

# Methylcyclohexane to Benzene Conversion over K-Promoted Pt(111)

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**Abstract:** The adsorption, desorption, and reaction of methylcyclohexane (MCH) were studied on clean and potassium-modified Pt(111) surfaces. The desorption of reversibly chemisorbed MCH on clean Pt(111) occurs at 240 K, and physisorbed MCH desorbs at 140–150 K. At 164 K, the MCH sticking coefficient is near unity and stays constant until about half-coverage of the chemisorbed layer before gradually dropping to 0, indicating precursor-mediated adsorption kinetics. Potassium at a coverage up to  $\theta_K = 0.15$  has almost no effect on the sticking coefficient or saturation coverage of MCH on Pt(111) at 164 K, but stabilizes chemisorbed MCH on the surface by about 20 K in TPD. At higher  $\theta_K$ , MCH is more weakly bound and no chemisorbed MCH is formed for  $\theta_K = 0.26$ . Potassium adatoms increase reversible MCH adsorption and promote the desorption of benzene as a product for  $0.1 < \theta_K < 0.25$ . The cleavage of the C–C bond between the ring and methyl group in MCH, which is responsible for the benzene formation, was observed for  $\theta_K = 0.19$  at a remarkably low temperature of less than 230 K. Preadsorbed carbon increases the amount of reversible MCH adsorption but does not change the bonding energy nor cause benzene desorption. These results indicate that MCH  $\rightarrow$  benzene conversion and particularly benzene desorption are enhanced by the combined electronic effect of coadsorbed alkali adatoms and the local postdosing effect of CH<sub>x</sub> from the methyl group.

## Introduction

Hydrocarbon conversion chemistry over metal surfaces represents an area of significant scientific and technological interest because of its importance in catalytic reforming. Platinum catalysts possess high activity for alkane dehydrogenation reactions to produce aromatic hydrocarbon molecules, but they are often too reactive at the high temperature required to carry out these largely endothermic reactions, and decomposition reactions reduce selectivity for the desired product formation. Certainly, desorption of strongly chemisorbed aromatic molecules such as benzene or toluene is a difficult step in the reaction mechanism, and further dehydrogenation of these species leads to lower selectivity and coking of the catalyst. In particular, the rate-limiting step for a prototypic endothermic reaction, methylcyclohexane (MCH) to toluene dehydrogenation over supported Pt catalysts, has been proposed to be desorption of the product.<sup>1</sup> We approach this problem by focusing on surface science studies of the selective dehydrogenation of MCH to benzene and toluene on unsupported, well-defined Pt(111) single crystals. Bimetallic catalysts containing Pt and a second metallic element are used industrially to increase selectivity and reduce carbon deposition, and the role of the second metal component is of fundamental interest. Modification of the Pt electronic properties due to alloying with other (particularly early) transition metals could lead to stronger metal–hydrogen bonds but weaker metal–carbon bonds and thereby facilitate dehydrogenation while inhibiting decomposition.<sup>2</sup>

Alkali adatoms strongly alter the electronic properties of late transition metal surfaces and can be used to probe the effects of changing the surface electronic structure on chemisorption and reaction. Coadsorption studies of K and ethylene<sup>3</sup> and benzene<sup>4</sup> on Pt(111) have shown that potassium adatoms increase the

barrier to C–H bond breaking and weaken  $\sigma$ -donation of these molecules to the surface, decreasing their dehydrogenation and heat of adsorption. Although Pt(111) readily dehydrogenates cyclohexane to form benzene on the surface below 300 K, benzene is essentially irreversibly adsorbed.<sup>5,6</sup> If K-modified surfaces can destabilize benzene or toluene sufficiently without shutting down the initial dehydrogenation to form these products, then the desorption of these products into the gas phase will be enhanced. Probing how K alters the hydrocarbon conversion chemistry of Pt surfaces can also reveal some insight into electronic effects that can occur in the chemistry of Pt alloys with early transition metals, which are often difficult to characterize and study.

