	—
<i>i</i> -Butane	6.1	—	—	14.8	2.2
<i>n</i> -Butane	1.4	—	—	—	—
<i>i</i> -Pentane	3.5	1.3	—	—	2.5
<i>n</i> -Pentane	2.4	1.3	—	—	—
Cyclopentane	—	6.0	—	—	1.3
2-Methylpentane	0.9	45.0	54.2	—	44.1
3-Methylpentane	0.9	27.4	24.6	—	22.3
<i>n</i> -Hexane	0.6	17.3	21.2	49.3	17.1
Benzene	29.6	—	—	—	5.6
Cyclohexane	52.9	—	—	35.9	4.9
RO TOF ( $s^{-1} \times 10^4$ )	1.6	29.6	37.1	—	21.3
RE TOF ( $s^{-1} \times 10^4$ )	55.2	—	—	—	2.7

sample was heated from 100 to 350°C, ramping at 8°C/min, and kept at 350°C for 20 min in flowing helium (30 ml/min). Mass spectrometer-monitored temperature-programmed decomposition of  $\text{NaN}_3$  on Pd/NaY (38) showed that  $\text{NaN}_3$  decomposition was complete under these conditions.

### B. Methylcyclopentane Conversion

The MCP reaction was carried out with 150 mg of catalyst at 275°C and atmospheric pressure in a continuous-flow microreactor described elsewhere (29). A reaction mixture with  $\text{H}_2/\text{MCP} = 16$  was obtained by passing purified  $\text{H}_2$  through a MCP saturator cooled to 0°C in an ice/water bath. In some cases, He was used as a carrier instead of  $\text{H}_2$  to investigate the effect of  $\text{H}_2$  on MCP reaction. The reaction flow rates were held constant at 20 ml/min. Reaction products were analyzed by an on-line HP 5794 gas

chromatograph equipped with a flame ionization detector (FID) detector and a 50-m crosslinked methylsilicone fused capillary column.

### C. Temperature-Programmed Surface Reaction (TPSR)

The TPSR experiments were carried out in the same flow system. A 500-mg sample of Pd/HY was calcined at 500°C and reduced with  $\text{H}_2$  at 350°C. After cooling in helium to RT, MCP was adsorbed by passing a mixture of helium and MCP through the catalyst bed for 20 min. The sample was then purged with pure helium at RT to remove physisorbed MCP until none was detectable by FID. This purge usually lasted about 50 min. The sample was then heated at 2°C/min in flowing He at 20 ml/min. The chemisorbed surface species desorbed and were analyzed using GC equipped with a FID.

TABLE 1B  
 Conversion, Turnover Frequencies, and Product Distributions after 30-Min TOS

Catalyst	Pd/HY	Pd/NaY	Pd/NaY-neutr(I)	HY(II)	Phys. mixt. (I + II)
Total conv. (%)	18.0	1.6	2.4	0.9	1.7
Total TOF ( $s^{-1} \times 10^4$ )	44.9	4.2	6.5	—	4.6
Product distribution					
Methane	—	—	—	—	—
Ethane	—	—	—	—	—
Propane	2.2	—	—	—	—
<i>i</i> -Butane	6.2	—	—	20.4	—
<i>n</i> -Butane	1.7	—	—	—	—
<i>i</i> -Pentane	3.8	—	—	21.5	10.5
<i>n</i> -Pentane	1.8	—	—	—	—
Cyclopentane	—	—	—	—	—
2-Methylpentane	—	5.1	53.0	—	6.0
3-Methylpentane	—	3.2	23.6	—	—
<i>n</i> -Hexane	—	0.2	23.4	4.9	—
Benzene	27.3	44.4	—	29.9	35.4
Cyclohexane	57.0	47.1	—	23.3	49.0
RO TOF ( $s^{-1} \times 10^4$ )	—	0.4	6.5	—	0.2
RE TOF ( $s^{-1} \times 10^4$ )	37.8	3.8	—	—	3.9

