JOURNAL OF CATALYSIS 151, 330–337 (1995)

The Effect of Hydrogen Partial Pressure on Methylcyclopentane Ring Opening

M. Vaarkamp,*,[1] P. Dijkstra,* J. van Grondelle,* J. T. Miller,† F. S. Modica,† D. C. Koningsberger,‡ and R. A. van Santen*

*Schuit Institute of Catalysis, Department of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands; †Amoco Oil Research Center, P.O. Box 3011, Naperville, Illinois 60566-7011; and ‡Debye Institute, Department of Inorganic Chemistry, Utrecht University, P.O. Box 80083, 3508 TB Utrecht, The Netherlands

Received April 25, 1994; revised September 8, 1994

The ring opening of methylcyclopentane (MCP) over well-characterized Pt/SiO_2 (EUROPT-1), $Pt/\gamma\text{-}Al_2O_3$, and Pt/K-LTL catalysts was studied as a function of hydrogen partial pressure and reduction temperature. The MCP ring opening selectivity did not change in the range of $H_2:MCP$ ratios studied (8–200). The turnover frequency (TOF) went through a maximum as the $H_2:MCP$ ratio increased. The maximum TOF of the $Pt/\gamma\text{-}Al_2O_3$ after reduction at 450°C is about three times higher than the maximum specific activity of the Pt/K-LTL and Pt/SiO_2 catalysts. The $H_2:MCP$ partial pressure ratio at which maximum activity is obtained increases in the series Pt/K-LTL $<$ $Pt/\gamma\text{-}Al_2O_3$ $<$ Pt/SiO_2. This sequence is rationalized using reported adsorption energies of H_2 and assuming a decreased adsorption energy of MCP on Pt/K-LTL. The data can be described with a reaction mechanism that includes the cleavage of a C–C bond as the rate-determining step. Kinetic analysis of the changes in specific reaction rate as a function of the $H_2:MCP$ ratio showed that the reaction proceeds through multiple adsorbed MCP species. The surface reaction rate is more than an order of magnitude higher for the $Pt/\gamma\text{-}Al_2O_3$ catalyst than for the Pt/K-LTL catalyst, but decreases with increasing reduction temperature for both catalysts. © 1995 Academic Press, Inc.

INTRODUCTION

Methylcyclopentane (MCP) ring opening has been widely used as a catalytic probe for the particle size in platinum catalysts. The ring opening is nonselective (statistical) when catalyzed by small platinum particles, but selective (nonstatistical) over large platinum particles (1). In particular, the selectivity toward *n*-hexane decreases when the particle size increases. Several mechanisms to account for the change in selectivity with particle size have been proposed (1–3). Much less attention has been paid to the changes in reactivity with hydrogen and MCP partial pressure.

An increase in MCP ring opening activity with partial pressure of hydrogen has been reported for Pt/C (4, 5), Pt black (4, 6), Pt/SiO_2 (4, 6, 7), Pt/Al_2O_3 (4, 8, 9), and Ir/Al_2O_3 (10) catalysts. If the experiments are carried out at temperatures below 300°C a maximum in activity is observed (8). The observation of maximum activity can be explained phenomenologically by the competition of the reactants for the same surface site. Frennet and coworkers (11, 12) showed that competition of hydrogen and hydrocarbon can account for the volcano-type activity plots and the broadening of the maximum at high temperature.

This paper reports a study on the ring opening of MCP as a function of hydrogen partial pressure over well-characterized Pt/SiO_2, Pt/K-LTL, and $Pt/\gamma\text{-}Al_2O_3$ catalysts. The selectivity is unaffected by the hydrogen partial pressure and only slightly different for catalysts reduced at higher temperatures. The specific activity changes with the support, hydrogen partial pressure, and reduction temperature. A kinetic model that describes the changes in activity with hydrogen partial pressure is presented and discussed.

EXPERIMENTAL

Catalyst Preparation

The K-LTL zeolite was obtained from Linde. The zeolite was repeatedly washed with water until the pH of the wash solution was 9.5. The resulting K–LTL zeolite contained 8.3 wt% Al and 13.0 wt% K. Subsequently the zeolite was impregnated with tetramine platinum (II) nitrate to yield a 1.2 wt% Pt/K-LTL catalyst. The impregnated catalyst was dried at 130°C. The activity of this catalyst for the aromatization of *n*-hexane has been reported previously (13).

The 1.0 wt% $Pt/\gamma\text{-}Al_2O_3$ catalyst was prepared by pore volume impregnation of the $\gamma\text{-}Al_2O_3$ (CK300, Ketjen) sup-

---

[1] Present address: Mitsubishi Chemical Corporation, Yokohama Research Center, 1000 Kamoshida-cho, Aoba-ku, Yokohama 227, Japan.

0021-9517/95 $6.00

port with a solution of H_2PtCl_6. After overnight drying at 120°C in air, the catalyst was reduced at 300°C (heating rate 3°C/min) for 4 h under flowing H_2 and passivated at RT.

The preparation, characterization, and catalytic properties of the 6.3 wt% Pt/SiO_2 catalyst (EUROPT-1) has been thoroughly described (14, 15).

Prior to the catalytic experiments the catalysts were dried *in situ* at 120°C for at least 1 h under flowing nitrogen, followed by *in situ* reduction under a stream of hydrogen for 1 h at the specified reduction temperature (heating rate 5°/min).

