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Adsorption and Reactive Desorption of C_6 Hydrocarbons on Pt/SiO_2

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C_6 hydrocarbons (*n*-hexane, 3-methylpentane, methylcyclopentane) were adsorbed on a well-dispersed Pt/SiO_2 catalyst ($d_{Pt} = 2.4$ nm) at 298 and 420 K and subsequently desorbed with a stream of hydrogen in the temperature range 298 to 620 K. Seventy-two to eighty percent of desorption occurred at 298 K and the remainder during heating to 470 K. After adsorption at 298 K, >93% of hydrocarbons desorbed unchanged, but after adsorption at 420 K, only methylcyclopentane desorbed largely unchanged, while *n*-hexane and 3-methylpentane desorbed predominantly as methylcyclopentane. Implications for the mechanism of nonselective ring opening of methylcyclopentane and cyclic isomerization of C_6 hydrocarbons are discussed.

INTRODUCTION

The transformation of alkanes over platinum catalysts has interested researchers ever since Kazanskii (*1*) and Anderson (*2*) demonstrated that skeletal rearrangements occur on Pt metal surfaces. Isomerization and cyclization of hexanes has been studied extensively and numerous mechanisms have been proposed (*3, 4*). More recently the effects of carbon overlayers on Pt surfaces on selectivity and activity for hydrocarbon conversions have attracted some attention (*5, 6*). Thus, Sarkany (*7*) measured *n*-hexane uptakes on platinum black from hydrogen/*n*-hexane gas mixtures at temperatures of 450 to 560 K and found that strongly bound surface species could be hydrogenatively desorbed. This process yielded predominantly *n*-hexane but some transformation to methylcyclopentane (MCP) was observed. Here, we report on the hydrogenative desorption from a well-dispersed platinum/silica catalyst of *n*-hexane, 3-methylpentane, and methylcyclopentane, adsorbed at 298 and 420 K, respectively.

EXPERIMENTAL

Catalysts and materials. Platinum (10 wt%) on SiO_2 (Aerosil/Degussa) was prepared by incipient wetness impregnation with hexachloroplatinic acid followed by drying at 380 K for 15 hr. The activation treatment consisted of heating at 380 K in flowing helium for 1 hr and in hydrogen for 2 hr, then slowly raising the temperature to 620 K and further reduction at that temperature for 16 hr. The catalyst showed a dispersion (H/Pt) of 42%, corresponding to an average particle size of 2.4 nm. All hydrocarbons used were research grade from Fluka.

Procedures. An all-glass flow apparatus was used, consisting of a gas purification train, flow and pressure regulators, a tubular reactor (8 mm i.d.) which could be heated to 770 K by an external oven, gas sampling loops, and traps for the collection of products. The products could be introduced either continuously by a saturator or in pulse form by injection. Product analysis was carried out by on-line gas chromatography using a 10% squalane on chromosorb column.

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Hydrogenolysis of methylcyclopentane was carried out under atmospheric pressure and at 470 K with a feed stream containing hydrogen and MCP in a ratio of 10.

In the thermal desorption experiments the catalyst was first treated in hydrogen at 620 K for 1 hr, cooled to adsorption temperature in hydrogen, and then flushed with helium at that temperature for 10 min. This pretreatment yielded a "hydrogen-covered" surface, corresponding to the "irreversibly adsorbed" hydrogen at room temperature (about 60% of total uptake) and a lower coverage (about 40%) at 420 K. Hydrocarbons were adsorbed on the catalyst surface by passing a helium–hydrocarbon mixture (ratio 250/1) over the catalyst at adsorption temperature. About 10 times the amount of hydrocarbon required for theoretical monolayer coverage was supplied to the catalyst in this manner. Then, gas-phase hydrocarbon and physisorbed hydrocarbon were removed by purging with helium, and in the case of adsorption at 620 K the sample was cooled in helium to room temperature. Desorption was carried out in flowing hydrogen, starting at room temperature (30 min) and slowly raising the temperature to 620 K. Desorption products were collected for gas chromatographic analysis in a cold trap at 77 K in three fractions: fraction 1, compounds desorbed at room temperature (30 min); fraction 2, compounds desorbed between room temperature and 470 K (35 min); and fraction 3, desorbed products between 470 and 620 K (30 min). After desorption, the catalyst was kept in flowing hydrogen for 1 hr and the procedure repeated. Desorption experiments proved very reproducible and no changes in the hydrogenolysis (selectivity, activity) of MCP were observed after each desorption run. In order to estimate possible support effects, thermal desorption runs were carried out with Aerosil alone. However, none of the three desorption fractions contained hydrocarbons. The amounts of hydrocarbons collected from the platinum catalysts are therefore entirely due to interaction of hydrocarbons with the metal surface.