The fraction of metal atoms exposed was determined by chemisorption of carbon monoxide, using the static adsorption technique. Previous results had ascertained that, for Pd/NaY after reduction at 350°C, CO adsorption correctly measures the number of surface exposed Pd atoms that are accessible to MCP (14), whereas for samples that

were reduced at much lower temperature and, therefore, contain isolated Pd atoms, Pd<sub>4</sub>, or Pd<sub>6</sub> clusters, CO promotes additional agglomeration of Pd atoms (51). All catalytic rate data will be based on measured metal dispersion; these turnover frequency (TOF) values are invariant with respect to errors of metal loading, determined from the ion-exchange procedure. The measured dispersions, CO/Pd, of our samples are 0.42 for Pd/HY; 0.30 for Pd/NaY; 0.29 for Pd/NaY-neutr.

### III. RESULTS

Data on MCP conversion, turnover frequencies, and product distributions at 275°C over Pd/NaY-neutr, Pd/NaY, Pd/HY, HY, and a physical mixture of Pd/NaY-neutr and HY are presented in Table 1 for two times on stream (TOS), viz. 5 and 30 min. As the accessible metal surface decreases during

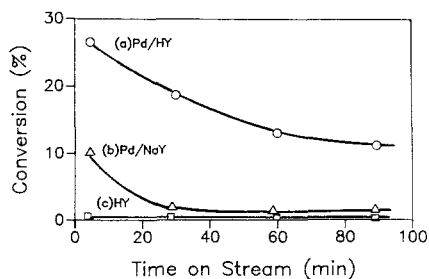


FIG. 1. The activity of Pd/HY, Pd/NaY, and HY for MCP reaction vs TOS.

catalyst deactivation, catalytic rates rather than turnover frequencies will be reported in the figures. Figure 1 shows the conversion of MCP vs TOS over Pd/HY, Pd/NaY, and HY. With a given palladium loading, Pd/HY evidently is much more active and has a lower deactivation rate than Pd/NaY (Fig. 1a,1b); under the same conditions, the activity of HY for MCP conversion is negligible (Fig. 1c).

Three types of reactions occur during MCP conversion (28):

- (1) Ring opening (RO), i.e., conversion to *n*-hexane and isohexanes;
- (2) Ring enlargement (RE), i.e., conversion to cyclohexane and benzene;
- (3) Cracking, i.e., production of molecules containing <6C atoms.

Since the cracking rate of MCP was always more than one order of magnitude lower than that of RO and RE, attention will further be focused on RO and RE. Whereas selectivity will, in general, vary with conversion if consecutive reactions are important, this is of little importance for the present conditions, as there is evidence that RO and RE are essentially parallel reactions; i.e., secondary interconversion of open chain alkanes and cyclohexane can be disregarded. Therefore, selectivity data measured outside the differential regime will be indicative also for the initial selectivity.

It can be seen from Table 1 that the MCP reaction rates differ widely for these catalysts. On Pd/NaY-neutr, ring opening is the sole reaction observed. On Pd/HY, the prevailing reaction is ring enlargement. Surprisingly, the physical mixture of Pd/NaY-neutr and HY does not display any significant activity for ring enlargement, although it contains both Pd<sub>n</sub> particles and acidic protons. On Pd/NaY, ring opening is initially dominant, but ring enlargement predominates at long TOS.

Figure 2 shows the rate of formation of RE products vs TOS. The strong effect of proton concentration is evident, but the strong difference between Pd/HY and the

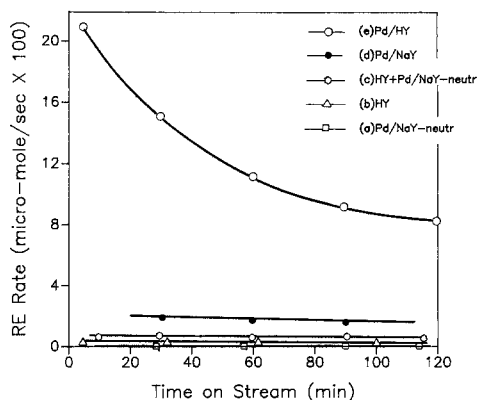


FIG. 2. Ring enlargement of MCP over Pd/HY, Pd/NaY, Pd/NaY-neutr, HY, and a physical mixture of HY + Pd/NaY-neutr.

physical mixture of Pd/NaY-neutr + HY illustrates the importance of proximity of metal and acid sites.

