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Enhanced benzene formation on Pt/H-mordenite and Pd/H-mordenite

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The distribution of methylcyclopentane (MCP) ring enlargement (RE) products between benzene (Bz) and cyclohexane (CH) provides information on the reaction mechanism. The Bz/CH ratio is in excess of the calculated and experimentally determined equilibrium ratio. This implies that benzene is a primary product; it eliminates the possibility of direct hydride ion transfer to carbenium ions as the prevailing mechanism. The results are consistent with the concept that metal–proton adducts are instrumental in bifunctional catalysis.

Keywords: MCP ring enlargement; proton adduct; Pt and Pd mordenites; benzene/cyclohexane equilibrium

1. Introduction

Cations in zeolites, necessary to compensate the negative charge of the aluminosilicate framework, significantly affect the physical, chemical, and catalytic properties of the zeolite. In particular protons, whether formed by decomposition of NH_4^+ ions or as a component of the reduction of metal ions, exert a strong influence on the catalytic performance. In hydrocarbon conversion processes the protons act as Brønsted acid sites, inducing the formation of carbenium or carbonium ion intermediates [1,2]. In bifunctional catalysis protons and transition metal atoms can act either as independent catalytic sites or interact with each other.

In early research by Rabo et al. [3] unusual chemisorption by Pt/CaY was discovered, the H/Pt stoichiometry significantly exceeded the predicted ratio of 1 : 1. This result was independently confirmed by others [4] illustrating the complexity of these systems. Boudart observed that for certain probe reactions such as neopentane conversion, Pt/Y was much more active than Pt/Al_2O_3. Neopentane is commonly thought to be a sensitive probe for metal sites in a metal/acid bifunctional medium due to the difficulty of forming a stable carbenium ion in the molecule. The results bear out that the Pt metal in this catalyst resembles the behavior of Ir, its left hand neighbor in the periodic table. This enhanced activity was ascribed to an electron transfer from Pt to the zeolite support and was termed "electron-deficiency" [5].

Since these initial papers the role of electron deficient metal particles in zeolites has been reviewed by Gallezot [6,7]. The observation that electron-deficiency of zeolite supported Pt or Pd increases with the proton concentration and vanishes when zeolite protons are neutralized, led Sachtler et al. to propose the model that a metal–proton adduct is formed [8,9].

The ability to transfer electron density from a metal center to the host support is not limited to Pt or Pd metal. Experimental and theoretical evidence show that Rh, Ru, and Ir may also act in a similar fashion [10–12].

A series of investigations in this laboratory have lent strong support to the metal–proton adduct model. Homeyer et al. found enhanced activity in neopentane conversion for zeolite supported Pd over silica supported Pd [13]. Bai and Sachtler observed that for the conversion of methylcyclopentane the catalytic functions of metal and acid were not additive. Ring enlargement products of benzene (Bz) and cyclohexane (CH) were formed, the ratio Bz/CH was higher on catalysts having a larger proton concentration. It was suggested that the proton adduct acts as a "collapsed bifunctional site", i.e. all molecular transformations may occur during a single adsorption [8]. This ability of Pd to form adducts and to be in contact with zeolite protons serving also as anchors has been characterized by IR, chemical, and other physical tests [14–16]. XPS results of Pd/NaY, Pd/NaHY, and Pd/HY clearly demonstrate the "electron-deficiency" of Pd in these adducts [17]. For very small values of n in $[Pd_n\text{–}H_x]^{x+}$, in particular $n = 1$, the chemisorption of H_2 was found to be rather dramatically affected: very high metal dispersion, verified by EXAFS data, results in low values of the H_{ads}/Pd ratio [18].

The research reported in this paper deals with Pt and Pd supported in mordenite (Mor). The characterization of these systems and the special relationship of metal particle formation and acidity have recently been reported [19,20]. Catalytic activity has been tested using methylcyclopentane conversion as a probe reaction. The activity sequence: Pt(Pd)/HMor > Pt(Pd)/NaMor > Pt(Pd)/SiO_2 has been found. MCP conversion is a bifunctional reaction in which products may be produced in three parallel paths, i.e. cracking (CR), ring opening (RO), and ring enlargement (RE). The specific selectivity of products in each group is pertinent to the reaction mechanism and the catalytic sites. Stereo-specificity in RO for Pt/mordenite has been recently described [19]; it is also dependent on the proton concentration.