In this paper, we explore the effects of K on the adsorption and reaction of MCH on Pt(111) by directly measuring the sticking coefficient and by using temperature-programmed desorption (TPD). To our knowledge, this is the first surface science study of MCH on a single-crystal metal surface. While no dehydrogenated products desorb during TPD of MCH on clean Pt(111), benzene desorbs as a product under ultrahigh vacuum (UHV) conditions on K-promoted Pt(111) for  $0.1 < \theta_K < 0.25$ .

## Experimental Section

The experiments were carried out in a UHV system which has been described previously.<sup>7</sup> Briefly, the system was equipped with instrumentation for TPD, Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED). The Pt(111) surface was cleaned by argon ion sputtering and annealing, followed by heating to 1000 K in  $2 \times 10^{-8}$  Torr of O<sub>2</sub> until no impurities were detected by AES and a sharp LEED pattern was obtained. Carbon that deposited due to MCH decomposition during TPD was removed by the same annealing and O<sub>2</sub> treatment. Potassium was evaporated from a thoroughly outgassed SAES getter source. The cleanliness and coverage of K were determined by AES and TPD. Methylcyclohexane (Aldrich, 99+%) was placed in a Pyrex container along with dried 3A molecular sieve granules to absorb H<sub>2</sub>O

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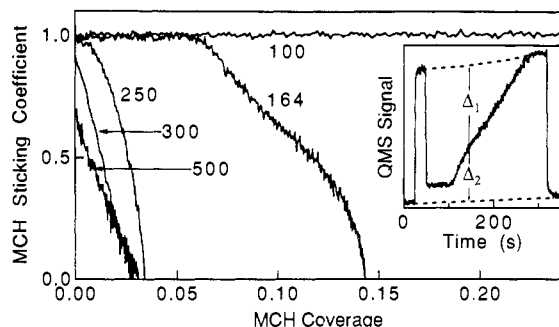
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**Figure 1.** Plot of the sticking coefficient versus coverage for MCH adsorption on clean Pt(111) at the indicated temperatures. The inset shows the raw data obtained at 164 K by the beam reflection techniques.

and was further purified by several freeze-pump-thaw cycles. The vapor of the room temperature liquid was used for adsorption experiments. The purity of MCH was checked by gas chromatography and by *in-situ* mass spectrometry. In TPD, the heating rate was 4.2 K/s and signals at 2, 55 (MCH), 78 (benzene), 91 (toluene), 81 (methylcyclohexene), 82 (cyclohexene), and 84 (cyclohexane) amu were routinely monitored.

The absolute sticking coefficient,  $S$ , was measured directly using a simple kinetic uptake technique described previously.<sup>7</sup> This is illustrated in the inset of Figure 1 for MCH adsorption on Pt(111) at 164 K. The incident effusive MCH beam from a collimated microcapillary array doser causes a rise in the MCH partial pressure in the chamber. This pressure drops when the sample is rotated in front of the beam due to the adsorption of MCH on the front face of the Pt(111) sample. The sticking coefficient is obtained by using  $S = \Delta_1/F(\Delta_1 + \Delta_2)$ , where  $F = 0.87$  is the fraction of the beam that impinges onto the sample. We should point out that  $S$  refers to both nondissociative and dissociative sticking. The MCH coverage,  $\theta_{\text{MCH}}$ , was calibrated using the known saturation coverage of 0.5 monolayer of CO on clean Pt(111)<sup>8</sup> at 300 K by the following equation:<sup>9</sup>

$$\theta_{\text{MCH}} = \frac{P_{\text{MCH}}}{P_{\text{CO}}} \left( \frac{m_{\text{CO}}}{m_{\text{MCH}}} \right)^{1/2} \frac{\int S_{\text{MCH}} dt}{\int S_{\text{CO}} dt} \theta_{\text{CO}}$$

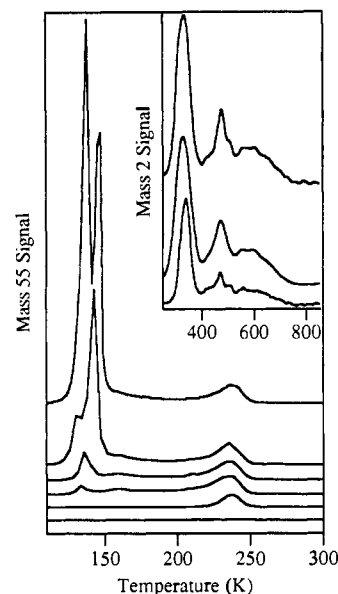
where  $m$  is the molecular weight and  $P$  is the doser backing pressure. Both MCH and K coverages are defined relative to the Pt(111) surface density of  $1.5 \times 10^{15}$  atoms/cm<sup>2</sup>.