Hydrogen Chemisorption

The desorption isotherms of hydrogen were measured in a conventional volumetric glass apparatus. Hydrogen was purified by passage over a reduced copper catalyst to remove oxygen and a 5A molecular sieve to trap water. Typically 0.5 g of catalyst was dried at 120°C prior to reduction. After reduction, the catalyst was cooled under H_2 to 200°C and the apparatus was evacuated to 10^{-2} Pa for 15 min. Subsequently a known amount of hydrogen was admitted to the sample (activated hydrogen adsorption) and the sample was cooled to room temperature. At room temperature the hydrogen desorption isotherm was measured between 10 and 80 kPa. The H/Pt value was calculated by extrapolating the hydrogen desorption isotherm to zero pressure (16).

Catalytic Measurements

Methylcyclopentane (Janssen Chimica, 99+% purity) ring opening experiments were carried out at atmospheric pressure in a fixed-bed, continuous flow reactor. The internal diameter of the stainless-steel reactor was 12 mm; inside the reactor a stainless steel tube of 6-mm diameter with a thermocouple was mounted. Typically 1 g of catalyst of particle size 125–450 μm was used. Reaction products were analyzed on-line using a HP5995 gas chromatograph, equipped with a FID detector and a 50-m Chrompack fused silica capillary column with an Al_2O_3/KCl coating.

The conversion was varied by changing the weighted hourly space velocity (WHSV) at a constant linear gas flow rate. The Pt/SiO_2 catalyst was diluted with silica. Conversion is defined as the fraction of MCP converted; selectivity is defined as the amount of a product divided by the amount of MCP converted. The turnover frequency (TOF) was calculated from the number of molecules of MCP converted and the H/Pt ratio, assuming that every site capable of chemisorbing hydrogen is a catalytically active site. The absence of diffusion limitations was verified by using different sieve fractions and linear gas flow rates.

TABLE 1

Hydrogen Chemisorption and Ring Opening Activity Results
H_2:MCP Ratio = 40, Conversion ≤10 wt%

Catalyst	T_{red} (°C)	H/Pt	WHSV (h^{-1})	E_{act} (kJ/mol)
Pt/K-LTL	300	1.42	0.22	158 ± 9
	450	1.27	0.22	162 ± 5
	600	0.84	0.22	159 ± 2
Pt/γ-Al_2O_3	300	1.48	0.27	138 ± 2
	450	1.16	0.27	143 ± 4
	600	1.03	0.27	129 ± 1
Pt/SiO_2	450	0.80[a]	1.37	138 ± 3

[a] Taken from Ref. (15).

Deactivation and initial selectivities were measured by storing samples in a 16 position loop selection valve (Valco ST16), positioned between the reactor and the gas chromatograph. By storing samples it is possible to take up to 15 samples within a minute.

RESULTS

Characterization

The Pt/K-LTL and Pt/γ-Al_2O_3 catalysts were extensively characterized by EXAFS and hydrogen TPD (17–19). Results are similar for both catalysts. The particle size increases with reduction temperature. After reduction at low temperature (300°C, LTR) the platinum clusters contain 5–7 atoms, while after reduction at high temperature (600°C, HTR) the clusters contain ≈11 atoms. Furthermore, the structure of the metal–support interface changes with reduction temperature. After LTR, hydrogen is present in the metal–support interface. This hydrogen is released by treatment above 500°C. Hence, the platinum particle has a more intimate contact with the support and will therefore be more influenced by the support after HTR than after LTR.

The 6.3 wt% Pt/SiO_2 catalyst has particles varying in size from 0.9 to 3.5 nm; the average size is 1.8 nm (14). Extensive characterization by EXAFS and TEM showed that the catalyst has an excellent thermal stability; no decrease in dispersion was observed after reduction at 600°C for a short period (14).

The hydrogen chemisorption capacity (Table 1) shows that the platinum is highly dispersed, even after reduction at 600°C. For both Pt/K-LTL and Pt/γ-Al_2O_3 the hydrogen chemisorption capacity decreases with the reduction temperature, consistent with the increase in particle size observed with EXAFS.

Stability

The catalysts deactivated during the catalytic runs. At high H_2 to MCP partial pressure ratio (H_2:MCP ratio)

TABLE 2

Product Selectivities (wt%) of MCP Ring Opening on the Pt/K-LTL Catalyst Reduced at 310°C after 0 and 12 h time on Stream (TOS)

	$H_2:MCP = 8$		$H_2:MCP = 40$	
Product	Initial	12 h TOS	Initial	12 h TOS
2MP	32	32	33	33
3MP	29	30	33	33
n-Hexane	13	20	30	30
Benzene	16	11	3	3
True *n*-hexane (nC_6 + benzene)	29	31	33	33

Note. Reaction Temperature 270°C, WHSV = 0.22 h^{-1} ($H_2:MCP$ = 8) and 0.44 h^{-1} ($H_2:MCP$ = 40).

this did not affect the product distribution. At low $H_2:MCP$ ratios the selectivity toward olefins and benzene decreased with time on stream (TOS).

The rate and extent of activity loss depend on the ratio of hydrogen to MCP partial pressure. At low values of this ratio (<15) 40% of the initial activity was lost in the first 3 h on stream. No further changes in activity or selectivity were observed with TOS. At high values of the $H_2:MCP$ ratio (>35), deactivation in the first hour is approximately 15%. After the first hour the catalyst was stable.