In Fig. 3, the RO selectivity is plotted versus TOS. It shows the characteristic difference between Pd/NaY and Pd/NaY-neutr. Though both catalysts deactivate with TOS, the RO selectivity stays at 100% for Pd/NaY-neutr, but decreases from 90% to about 10% for Pd/NaY, indicating that RE becomes dominant. The RO selectivity on Pd/HY is always near zero (Fig. 3c).

The two products of the RE reaction are

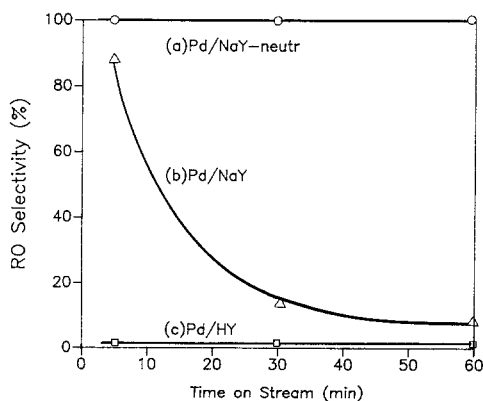


FIG. 3. Ring-opening selectivity of Pd/HY, Pd/NaY, and Pd/NaY-neutr.

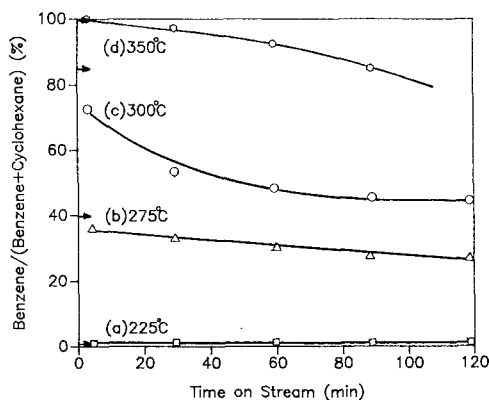


FIG. 4. The effect of reaction temperature on benzene/cyclohexane ratio on Pd/HY. The arrows are the equilibrium ratios.

cyclohexane and benzene. The benzene/cyclohexane ratio on partially deactivated catalysts is higher on Pd/NaY than on Pd/HY. The effect of the reaction temperature on this ratio is shown for Pd/HY in Fig. 4. At 225°C, only cyclohexane was detectable, but at 350°C, only benzene was detected in the initial stage of the reaction. The equilibrium ratios are indicated by arrows.

It is likely that reaction intermediates or products of RE are strongly adsorbed on metal sites, blocking them for the RO path. Therefore a TPSR experiment was carried out with Pd/HY. Cyclohexane, benzene and traces of lower MW products were detected besides MCP. The peak desorption temperature for MCP is about 125°C. After the desorption of MCP, cyclohexane was released at higher temperature followed by benzene. The relative concentration of MCP, cyclohexane (CH) and benzene (BZ) are shown in Fig. 5. Above 230°C, only benzene is observed. The TPSR results suggest that cyclohexane is a primary product of MCP ring enlargement, but benzene will predominate on the surface of the metal under steady-state conditions. To support this finding, the MCP reaction was carried out at 275°C, using He as a carrier instead of H<sub>2</sub>. It was found that the benzene content of the RE products is 95% in He, as opposed to only

35% in H<sub>2</sub>. This could mean that an adsorbed cyclohexane precursor is formed first and subsequently converted to adsorbed benzene while H<sub>2</sub> is desorbed.