## Results and Discussion

Figure 1 clearly shows that  $S$  is unity and independent of coverage for MCH adsorption and condensation on Pt(111) at 100 K, just like many other hydrocarbon molecules.<sup>9</sup> For adsorption at 164 K, which is between the multilayer and monolayer desorption temperatures as shown by TPD, the sticking coefficient is unity almost to half-coverage before dropping to 0, indicating a strong effect of a precursor state in the adsorption mechanism. The monolayer saturation coverage of 0.14 indicates that each MCH molecule occupies about seven Pt surface sites. This is quite reasonable if we consider the flat-lying MCH molecule as a distorted hexagon with a van der Waals diameter of 6.6 Å and stretched to 8.1 Å in one direction due to the methyl group. For  $T \geq 250$  K, molecular desorption of MCH from the monolayer occurs so that  $S$  represents a reactive sticking coefficient, which is initially also high but decreases rapidly with coverage as desorption and decomposition compete with adsorption. The shorter lifetime of the precursor state at higher temperature might be responsible for the drop in  $S_0$  and the more nearly linear decrease in  $S(\theta)$  for  $T \geq 250$  K. The insensitivity of the saturation coverage with temperature for  $T > 250$  K suggests that the reactive adsorption is limited by a fixed carbon coverage beyond which no decomposition of MCH occurs.

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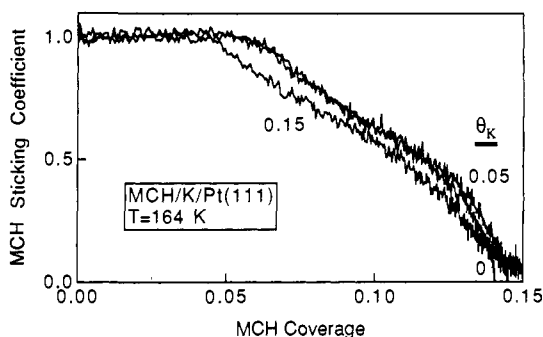


**Figure 2.** MCH TPD spectra for MCH adsorbed on clean Pt(111) at 100 K with  $\theta_{\text{MCH}} = 0.02, 0.08, 0.16, 0.2, 0.4, 0.8$  (from bottom to top). The inset shows the H<sub>2</sub> TPD for  $\theta_{\text{MCH}} = 0.02, 0.08, 0.8$  (from bottom to top).

Figure 2 shows the TPD spectra of MCH and H<sub>2</sub> (as inset) after exposing Pt(111) to various coverages of MCH at 100 K. We used  $m/e = 55$  to monitor MCH since it had the highest intensity in the cracking pattern of MCH. The MCH desorption state at  $\approx 240$  K was observed first and saturated at a coverage of  $\approx 0.14$ . This peak can be assigned to the desorption of reversibly adsorbed MCH from the chemisorbed monolayer. Using the desorption peak temperature of 235 K, appropriate for a monolayer coverage of 0.14 and the heating rate of 4.2 K/s used in TPD, first-order Redhead analysis yields an activation energy for desorption of 14 kcal/mol. For coverages of 0.16 and above, another desorption state appears at 143 K and saturates at  $\theta_{\text{MCH}} \approx 0.4$ . The activation energy for the desorption of this state is 8.6 kcal/mol, corresponding to desorption of MCH with an adsorption energy between that for a monolayer and multilayer, possibly a second-layer state or more generally a physisorbed state which is beyond monolayer but is still partially stabilized by the Pt(111) substrate. A similar desorption state has been observed by Rodriguez and Campbell<sup>6</sup> for cyclohexane desorption from Pt(111). For coverages of  $\approx 0.4$  and above, another desorption state appears at 139 K, and it continues to grow without saturating with increasing MCH coverage. This is attributed to a condensed multilayer of MCH with an activation energy for desorption of 8.3 kcal/mol, which agrees (within experimental error) with the sublimation energy of 8.45 kcal/mol for MCH. All of these desorption activation energies should be equal to the adsorption energies since adsorption occurs readily at 100 K with little or no barrier.