The changes in selectivity were similar for all catalysts; therefore, only results for a Pt/K-LTL catalyst reduced at 310°C (Table 2) will be reported. At high $H_2:MCP$ ratios, selectivities are independent of the TOS. The selectivity toward ring opening products is higher than 97%; the other product is benzene (3%). At low H_2:MCP ratios the selectivity toward ring opening products changes with TOS, (initially 74%, after 12 h 82%) and the selectivity toward benzene decreases with TOS from 16 to 11%. The remaining products are unsaturated C_6.

Analysis of the results obtained with the Delplot technique (20) showed that benzene is a secondary product. Recently, Lane *et al.* (13) showed that the formation of benzene is only possible via 1,6-ring closure for nonacidic catalysts. Therefore, the combined benzene and *n*-hexane selectivity is regarded as the true *n*-hexane selectivity. The true selectivity for *n*-hexane does not change with TOS.

The constant true *n*-hexane selectivity of the Pt/K-LTL catalyst with TOS (deactivation) differs from the increase reported by Ponec and co-workers (21) for Pt/SiO_2 catalysts. They related the increased *n*-hexane formation to the increasing amount of coke on the surface of the catalyst. The higher resistance of the Pt/K-LTL catalysts to coke formation (22) is the explanation for this difference in behavior.

Selectivity

The selectivities in the ring opening products varied for conversions higher than 10%, due to isomerization of the ring opening products (consecutive reactions) on the platinum surface. To minimize consecutive reactions the conversion was kept below 10%.

All catalysts produce mainly ring opening products and varying amounts of hydrogenolysis and aromatization products (Table 3). Selectivity toward olefins is negligible. Increasing the reduction temperature from 300 to 550 or 600°C has only minor effects on the selectivity.

The *n*-hexane selectivity obtained for the EUROPT-1 catalyst (29%) agrees with reported values. Kramer and Fischbacher reported on *n*-hexane selectivity of 34% after reduction at 400°C; the selectivity drops to 23% after sintering at 950°C (23).

The *n*-hexane selectivity of the Pt/γ-Al_2O_3 catalyst decreases from 13.2% to 8.5% when the reduction temperature is raised from 300 to 550°C, consistent with trends observed in the literature (23). Adding a pulse of pyridine to the reactant stream did not change the product selectivities. Hence, no isomeriation on acidic sites on the alumina surface occurs. Literature values for the *n*-hexane selectivity range from 38% for a 0.2 wt% Pt/Al_2O_3 catalyst (24) to 13% for the sintered standard 0.3 wt% Pt/Al_2O_3 catalyst (23). An *n*-hexane selectivity of 5% was reported for a 10 wt% Pt/Al_2O_3 catalyst (24).

Comparison of the selectivity of the Pt/K-LTL catalyst with the selectivity pattern obtained for the Pt/SiO_2 catalyst shows that the selectivity toward 2MP is diminished

TABLE 3

Selectivities of MCP Ring Opening at 270°C and $H_2:MCP$ Ratio of 40, Conversion ≤10 wt% (Pt/γ-Al_2O_3 Results at $H_2:MCP$ Ratio of 22)

	Catalyst						
	Pt/SiO_2	Pt/γ-Al_2O_3			Pt/K-LTL		
T_{red} (°C)	450	300	450	550	300	450	600
Crack	0.5	3.8	1.7	0.5	6	1	11
2MP	51.8	62	66	68	32	39	33
3MP	16.6	21	23	23	34	30	28
n-Hexane	29.3	13	9	8	24	25	24
C_6 Olefins	0.2	—	—	—			
Benzene	1.6	0.2	0.3	0.5	4	5	4
True nC_6	30.9	13.2	9.3	8.5	28	30	28
2MP : 3MP	3.1	3.0	2.9	3.0	0.9	1.3	1.2
nC_6 : 3MP	1.9	0.6	0.4	0.4	0.8	1.0	1.0