RESULTS AND DISCUSSION

Hydrogenolysis of MCP. At 470 K products consisted of 2-methylpentane (46 mol%), 3-methylpentane (22 mol%), and *n*-hexane (32 mol%). No measurable amounts of cracked products were detected. The high *n*-hexane values indicate that the predominant reaction (about 80%) is nonselective ring opening as expected for a catalyst with a high degree of Pt dispersion (*3*).

Adsorption–thermal desorption experiments. The results of hydrogenative thermal desorption of adsorbed *n*-hexane, 3-methylpentane, and methylcyclopentane are summarized in Table 1.

Adsorption of MCP at 298 K yields surface species which can be desorbed quantitatively in hydrogen without any conversion to other hydrocarbons. Fraction 1 contained 80% of desorbed MCP and fraction 2 contained the remaining 20%. After adsorption at 420 K, 82% was desorbed at 298 K, the products being 96% MCP and 4% 2-MP. Fraction 2 contained 18% of desorption product with a product distribution of 43% MCP, 29% 2-MP, 11% 3-MP, 5% *n*-H and 12% C_1–C_5 hydrocarbons. This product distribution differs somewhat from that obtained for the reaction of MCP. However, we emphasize the different conditions under which both experiments were conducted. Product distributions have been shown to depend on hydrogen partial pressure and temperature.

When *n*-hexane was adsorbed at 298 K, desorption fraction 1 contained 72% of total desorbed hydrocarbon, 98% of which was the parent hydrocarbon, but 2% was converted to MCP. Fraction 2 (28% of desorption products) consisted of 81% *n*-hexane, 2% 2-MP, and 17% cracking products. Desorption of *n*-hexane adsorbed at 420 K yielded 76% in fraction 1 with a distribution of 18% parent, 81% MCP, and 1% 2-MP. The remaining 24% desorbed in fraction 2 (55% parent, 28% cracked products, and

TABLE 1

Summary of Adsorption/Desorption Data

Hydrocarbon	T_{ads}/K	Desorption[a]							Overall conversion (%)	Total amounts desorbed (mole/g_{cat})	HC_{ads}/Pt_s
		Fraction[b]	% of total	Products[c]							
				MCP	*n*-H	3-MP	2-MP	C_1–C_5			
MCP	298	1	80	80.0	—	—	—	—			
		2	20	20.0	—	—	—	—	0.0	1.9×10^{-5}	0.088
	420	1	82	78.7	—	—	3.3	—			
		2	18	7.7	0.9	2.0	5.3	2.1	13.6	2.5×10^{-5}	0.116
n-H	298	1	72	1.2	70.8	—	—	—			
		2	28	—	22.7	—	0.6	4.7	6.5	1.9×10^{-5}	0.088
	420	1	76	61.6	13.6	—	0.8	—			
		2	24	4.1	13.2	—	—	6.7	73.2	2.4×10^{-5}	0.111
3-MP	298	1	80	1.4	—	78.6	—	—			
		2	20	—	—	16.0	—	4.0	5.4	2.0×10^{-5}	0.093
	420	1	81	59.1	—	21.1	0.8	—			
		2	19	3.0	—	6.0	1.2	8.8	72.9	2.4×10^{-5}	0.11

[a] Concentrations are given in wt%.

[b] Fraction 1: desorption at 298 K; fraction 2: desorption at 298–470 K; fraction 3: desorption to 620 K never contained hydrocarbons.

[c] MCP, methylcyclopentane; *n*-H, *n*-hexane; 3-MP, 3-methylpentane; 2-MP, 2-methylpentane; C_1–C_5, C_1 to C_5 hydrocarbons.

17% MCP). The overall conversion of adsorbed *n*-hexane was 73%. The products were MCP (90%), cracked products (9%), and 2-MP (1%).

3-Methylpentane adsorbed at 298 K yielded 80% desorption in fraction 1 (98% 3-MP, 2% MCP) and 20% in fraction 2 (80% 3-MP, 20% cracked products). After adsorption at 420 K 81% desorbed at 298 K (fraction 1) as MCP (73%), 3-MP (26%), and 2-MP (1%) while 19% desorbed in fraction 2 (16% MCP, 32% 3-MP, 6% 2-MP, and 46% cracking products). The overall conversion of 3-MP adsorbed at 420 K was 72.9%, 85.2% to MCP, 2.7% to 2-MP, and 12.1% to C_1–C_5.