The inset of Figure 2 shows that H<sub>2</sub> desorption increases with MCH coverage and saturates at  $\theta_{\text{MCH}} = 0.08$ . Similar to cyclohexane,<sup>6</sup> no gas-phase products other than hydrogen were observed during TPD of MCH adsorbed on clean Pt(111), and hydrogen desorbs in three distinct regions at around 330, 475, and 600 K. Apparently MCH decomposes sequentially as the temperature increases. The 330 K peak is rate-limited by H<sub>2</sub> desorption rather than C-H bond scission, since it is very similar to the desorption peak of hydrogen adsorbed on clean Pt(111) from H<sub>2</sub> exposure.<sup>10</sup> MCH dehydrogenation thus takes place on the surface below 300 K. This is consistent with previous laser-induced thermal desorption studies showing that the dehydrogenation of cyclohexane to form C<sub>6</sub>H<sub>9</sub> and benzene on Pt(111)

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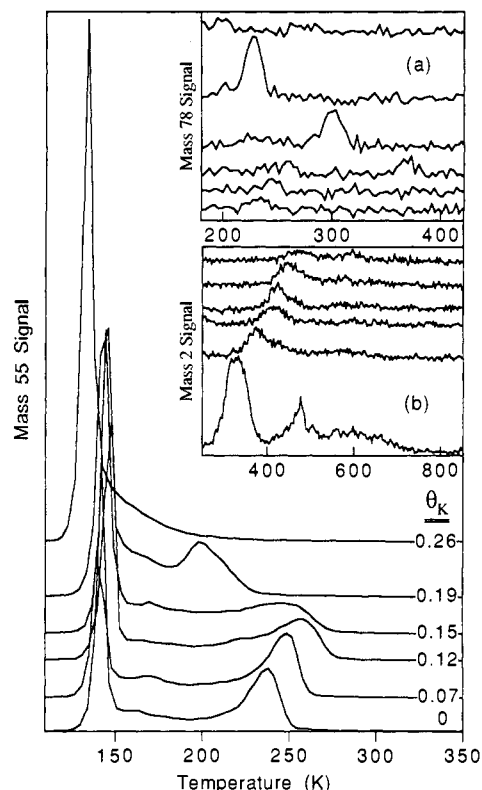


**Figure 3.** MCH sticking coefficient as a function of coverage on Pt(111) at 164 K precovered by the indicated amounts of potassium.

occurs at  $\approx 180$  K.<sup>5</sup> The 475 and 600 K peaks, which are well above the normal H<sub>2</sub> desorption temperature, are reaction rate-limited due to the C–H bond scission from the dehydrogenation of reaction intermediates. The areas of the H<sub>2</sub> desorption-rate-limited peak at 330 K and the reaction-rate-limited region between 400 and 750 K are in a ratio of 1.08 and independent of coverage. This ratio of near unity suggests the benzyl species is an important intermediate of MCH dehydrogenation:  $C_7H_{14,a} \rightarrow C_7H_{7,a} + 7H_a + 2H_a \rightarrow H_{2,gas}$  near 330 K. Vibrational spectroscopy studies<sup>11</sup> confirmed the presence of the benzyl intermediate above 330 K. By comparing the saturation H<sub>2</sub> TPD area with that of toluene on Pt(111), where we know that the monolayer coverage is 0.11 from sticking coefficient measurements and that 95% of the toluene decomposes,<sup>11,12</sup> we conclude that 35% of the MCH monolayer decomposes on Pt(111) during heating. This is similar to cyclohexane on Pt(111), where 32% of the adsorbed monolayer decomposes.<sup>5</sup> On the basis of the areas of the MCH TPD peaks at 240 and 143 K, and the fact that 65% of the MCH monolayer desorbs, the desorption state at 143 K corresponds to a much more densely packed layer that is equivalent to about two monolayers of MCH.