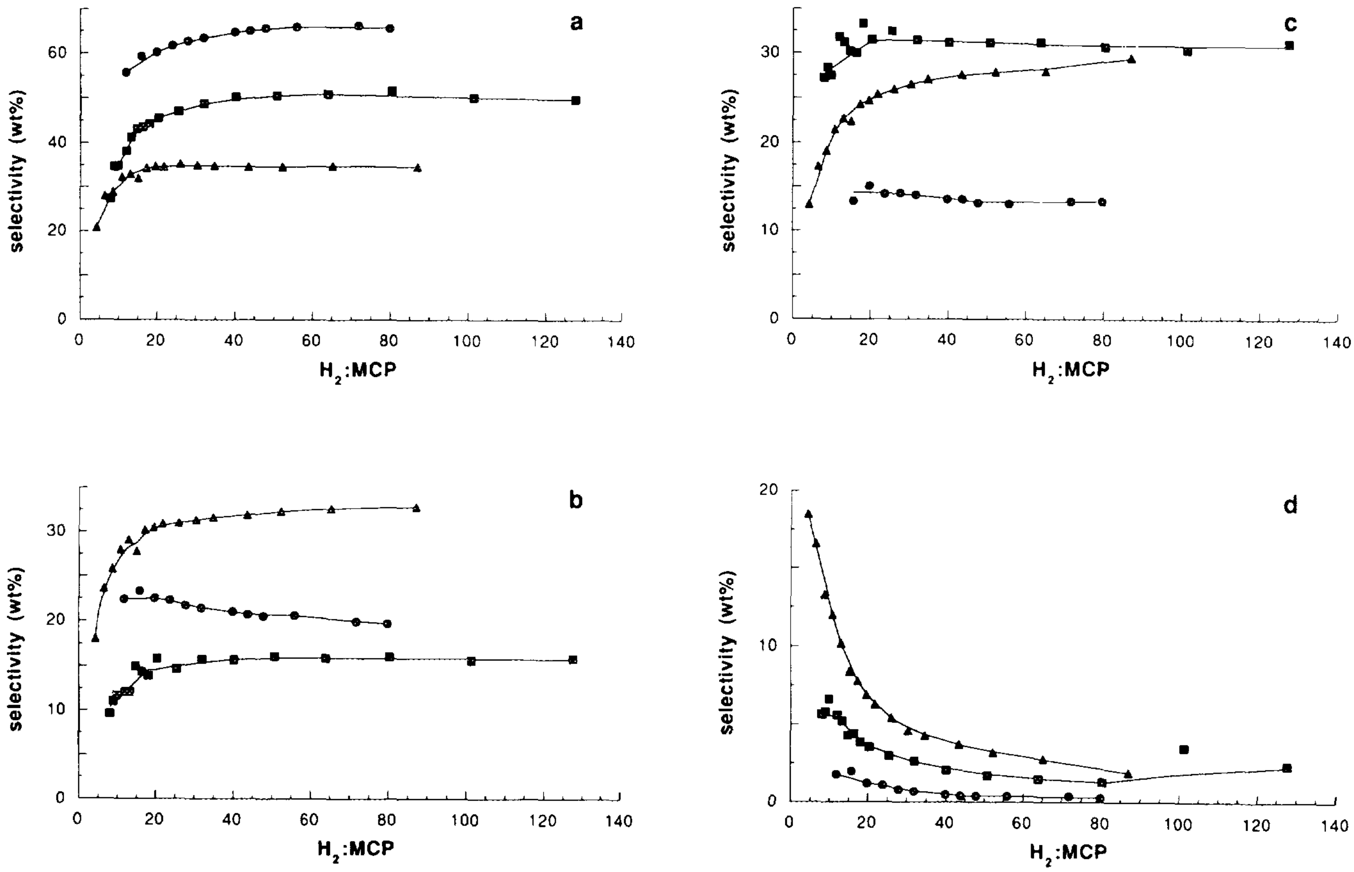

FIG. 1. Selectivity of MCP ring opening as a function of H_2 : MCP partial pressure ratio for Pt/SiO_2 (square), Pt/K-LTL (triangle) and Pt/γ-Al_2O_3 (circle). All catalysts reduced at 400–450°C. (a) 2-methylpentane, (b) 3-methylpentane, (c) n-hexane, and (d) benzene. The lines are drawn as a visual guide.

and that toward 3MP is increased. The higher selectivity toward 3MP has been reported for Pt/FAU (25, 26) and Pt/LTL (27) catalysts and is attributed to the constraint that the zeolite pore imposes on the orientation of the MCP molecule (26) and, hence, the adsorption geometry.

The changes in selectivity toward ring opening products and benzene with the H_2 : MCP partial pressure ratio are shown in Fig. 1. The benzene selectivity decreases with increasing H_2:MCP ratio. The selectivity toward n-hexane increases with hydrogen partial pressure for the Pt/K-LTL catalyst, whereas it is constant for the Pt/SiO_2 and Pt/γ-Al_2O_3 catalysts. However, the true n-hexane selectivity (n-hexane + benzene) is invariant with changing H_2 : MCP ratio for all catalysts (Fig. 2). In general, the selectivity toward ring opening products increases with H_2:MCP ratio. This trend is stronger for the Pt/SiO_2 and the Pt/K–LTL catalyst than for the Pt/γ-Al_2O_3 catalyst.

The ratio of 2MP to 3MP selectivity, i.e., 3, is similar to reported values for silica or alumina catalysts (1, 23, 28), but much higher than predicted by both the selective and the nonselective mechanism, i.e., 2. The 2MP : 3MP selectivity ratio is constant over the H_2 : MCP ratio studied for the Pt/SiO_2 and the Pt/K-LTL catalyst (Fig. 3). It increases slightly for the Pt/γ-Al_2O_3 catalyst, indicating a minor influence of the hydrogen surface coverage on the selectivity of the ring opening reaction.

Activity

The apparent activation energy for the ring opening of MCP for the catalysts studied is shown in Table 1. The highest temperature data were measured first. The activation energy of the Pt/K-LTL catalyst is the highest (≈160 kJ mol^{-1}); for the Pt/γ-Al_2O_3 catalyst and the Pt/SiO_2 catalyst it is about 20 kJ mol^{-1} lower. The influence of the reduction temperature on the activation energy is negligible for Pt/K-LTL. Increasing the reduction temperature from 300 to 450°C for the Pt/γ-Al_2O_3 catalyst increases the activation energy slightly (5 kJ mol^{-1}); further increase of the reduction temperature from 450 to 600°C decreases the activation energy significantly (14 kJ mol^{-1}).