#### IV. DISCUSSION

The results in Table 1 show significant differences in the catalytic properties of Pd/NaY-neutr, Pd/NaY, and Pd/HY. These differences are apparently related to the widely differing proton concentrations in these samples. Most remarkably, the results in Fig. 2 reveal that the mere coexistence of Pd<sub>n</sub> clusters and protons in a physical mixture is insufficient to efficiently catalyze the ring enlargement of MCP. It appears that metal clusters and protons must be present in the same solid, preferentially in the same zeolite cage, for the RE reaction to occur at a high rate. The question arises whether the superior RE activity of Pd/HY is merely due to the smaller average distance between metal and acid sites. The zeolite particle size of the physical mixture is about 1 μm; therefore, the average distance between metal and acid sites is about 4 to 5 orders of magnitude larger in the physical mixture than it is in Pd/HY. Previously, Chow *et al.* (29) compared Pt/HY with a physical mixture of Pt/SiO<sub>2</sub> and HY for the same probe reaction at 250°C. Their results show a much smaller difference in RE rate between Pt/HY and

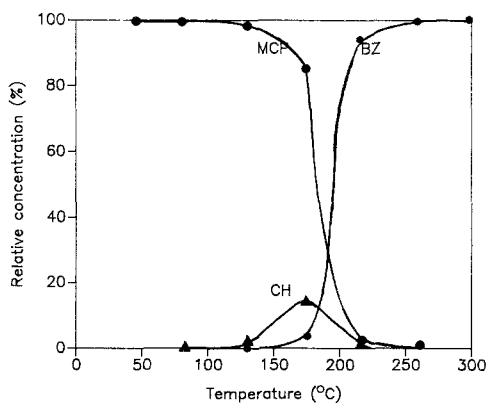


FIG. 5. TPSR results of MCP on Pd/HY.

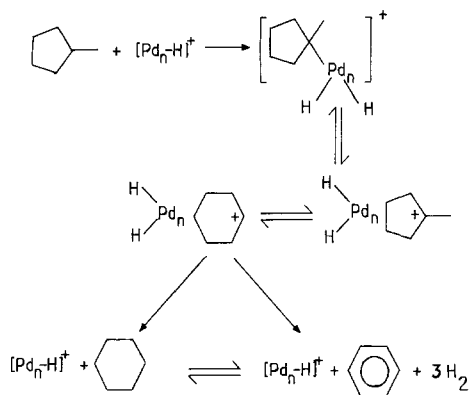


FIG. 6. Mechanistic model for MCP ring enlargement over  $[Pd_nH]^+$  adducts.

the physical mixture. For both catalyst systems, ring enlargement was the predominant process, and the RE rates differed only by about 20.5%. The authors attributed this minor difference to the longer average distance between metal and acid sites in the physical mixture. For the Pd catalysts studied in this paper, however, the RE rate of MCP on Pd/HY is about 20 times greater than that of the physical mixture of Pd/NaY-neutr and HY (Table 1a). As the geometry of the zeolite is equal in the experiments with Pt/Y and Pd/Y catalysts, it is difficult to attribute the large activity difference between Pd/HY and the physical mixture solely to different distances between the sites. The results thus suggest that, for palladium, an interaction of Pd clusters and protons is beneficial for a high RE rate of MCP. The classical model of bifunctional catalysis as proposed by Mills *et al.* (39) for many isomerization and cracking reactions fails to account for this. We, therefore, propose a different model, which does not require shuttling of intermediates between metal sites and acid sites. Instead, the present results seem to suggest that the RE reaction of MCP is catalyzed by  $[Pd_nH]^+$  adducts, rather than by separate metal and acid sites. The proposed model is sketched in Fig. 6.