Figure 3 shows the sticking coefficient as a function of coverage for MCH adsorption on clean and K-modified Pt(111) surfaces at 164 K with  $\theta_K = 0.05$  and 0.15. This adsorption temperature was chosen to avoid MCH multilayer formation, which occurs with unity sticking coefficient independent of  $\theta_K$  at 100 K. At  $\theta_K = 0.05$ , potassium has no effect on the adsorption kinetics of MCH on Pt(111) and  $S$  is unity up to  $\theta_{MCH} = 0.05$ , i.e., about one-third of the saturation coverage for MCH monolayer adsorption. For  $\theta_K = 0.15$ ,  $S$  starts to decrease at a slightly smaller coverage, but K causes no change in the saturation coverage. Remarkably, preadsorbed K in this range of  $\theta_K$  (up to one-half of a monolayer of K) has almost no effect on the overall adsorption kinetics of MCH on Pt(111).

Figure 4 shows the MCH TPD spectra after adsorbing MCH to a coverage of 0.2 on K/Pt(111) surfaces at 100 K. On the clean Pt(111) at this coverage, physisorbed MCH desorbs at 140 K in addition to the chemisorbed peak at 240 K. The monolayer desorption peak shifts to higher temperature for increasing K coverage up to  $\theta_K \approx 0.12$  and then shifts back to lower temperature with further increases of  $\theta_K$ . The stabilization of MCH by coadsorbed K at low coverages suggests attractive lateral interactions between MCH and K. This behavior is very similar to that observed by Davidsen et al.<sup>13</sup> for cyclohexane desorption from Cs/Pt(111) surfaces, and it can be explained by the dipole-reversal model proposed by Ernst and Campbell<sup>14</sup> based on their work function measurements. The strong dipole field due to an adsorbed alkali atom induces a dipole of the opposite direction



**Figure 4.** TPD spectra of MCH, benzene (inset a) and H<sub>2</sub> (inset b) for MCH adsorption on K/Pt(111) surfaces at 100 K with  $\theta_{MCH} = 0.2$ .

in a coadsorbed, highly polarizable hydrocarbon such as MCH or cyclohexane, giving rise to the attractive dipole–dipole interactions between the alkali and the hydrocarbons as observed. At higher  $\theta_K$ , MCH cannot fit between K adatoms and instead adsorbs tilted or on top of the K layer with a reduced heat of adsorption, leading to MCH desorption at lower temperature. It is interesting to note that the second-layer MCH is even influenced by preadsorbed K at a coverage of  $\theta_K = 0.26$ , as indicated by the shift to lower temperature in the desorption. As shown quantitatively in Figure 5, potassium increases the amount of reversibly adsorbed MCH.

Among the many masses monitored for possible products during TPD, only signals from mass 78 and 2 were observed, and these are plotted as insets a and b of Figure 4, respectively. Hydrogen desorption decreases with increasing  $\theta_K$ , indicating a reduced propensity for dehydrogenation of MCH induced by preadsorbed K. This is shown quantitatively in Figure 5. Meanwhile, preadsorbed K stabilizes the surface hydrogen produced from initial low-temperature MCH dehydrogenation, as evidenced by shifts of the H<sub>2</sub> desorption-rate-limited peak at 330 K to higher temperature with increasing  $\theta_K$ , in agreement with our earlier study of H<sub>2</sub>/K(Pt(111)).<sup>10</sup> Similar behavior has been seen by Davidsen et al.<sup>13</sup> for cyclohexane on Cs/Pt(111).