The turnover frequency (TOF) for the MCP conversion

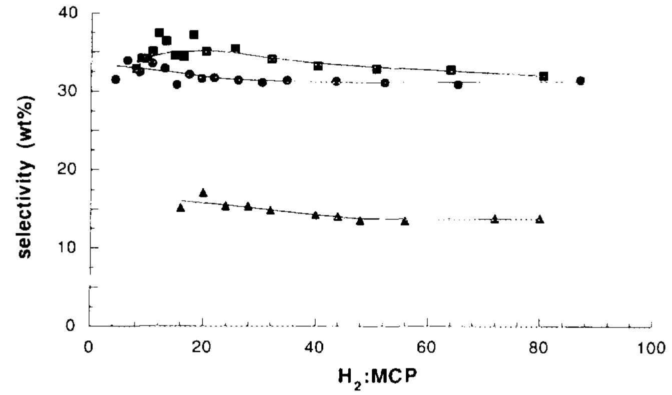

FIG. 2. Selectivity toward *n*-hexane plus benzene of the Pt/SiO$_2$ (square), Pt/K-LTL (triangle), and Pt/γ-Al$_2$O$_3$ (circle) catalysts after reduction at 400–450°C. The lines are drawn as a visual guide.

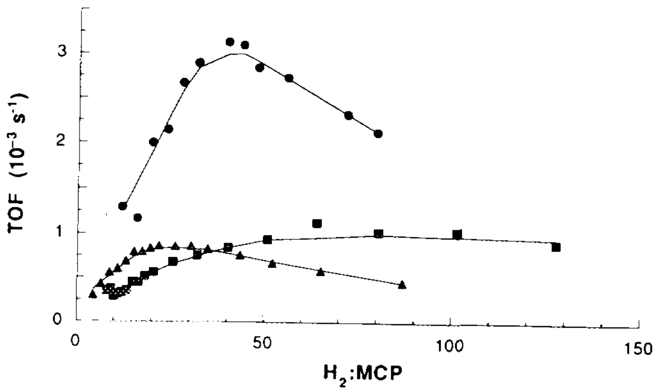

FIG. 4. Variation of turnover frequency (TOF) with H$_2$: MCP partial pressure ratio at 270°C for Pt/SiO$_2$ (square), Pt/K-LTL (triangle), and Pt/γ-Al$_2$O$_3$ (circle). All catalysts reduced at 400–450°C. The lines are drawn as a visual guide.

increases in the order Pt/K-LTL < Pt/SiO$_2$ < Pt/γ-Al$_2$O$_3$ (Table 1). The relative activities are the same as those for hydrogenolysis of propane (29). The difference in TOF between the Pt/γ-Al$_2$O$_3$ and Pt/SiO$_2$ catalysts is similar to the difference in TOF between the standard Pt/Al$_2$O$_3$ (EUROPT-3) and the standard Pt/SiO$_2$ (EUROPT-1) catalysts (23, 30).

The rate of MCP ring opening as a function of H$_2$: MCP partial pressure ratio is different for the Pt/K-LTL, Pt/γ-Al$_2$O$_3$, and Pt/SiO$_2$ catalysts (Fig. 4). The TOF of the Pt/K-LTL and Pt/γ-Al$_2$O$_3$ catalysts exhibits a maximum at different H$_2$: MCP ratios. The TOF of the Pt/SiO$_2$ catalyst shows a very broad plateau. The maximum activity is reached at different H$_2$: MCP ratios, indicating that adsorption of either MCP or H$_2$ is affected by the support used. The maximum in the TOF is not affected by the reduction temperature (Fig. 5).

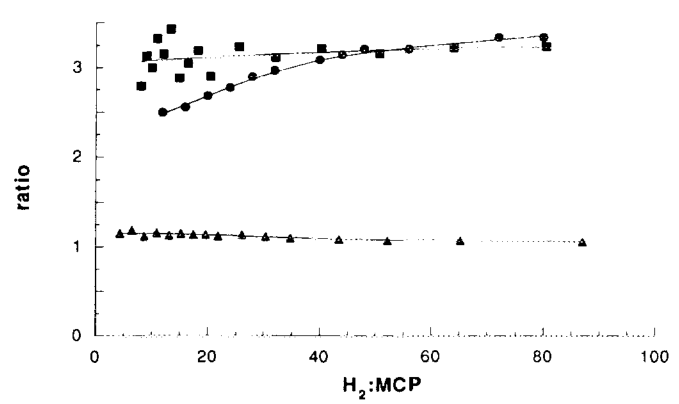

FIG. 3. Ratio of the selectivity toward 2MP and 3MP of the Pt/SiO$_2$ (square), Pt/K-LTL (triangle), and Pt/γ-Al$_2$O$_3$ (circle) catalyst after reduction at 400–450°C. The lines are drawn as a visual guide.