A possible objection against this model is that an alkyl group adsorbed on a  $Pd_n$  cluster

carrying a positive charge is not a carbenium ion. However, V. B. Kazansky *et al.* (40, 41) found that olefins adsorbed on Brønsted protons on zeolite walls are not true carbenium ions, either. They are described as slightly polarized alkoxy groups. The classical carbenium ion intermediate in skeletal isomerization of hydrocarbon is merely an excited state of the alkoxy group (on zeolite walls) or the alkyl group (on positively charged  $Pd_n$  clusters). Likewise, the carbenium ions on the Pd particles are depicted in Fig. 6 as limiting cases of an alkyl group on a  $Pd_nH_2$  adduct carrying a positive charge.

In the new model, as in the classical bifunctional model, proton-free Pd/NaY is unable to catalyze RE of MCP. Comparing the  $H^+$  concentration in Pd/HY and Pd/NaY and their RE activity, a reasonably high activity of Pd/NaY might be expected, because the reduced sample contains two Brønsted acid protons per Pd atom. However, for the formation of  $[Pd_nH]^+$  adducts, the location of  $Pd_n$  and  $H^+$  is also important. The genesis of metal clusters from  $Pd(NH_3)_4^{2+}/NaY$  has been studied by X-ray diffraction (42), TPO, TPR (43), UV-Vis, and EXAFS (44). It follows from these data that 500°C calcination of  $Pd(NH_3)_4^{2+}/NaY$  leads to bare  $Pd^{2+}$  ions located in sodalite cages and hexagonal prisms. During reduction with  $H_2$ , Pd atoms and protons are formed in these cages. The Pd atoms migrate subsequently to the supercages, where they form  $Pd_n$  clusters, while protons will be left behind in the small cages. Therefore, the formation of  $[Pd_nH]^+$  adducts in the supercages remains limited; the majority of the palladium exists as neutral  $Pd_n$  clusters. This situation differs strongly from that in Pd/HY, where the  $Pd_n$  clusters share their supercages with many protons and a large fraction of the palladium will form  $[Pd_nH]^+$  adducts with high activity for MCP RE reaction (Fig. 2e).

Pd/NaY-neutr is only able to catalyze the RO of MCP (see Table 1). This is in agreement with Gault's basic conclusion

that RO of MCP is specific for the metal function (45). Models have been proposed to rationalize the distribution of the three RO products (46–49). This is, however, not part of the objectives of the present paper and will, therefore, not be discussed here. In Pd/HY RO and RE are both catalyzed, however, benzene which is formed as a major RE product, is likely to deactivate the metal sites for RO. It is known that RO hydrogenolysis of MCP is an ensemble-sensitive reaction (50); the number of large Pd ensembles rapidly decreases due to site blocking. The results in Fig. 3 show that decrease of the selectivity differentiates between Pd/NaY-neutr and Pd/NaY. This could be due to the total absence of adsorbed benzene in the case of Pd/NaY-neutr.

As indicated by the arrows in Fig. 4, the benzene/cyclohexane ratio is slightly below the equilibrium ratio. This and the TPSR results suggest that the primary product of MCP RE on Pd/HY is cyclohexane which is subsequent dehydrogenated to benzene. Formation of cyclohexane takes place at rather low temperature on  $[Pd_nH]^+$  adducts. The mechanism in Fig. 6 assumes that both six-ring products are formed on the  $[Pd_nH]^+$  adducts in either a parallel or consecutive fashion. Irrespective of the assumed mechanism, an increase of the reaction temperature and a decrease of the  $H_2$  pressure will thermodynamically favor benzene over cyclohexane.

## V. CONCLUSIONS

A high proton concentration in the proximity of  $[Pd_n]$  particles converts  $[Pd_n]$  clusters to  $[Pd_nH]^+$  adducts. The RE of MCP is catalyzed by these "electron-deficient"  $[Pd_nH]^+$  adducts more effectively than by separate metal and acid sites. Hydrogenolytic ring opening of MCP is catalyzed by neutral  $[Pd_n]$  clusters.

## VI. ACKNOWLEDGMENT

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