The present paper focuses on the unusual selectivity of MCP ring enlargement. The ratio of ring enlargement products, benzene (Bz) and cyclohexane (CH), has been evaluated for a variety of Pt and Pd mordenite catalysts following various pretreatment programs.

2. Experimental

0.5% and 1% Pt and 0.3% Pd H-mordenites were prepared by ion exchange. A dilute solution of the metal tetraammine nitrate was added dropwise at room temperature over 48 h to a slurry of zeolite (2000 ml DDI H_2O/g zeolite). The precursor zeolite was ammonium mordenite (UOP, LZ-M-8) which was converted to H-mordenite during calcination as described below. Ion exchanged samples were filtered, collected, and dried at room temperature and stored in a desiccator over a NH_4Cl/H_2O solution until a constant weight was maintained. Samples were calcined in a quartz reactor from room temperature (RT) to 510°C at 0.5°C/min in UHP oxygen (Linde, >1000 ml/min g) and were held at 510°C for 2 h. Samples were subsequently purged at 510°C for 20 min with UHP helium (Linde, 50 ml/min) and then cooled in He to RT.

Samples denotes as "wet" have been exposed to water vapor after calcination but prior to reduction. Water is brought to the catalyst at RT as a saturated helium vapor (50 ml/min) which passes through a double jacketed saturator containing water and maintained at 8°C. This stream is passed for a sufficient time as to allow restoration of 12 wt% of the catalyst load as water, assuming the catalyst takes up all the water supplied.

Reduction is performed from RT to 350°C at 8°C/min in UHP hydrogen (Linde, 20 ml/min) and held at 350°C for 30 min. The system is then cooled to the reaction temperature of 240°C in flowing hydrogen.

The MCP probe reaction is carried out with 100 mg of catalyst at 240°C and atmospheric pressure. MCP is brought to the catalyst as a saturated hydrogen vapor (20 ml/min) that passed through a saturator containing MCP and which is maintained at 0°C. This provides for an $H_2/MCP = 16$. The space velocity is therefore approximately 3400 h^{-1}. Conditions are such that conversions are always less than 12% and are considered to be in the differential regime. On-line gas analysis of reaction products is made by a Hewlett Packard 5790 gas chromatograph equipped with a capillary column and a flame ionization detector.

The equilibrium ratios of benzene to cyclohexane were calculated from thermodynamic data and verified experimentally by reacting either pure benzene with hydrogen or pure cyclohexane over Pt/SiO_2 for 24 h and varying the space velocity to determine the true equilibrium ratio independent of flow rate. Values of the experimental measurements were within 10% of the theoretical value which is within the estimated experimental error of the apparatus.

3. Results and discussion

Table 1 gives the initial and steady-state conversions for the catalysts studied as well as the product distributions. Both zeolite catalysts deactivate rapidly over

Table 1
Product distributions for 0.3% Pd and 0.5% Pt H-mordenite catalysts

	Catalyst			
	Pd/HMor dry	Pd/HMor wet	Pt/HMor dry	Pt/HMor wet
init. conv.[a]	5.92	3.54	6.80	3.84
s.s. conv.	3.13	2.73	3.38	1.80
selectivity (%)				
C_1	0.51	0.37	–	–
C_2	–	–	–	–
C_3	1.01	0.71	1.29	–
i-C_4	3.37	2.24	3.29	2.68
C_4	0.66	0.81	0.97	–
i-C_5	2.28	1.53	2.34	–
C_5	0.92	0.75	–	–
Cp	0.62	0.79	–	–
nH	0.86	0.64	3.02	2.12
2MP	4.41	3.38	6.25	6.39
3MP	1.55	1.28	4.21	2.52
CH	80.59	83.28	76.81	83.11
Bz	3.24	4.21	1.82	3.18

[a] After 10 min on stream.

time, most severely in the first minutes of reaction. Steady-state performance is therefore achieved quickly.

The product distribution is skewed toward ring enlargement with selectivities in this fraction being greater than 80%. Physical characterizations of these catalysts have been reported elsewhere [19,20]. In summary, the pretreatment conditions are such that all metal is reduced. Particle sizes are less than 10 Å and may reside in side pockets of the mordenite. The dispersion for all catalysts is greater than 90%.