While increasing the reduction temperature from 300 to 450°C does not affect the TOF of the Pt/K-LTL catalyst, the TOF of the Pt/γ-Al$_2$O$_3$ catalyst increases three

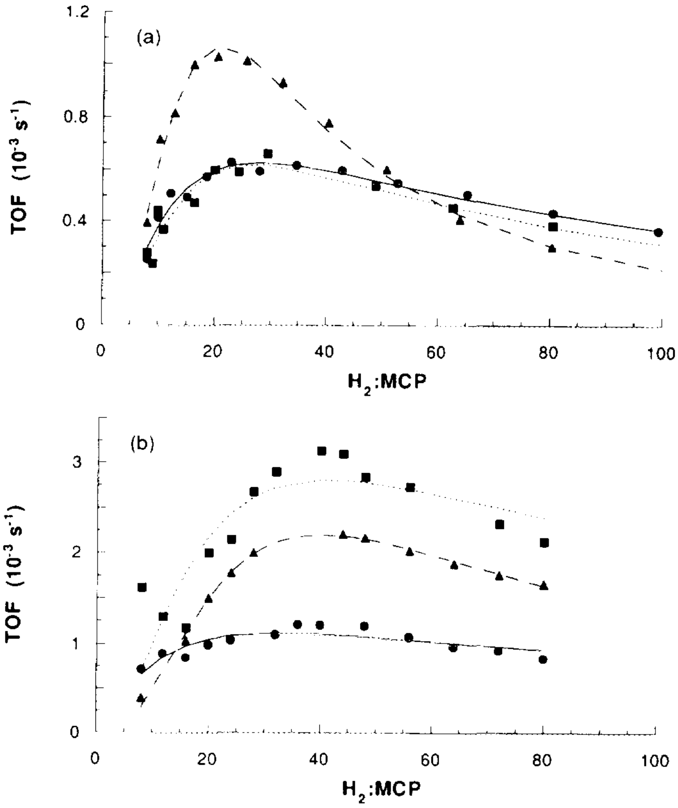

FIG. 5. Turnover frequency of MCP ring opening at 270°C and a MCP partial pressure of 0.5 kPa: (a) Pt/K-LTL and (b) Pt/γ-Al$_2$O$_3$. Reduction at 300°C (circle), 450°C (square), and 600°C for Pt/K-LTL or at 550°C for Pt/γ-Al$_2$O$_3$ (triangle). The lines represent the fits of the rate equation for the twofold adsorption of MCP.

times. Further increase of the reduction temperature lowers the specific activity of the Pt/γ-Al_2O_3 catalyst, whereas it increases the specific activity of the Pt/K-LTL catalyst.

Kinetic Analysis

The changes in specific activity with H_2 : MCP ratio were analyzed quantitatively using assumptions shown to hold for the hydrogenolysis of alkanes on iridium single crystals (31): (i) pseudoequilibrium is maintained for the adsorption of hydrogen and MCP onto the catalyst surface, and (ii) the rate-limiting step is the irreversible cleavage of a C–C bond. The pseudoequilibrium is described by two reactions:

$$H_2\,(g) + 2\# \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,H^{\#} \qquad [1]$$

$$MCP\,(g) + yn\# \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MCP^{\#} + n\,H^{\#}. \qquad [2]$$

In these reactions # represents an empty surface site, y represents the size of the "landing site" needed for dissociative adsorption of MCP, and n is the number of hydrogen atoms that split off from the MCP upon adsorption on the catalyst surface. It is assumed that the carbon atoms of MCP form only single bonds with surface platinum atoms and that the neighboring surface sites are not affected by MCP adsorption. Thus, the number of free surface sites needed for dissociative MCP adsorption is twice the number of split off hydrogen atoms ($y = 2$). Hydrogen–deuterium exchange experiments with cyclopentane have shown that MCP can adsorb onto the surface in one-, two-, three-, or fourfold mode (32), corresponding to values of n equal to 1, 2, 3, or 4 respectively. Hence, n is a measure for the degree of dehydrogenation of the surface species. The assumption that C–C bond breaking is the rate-determining step is expressed by

$$MCP^{\#} + (n+2)\,H^{\#} \xrightarrow{k_c} C_6\,(g) + (2n+2)\,\#. \qquad [3]$$

These three reactions result in the overall rate equation

$$r = k_c a^2 b \#^{2(n+1)}, \qquad [4]$$

with

$$a = \sqrt{K_1 p(H_2)} \qquad [5]$$

$$b = K_2 p(\mathrm{MCP}). \qquad [6]$$

The number of empty surface sites (#) for various values of n can be determined from

$$\#(a + 1 + na^{-n}b\#^{n-1}) = 1. \qquad [7]$$

No general solution of Eq. [7] can be obtained. For one-, two-, three-, and fourfold adsorption (n = 1–4) Eq. [7] was solved substituting the values of n in the equation and solving the resulting polynomial. The unique solutions for $n \geq 2$ are obtained by requiring that the number of sites is neither imaginary nor negative. Combination of the result for twofold adsorption of MCP with Eq. [4] gives

$$r = k_c a^2 b \left(\frac{a^2(a+1) - a^2\sqrt{(a+1)^2 + 8a^{-1}b}}{-4b} \right)^6. \qquad [8]$$

Each of the obtained rate equations was fitted to the experimental data. Onefold adsorption does not describe the data as well as multifold adsorption and is therefore rejected. The obtained curves are similar for two-, three-, and fourfold adsorption of MCP to the platinum surface. The fits for twofold adsorption are shown in Fig. 5 for the Pt/K-LTL and the Pt/γ-Al_2O_3 catalyst, results for three- and fourfold absorption are omitted for clarity. The agreement between model and data is good. The refined values for K_1, K_2, and k_c are listed in Table 4. The equilibrium constants for MCP and H_2 adsorption are higher for the Pt/K-LTL catalyst than for the Pt/γ-Al_2O_3 catalyst, indicating a higher apparent adsorption energy of both H_2 and MCP toward the platinum in the zeolite. The surface reaction rate (k_c) is at least one order of magnitude higher for the γ-Al_2O_3 supported platinum than for the zeolite supported platinum, suggesting a higher intrinsic activity.