The coverage of the platinum surface with hydrocarbon at 298 K, as calculated from the sum of desorbed products (see Table 1), of 1.9×10^{-5} mole for *n*-hexane and methylcyclopentane and 2.1×10^{-5} mole for 3-methylpentane corresponds to hydrocarbon/Pt_s ratios of 0.088 and 0.098, respectively. At 420 K this ratio increased to 0.11. Those values are close to the values expected for monolayer coverage. Avery (*8*) observed saturation coverage of cyclopentadienyl on Pt(111) at a hydrocarbon/Pt_s ratio of 0.1. The ratios of *n*-hexane/Pt_s measured by Sarkany (*7*) on Pt-black was 0.08 at 453 K under an atmosphere containing hydrogen and hydrocarbon in a ratio of 19/1, but their data at 563 K showed a strong dependence of hydrocarbon uptake on hydrogen pressure. Therefore, it is expected that hydrocarbon coverages are higher at the lower hydrogen pressures of our adsorption experiment.

Reactive desorption in a stream of hydrogen removed 72–80% of strongly bound hydrocarbon at 298 K (fraction 1). The remaining species were hydrogenated off the Pt surface in the temperature range 298–473 K (fraction 2). The third fraction, between 473 and 620 K, never contained measurable amounts of hydrocarbons. We do not believe that substantial hydrocarbon residues remained on the surface after hydrogenative desorption, because (i) repeating the experiment reproduced uptake values and desorption product distributions and (ii) desorption data were identical also for catalysts exposed to an oxidation–reduction cycle at 620 K.

Of all the hydrocarbons adsorbed at 298 K well over 90% desorbed unchanged (MCP 100%, *n*-H 93.5%, 3-MP 94.6%). The remaining products were predominantly C_1–C_5 hydrocarbons and C_6 isomers. This changed dramatically when the adsorption temperature was raised to 420 K. The conversion of MCP was still only 13%, mainly to C_6 isomers (60%), but in the case of *n*-hexane and 3-methylpentane around 73% of the parent hydrocarbon was converted to products, predominantly to MCP (85–90%), to small amounts of isomers, and to around 10% C_1–C_5 hydrocarbons. It is notable that the major amount of MCP was obtained in fraction 1 (desorption at 298 K). Thus, it appears that during adsorption of hexanes in the absence of hydrogen, a surface species is formed which desorbs primarily or preferentially as MCP. The concentration of this species is low at 298 K (only 1.5% desorbs as MCP) but seems to be the major species at 420 K. Although the carbon skeletal configuration required to facilitate the cyclization of hexanes might arise either in the primary adsorption step or in the hydrogenative desorption process, we deduce that the MCP precursor is formed already in the primary adsorption step from the fact that in the temperature range of interest the equilibrium constants for the formation of MCP from hexanes under 0.1 MPa hydrogen are quite small—around 10^{-7} at 298 K and 10^{-4} at 420 K. The similarity of initial coverages and the nature of the product distributions indicate further that upon adsorption of *n*-hexane, 3-methylpentane, and methylcyclopentane at 420 K the predominant surface species are identical or at least very similar.

Implications for "cyclic mechanism" in hexane isomerization. (1) A systematic study of adsorption–hydrogenative desorption of C_6 hydrocarbons over a series of catalysts with varying dispersions would be required to substantiate the link between MCP production upon adsorption of open chain hexanes at temperatures <420 K on Pt catalysts and isomerization of C_6 hydrocarbons via a cyclic mechanism and nonselective ring opening of MCP. Nevertheless, it is interesting to note that on our well-dispersed platinum catalyst (d_{Pt} = 2.4 nm), nonselective ring opening of MCP was dominant, and during adsorption 60–65% of open chain hexanes at 420 K were converted to MCP. In contrast, on platinum black of low dispersion used by Sarkany (*7*) significantly lower conversions were observed during adsorption and hydrogenative desorption of *n*-hexane at adsorption temperatures of around 550 K.

(2) In studies of skeletal reactions of hexanes over platinum catalysts, a strong dependence of the yields of MCP on hydrogen partial pressures has been reported (*9–10*). Chow and McVicker postulated a sequential mechanism for isomerization of hexanes of the type

$$(n\text{-H, 2-MP, 3-MP}) \rightarrow [\text{MCP}] \rightarrow (C_6 \text{ isomers})$$

with C_5 ring closure being rate-controlling for the overall reaction. According to the equation

$$C_6H_{14} \underset{r_2}{\overset{r_1}{\rightleftharpoons}} \text{MCP} + H_2$$

the rate for ring closure (r_1) increases with decreasing hydrogen partial pressure while the rate for ring opening (r_2) decreases. Thus, in agreement with Chow and McVicker, high MCP concentrations and low isomer concentrations result at the low hydrogen partial pressures at which hydrocarbon adsorptions were carried out in the present study. However, we believe it worthwhile to point out that the low temperatures (370–420 K) at which skeletal rearrangements occurred during the adsorption experiments are substantially lower than those at which reactions have been reported.

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