The equilibrium constant for the reaction forming Bz and CH was calculated by using van 't Hoff's relation for the Gibbs free energy for the equilibrium of gases which can be considered as ideal: $\Delta G^0 = -RT \ln K_p$ with $\Delta G^0 = \Delta H^0 - T\Delta S^0$. The values of ΔH^0 and ΔS^0 at the temperature of our experiments were calculated from the standard enthalpy and entropy and the integrals of $\Delta C_p\,dT$ and $\Delta C_p/T\,dT$ respectively over the temperature range. C_p and other standard thermodynamic data were obtained from the literature [21]. The C_p data are given as a power series $C_p = a + bT + cT^2 + dT^3$. Calculated values for the free energy, enthalpy, and entropy at 240°C are given in table 2.

Per definition K_p is given by

$$K_p = [(P_{Bz}/P^0_{Bz})(P_{H_2}/P^0_{H_2})^3]/(P_{CH}/P^0_{CH}),$$

Table 2
Thermodynamic data for the conversion of cyclohexane to benzene at 513 K

ΔG_{rxn} (kcal/mol)	ΔH_{rxn} (kcal/mol)	ΔS_{rxn} (cal/mol)
3.9336	51.7304	93.1440

where $P^0_{CH} + P^0_{Bz} + P^0_{H_2} = 1$ atm. In order to calculate the dimensionless quantity $(P_{Bz}/P_{CH})_{eq.}$ we need to insert $(P_{H_2}/P^0_{H_2})$. Our reaction system operates at an initial H_2/MCP ratio of 16, so that 6% of the feed is hydrocarbon and $P_{H_2} = 0.94$ atm. From these numbers a value of 0.024 is obtained (at $P_{H_2} = 0.94$ atm) for the equilibrium Bz/CH ratio. The experimental values of the Bz/CH for the product of MCP over zeolite supported Pt catalysts and the results of Bz hydrogenation and CH dehydrogenation of Pt/SiO_2 are shown in table 3 together with the theoretical value.

It is evident from these data that the Bz/CH value of the RE of MCP over all Pt/HMor and Pd/HMor catalyst samples is in excess, in some cases greatly, of the equilibrium value. Addition of water to the pretreatment schedule results in a further increase in the Bz/CH ratio. The possibility of the Bz/CH ratio being increased due to a conversion of cyclohexane in a secondary reaction can be ruled out. First, the reactions were carried out at low conversion in the differential regime. Secondly, even if we assume that *n*-hexane and all cracking products of the reaction stem from reactions consecutive to the formation of cyclohexane, the corrected ratio of Bz/CH is still in excess of that predicted by equilibrium. These values are listed in table 4.

It is not unusual that two products from the same reactant are formed in non-equilibrium ratio. If both products are formed in *parallel* paths, the product formed via the transition state of lowest free energy will prevail. If products are formed in a *consecutive* way, the ratio of secondary to primary product will be lower than the equilibrium ratio if the rate constant for the latter step is significantly smaller than that leading to the primary product. A secondary/primary product ratio high-

Table 3
Benzene/cyclohexane ratios for wet and dry Pd and Pt mordenite catalysts

Catalyst	Wet Bz/CH (+/−S.D.)	Dry Bz/CH (+/−S.D.)
0.5% Pt/HMor	0.038 (0.004)	0.028 (0.004)
1% Pt/HMor	0.065 (0.002)	0.050 (0.001)
0.3% Pd/HMor [a]	0.048 (0.005)	0.038 (0.003)
theoretical [b]	0.024	0.024
1% Pt/SiO_2 from Bz	0.023	0.023
1% Pt/SiO_2 from CH	0.023	0.023

[a] 0.3 wt% Pd is approximately the same mole quantity as 0.5 wt% Pt.

[b] Corrected to the actual H_2 partial pressure of the reactor.

Table 4
Benzene/cyclohexane ratios for various catalysts adjusted for contributions from 2° reactions

Catalyst	Bz/CH (original) (wet/dry)	Bz/CH (CH + CR + n-2C$_6$) (wet/dry)
0.5% Pt/HMor	0.038/0.028	0.038/0.027
1% Pt/HMor	0.065/0.050	0.061/0.047
0.3% Pd/HMor	0.048/0.038	0.046/0.035

er than the equilibrium ratio would violate the principle of microscopic reversibility. The results, therefore, unambiguously rule out the possibility that benzene is formed via a secondary dehydrogenation of cyclohexane.