DISCUSSION

The threefold increase in TOF of the Pt/γ-Al_2O_3 catalyst when the reduction temperature is raised from 300 to 450°C indicates that the intrinsic activity of the catalytically active site changes. The EXAFS characterization of this catalyst (19) has shown that by increasing the reduction temperature from 300 to 450°C the structure of the metal–support interface is changed and the shape of the particles changes from 3D to flat. At the same time hydrogen atoms at the metal–support interface are lost, placing the Pt in contact with the oxygen atoms of the support. The absence of the third shell in the EXAFS spectrum after reduction at 450°C indicates that a raft with fourfold symmetry is formed. This square surface might exhibit increased MCP ring opening activity in agreement with a study on the MCP ring opening activity of platinum single crystal surfaces (33). The sintering of the platinum particles at higher reduction temperatures, as indicated by the decreased hydrogen chemisorption capacity, will result in (hemi)spherical particles that expose a surface with sixfold symmetry and therefore ex-

TABLE 4

Reaction Rate Constants of MCP Ring Opening for Twofold Adsorbed MCP at 270°C

	Pt/K-LTL			Pt/γ-Al_2O_3		
T_{red} (°C)	K_1	K_2	k_c	K_1	K_2	k_c
300	5.0×10^{-2}	1.1×10^{-2}	7.9×10^{-1}	8.2×10^{-4}	4.4×10^{-4}	1.0×10^{1}
450	8.7×10^{-3}	3.8×10^{-2}	3.3×10^{-1}	1.5×10^{-3}	5.6×10^{-3}	3.1
600[a]	2.6×10^{-1}	2.3×10^{1}	5.4×10^{-2}	1.8×10^{-2}	4.4×10^{-1}	3.4×10^{-1}

[a] 550°C for Pt/γ-Al_2O_3.

hibit the observed lower specific MCP ring opening activity.

All catalysts show a maximum in the MCP ring opening activity, regardless of the support or the reduction temperature. The H_2 : MCP ratio at which maximum activity is obtained is a function of the support, but is not affected by the reduction temperature, i.e., particle size, morphology, and structure of the metal–support interface.

The rate of MCP ring opening is a function of the surface reaction rate and the surface concentration of hydrogen and MCP. Therefore, the optimal H_2:MCP ratio at which maximum activity is reached is affected by the adsorption energies of H_2 and MCP. Recent calorimetric measurements showed that the heat of adsorption of H_2 on Pt/K-LTL is up to 10 kJ/mol higher than for Pt/SiO_2 or acidic Pt/H-LTL (34), consistent with the observed lower H_2 : MCP ratio at which maximum activity is reached for the Pt/K-LTL catalyst. The 2MP : 3MP ratio of 3 obtained here and reported extensively in literature (1, 23, 28) suggests that the adsorption energy for the MCP species that leads to 2MP is higher than for the species that leads to 3MP. The observed increased production of 3MP for the Pt/K-LTL catalyst will therefore result in a lower average MCP adsorption energy and hence also a lower H_2:MCP ratio at which maximum activity is reached.

The reaction sequence derived from the assumptions that (i) adsorption of hydrogen and MCP is in pseudoequilibrium and (ii) the rate of C–C bond cleavage is rate limiting describes the obtained results within the experimental limits of accuracy. The pseudoequilibrium constants for H_2 and MCP adsorption cannot be related to the actual adsorption energies, because they are affected by the surface reaction rate. From the pseudoequilibrium constants for MCP and hydrogen adsorption it is clear that the surface of the Pt/γ-Al_2O_3 catalyst will have a higher hydrogen coverage than the surface of the Pt/K-LTL catalyst at the same H_2 : MCP ratio. This suggests that optimum activity is reached at lower H_2 : MCP ratio for the of the Pt/γ-Al_2O_3 catalyst than for the Pt/K-LTL catalyst. However, the at least 10 times higher surface reaction rate of the Pt/γ-Al_2O_3 catalyst shifts the optimum H_2 : MCP ratio to higher values. The difference in reaction rate for C–C bond breaking between the Pt/γ-Al_2O_3 and the Pt/K-LTL catalyst as well as the decrease in C–C bond breaking rate with increasing reduction temperature are consistent with reported results for hydrogenolysis of alkanes (29, 30, 35, 36).

At low H_2 : MCP partial pressure ratio (H_2 : MCP ratio), the surface reaction rate is limited by the rate of hydrogen dissociation, at higher H_2 : MCP ratio the surface is saturated with hydrogen. Clearly, this decreases the aromatics production at a higher H_2 : MCP ratio. The decreased stability of the catalysts at low H_2 : MCP ratio is consistent with these features, viz., due to the larger rate of coke deposition on hydrogen dificient platinum particles.

CONCLUSION

In the H_2 : MCP partial pressure ratio range of 8–200 the selectivity toward the various MCP ring opening products is invariant with H_2 : MCP ratio for the catalysts studied. A reaction sequence, in which the cleavage of a C–C bond is the rate-determining step, MCP is multiply adsorbed, and H_2 and MCP compete for the same surface sites, describes the data well. The H_2 : MCP ratio at which the maximum turnover frequency is reached, increases in the sequence Pt/K-LTL < Pt/Al_2O_3 < Pt/SiO_2. The position of the maximum is not affected by the particle size, morphology of the platinum particles, or the structure of the metal–support interface. The results can be rationalized from the differences in heat of adsorption of hydrogen and MCP.