In the classical mechanism of bifunctional catalysis [22] MCP is dehydrogenated over a metal site to methyl cyclopentene; this molecule migrates to a Brønsted acid site and becomes a methyl cyclopentyl carbenium ion which isomerizes to a cyclohexyl carbenium ion. In the next step a cyclohexene molecule leaves the acid site and is adsorbed on a metal site. Up to this point all steps are consecutive; once the cyclohexene molecule is adsorbed on the metal, two parallel paths lead to cyclohexane or benzene.

An alternative mechanism has been proposed by Kouwenhoven [23]. When applied to the present reaction, it assumes that a MCP molecule transfers a hydride ion to a cyclohexyl carbenium ion on the catalyst surface. The result of this step is that a new cyclopentyl carbenium ion and a cyclohexane molecule are formed. The latter molecule may, in a subsequent step, interact with a metal site, where it is dehydrogenated to benzene. In this scheme cyclohexane is a primary and benzene a secondary product. On the basis of the present results this mechanism can be ruled out for the present catalyst system.

The data are in agreement with the "collapsed bifunctional site" model proposed previously [8]. Dissociative adsorption of MCP on a metal–proton adduct will lead to a complex consisting of a methylcyclopentyl group held on a metal site via a metal carbon bound, but the complex carries a positive charge as schematically shown in fig. 1.

In this scheme, all structural changes to convert the five-membered to a six-membered ring and all C–H bond formations or ruptures required to form the reaction products take place without intermediate desorption. In this scheme, just as in the classical bifunctional mechanism, benzene and cyclohexane appear as parallel reaction products.

The conclusion that the transition state leading to Bz is lower than that leading to CH is not unreasonable as it is likely that electron-deficiency of the adsorption complex (i.e. adsorbing metal atoms and adsorbed hydrocarbon fragment) will favor the formation of unsaturated intermediates (cyclopentene, cyclopentadiene, cyclohexene, cyclohexadiene, benzene). For these molecules the formation of positive ions, in particular when complexing with metal atoms, has been amply demonstrated [24]. Resonance between states where the molecule is neutral and the

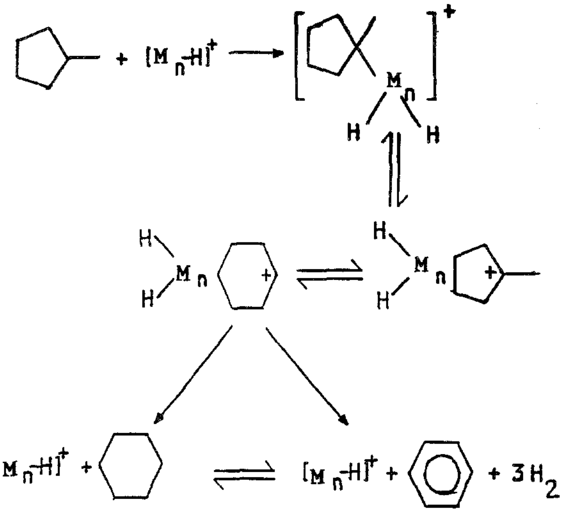

Fig. 1. Proposed mechanism for the ring enlargement of MCP to benzene or cyclohexane by a proton adduct. Me = Pt or Pd and *n* is the number of metal atoms.

metal carries the positive charge and other states where neutral metal atoms interact with cyclic carbocations, lowers the energy of these complexes. This will also result in a lowering of the corresponding transition states in comparison to the situation where a neutral alkyl group is adsorbed on a neutral metal surface. It is therefore possible that the favorable interaction of unsaturated molecules leads to a kinetic preference for the path(s) leading to dehydrogenation of the six-membered ring. The model could be further tested by reacting MCP over other catalysts such as Rh/HY [10] where proton adducts are also believed to exist.

4. Conclusions

Metal particles in zeolites interact with protons to form special species, perhaps metal–proton adducts. The number and/or activity of these species is promoted by addition of water. These species do not catalyze ring enlargement by a direct hydride ion transfer mechanism. Benzene is the primary product of MCP ring enlargement over these catalysts due to stabilization of the transition-state leading to its formation.

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