REFERENCES

1. Gault, F. G., *Adv. Catal.* **30,** 1 (1981).
2. Kramer, R., and Zuegg, H., *J. Catal.* **85,** 530 (1984).
3. Finlayson, O. E., Clarke, J. K. A., and Rooney, J. J., *J. Chem. Soc. Faraday Trans.* **80,** 191 (1984).
4. Bragin, O. V., Karpinski, Z., Matusek, K., Paál, Z., and Tétényi, P., *J. Catal.* **56,** 219 (1979).
5. Olfer'eva, T. G., Krasavin, S. A., and Bragin, O. V., *Izv. Akad. Nauk SSSR Ser. Khim.* **3,** 605 (1981).
6. Zimmer, H., and Paál, Z., *J. Mol. Catal.* **51,** 261 (1989).
7. Brandenberger, S. G., Callender, W. L., and Meerbott, W. K., *J. Catal.* **42,** 282 (1976).

8. Krasavin, S. A., and Bragin, O. V., *Izv. Akad. Nauk SSSR Ser. Khim.* **6,** 1314 (1982).
9. Garin, F., and Gault, F. G., *J. Am. Chem. Soc.* **97,** 4466 (1975).
10. Sárkány, A., *J. Chem. Soc. Faraday Trans. I* **85,** 1523 (1989).
11. Frennet, A., Lienard, G., Crucq, A., and Degols, L., *J. Catal.* **53,** 150 (1978).
12. Frennet, A., *in* "Hydrogen Effects in Catalysis" (Z. Paál and P. G. Menon, Eds.), p. 399. Dekker, New York, 1988.
13. Lane, G. S., Modica, F. S., and Miller, J. T., *J. Catal.* **129,** 145 (1991).
14. Bond, G. C., Garin, F., and Maire, G., *Appl. Catal.* **41,** 313 (1988).
15. Bond, G. C., and Wells, P. B., *Appl. Catal.* **18,** 221 (1985).
16. Benson, J. E., and Boudart, M., *J. Catal.* **4,** 704 (1965).
17. Vaarkamp, M., van Grondelle, J., van Santen, R. A., Miller, J. T., Modica, F. S., Lane, G. S., and Koningsberger, D. C., *in* "Proceedings, 9th International Zeolite Conference, Montreal, 1992" (R. von Ballmoos, J. B. Higgins, and M. M. J. Treacy, Eds.), Vol. II, p. 443. Butterworth–Heinemann, London, 1993.
18. Vaarkamp, M., Modica, F. S., Miller, J. T., and Koningsberger, D. C., *J. Catal.* **144,** 394 (1993).
19. Vaarkamp, M., Ph.D. Thesis, Eindhoven University of Technology, Eindhoven, The Netherlands, 1993.
20. Bhore, N. A., Klein, M. T., and Bischoff, K. B., *Ind. Eng. Chem. Prod. Res. Dev.* **29,** 313 (1990).
21. van Wijk, A. P., van Broekhoven, E. H., and Ponec, V., *J. Chem. Soc. Chem. Commun.*, 1263 (1986).
22. Iglesia, E., and Baumgartner, J. E., *in* "Proceedings, 9th International Zeolite Conference, Montreal, 1992" (R. von Ballmoos, J. B. Higgins, and M. M. J. Treacy, Eds.), Vol. II, p. 421. Butterworth–Heinemann, London, 1993.
23. Kramer, R., and Fischbacher, M., *J. Mol. Catal.* **51,** 247 (1989).
24. Maire, G., Plouidy, G., Prudhomme, J. C., and Gault, F. G., *J. Catal.* **4,** 556 (1965).
25. Jiang, H. J., Tzou, M. S., and Sachtler, W. M. H., *Appl. Catal.* **39,** 255 (1988).
26. Moretti, G., and Sachtler, W. M. H., *J. Catal.* **116,** 350 (1989).
27. Alvarez, W. E., and Resasco, D. E., *Catal. Lett.* **8,** 53 (1991).
28. Anderson, J. B. F., Burch, R., and Cairns, J. A., *J. Catal.* **107,** 351 (1987).
29. Miller, J. T., Meyers, B. M., Modica, F. S., Vaarkamp, M., and Koningsberger, D. C., *J. Catal.* **143,** 395 (1993).
30. Bond, G. C., and Hui, L., *J. Catal.* **132,** 462 (1992).
31. Engstrom, J. R., Goodman, D. W., and Weinberg, W. H., *J. Am. Chem. Soc.* **110,** 8305 (1988).
32. Clarke, J. K. A., Hegarty, B. F., and Rooney, J. J., *J. Mol. Catal.* **62,** L39 (1990).
33. Dauscher, A., Garin, F., and Maire, G., *J. Catal.* **105,** 233 (1987).
34. Sharma, S. B., Miller, J. T., and Dumesic, J. A., *J. Catal.* **148,** 198 (1994).
35. Menon, P. G., and Froment, G. F., *J. Catal.* **59,** 138 (1979).
36. den Otter, G. J., and Dautzenberg, F. M., *J. Catal.* **53,** 116 (1978).