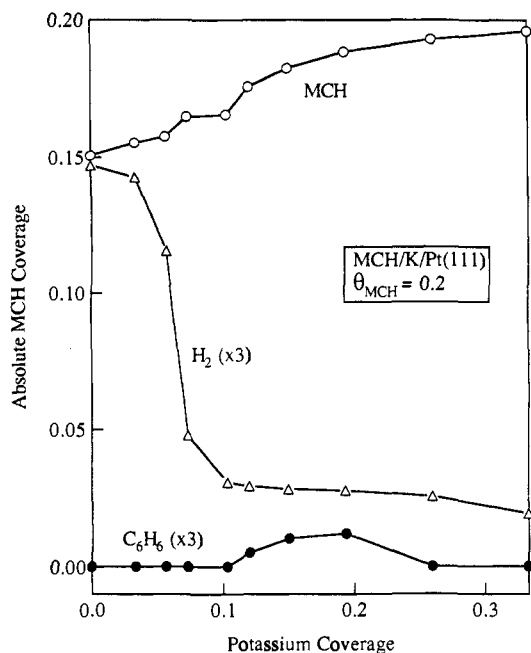
The most interesting observation for the MCH/K/Pt(111) system is benzene formation and desorption from the surface, as shown in inset a of Figure 4. We should point out that the mass 78 signal in TPD is not due to K<sub>2</sub> desorption because it does not follow that of K at mass 39 and occurs even below the potassium sublimation temperature. Benzene desorption was seen first at  $\theta_K = 0.12$ , and it increases in intensity and decreases in peak temperature from 370 to 230 K with increasing  $\theta_K$  from 0.12 to 0.19. Potassium coverages in this range cause the MCH molecular desorption peak to shift to lower temperature, and further increasing  $\theta_K$  shuts down the desorption of benzene as formation of chemisorbed MCH is inhibited. On the basis of the benzene TPD peak area, the amount of benzene desorbed from MCH/K/Pt(111) for  $\theta_K = 0.19$  is about 2.5% of the benzene mono-

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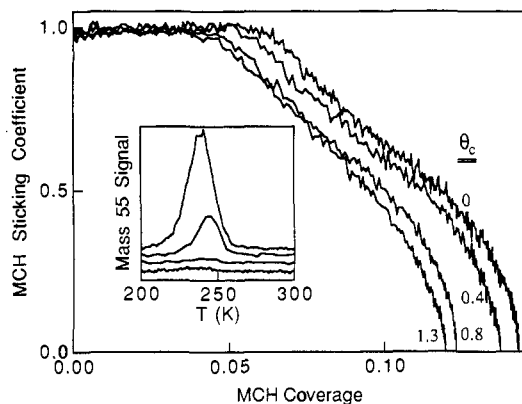
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**Figure 5.** The yield of reversibly adsorbed MCH, benzene, and  $H_2$  (based on the peak area of the TPD curves in Figure 4) as a function of K coverage. The  $H_2$  yield is expressed in terms of MCH absolute coverage.



**Figure 6.** The MCH sticking coefficient as a function of coverage on Pt(111) at 164 K precovered by varying amounts of carbon. The inset shows MCH TPD spectra after adsorbing  $\theta_{MCH} = 0.02$  on carbon-precovered Pt(111) at 100 K with  $\theta_C = 0, 0.4, 0.8,$  and  $1.3$  (from bottom to top).

layer coverage on clean Pt(111).<sup>11</sup> Considering the small amount (as can be seen from Figure 5) of irreversibly adsorbed MCH at this  $\theta_K$ , benzene production from MCH conversion is actually quite efficient, about 37%.

In order to see whether electronic or site-blocking effects are mainly responsible for the enhanced MCH  $\rightarrow$  benzene conversion over K-promoted Pt(111) surfaces, we also studied the effects of carbon precoverage on the adsorption and desorption of MCH. Graphitic-like carbon as indicated by Auger line-shape analysis was prepared during TPD of MCH to 850 K. We note that in all studies like these, however, the chemical nature and structure of this carbon residue have not been well characterized. The amount of carbon was calibrated using the C(272 eV) and Pt-(235 eV) peak-to-peak Auger ratio of the toluene monolayer with a known coverage of 0.11 on clean Pt(111). A carbon coverage of 0.4 is obtained for the surface following the TPD of a MCH monolayer on clean Pt(111). This further supports the conclusion that about 35% of the MCH monolayer decomposes during TPD on the basis of hydrogen desorption. Figure 6 shows that at 164 K both the saturation MCH coverage and the plateau region corresponding to unity sticking coefficient were

reduced with increasing carbon coverage, indicating a weakening of the precursor effect and a loss of adsorption sites due to surface carbon. Surprisingly, the initial MCH sticking coefficient is close to unity and the saturation coverage is still quite high even for  $\theta_C > 1$ . We found that preadsorbed carbon suppressed the dehydrogenation pathway in favor of molecular desorption of MCH (as shown in the inset of Figure 6), but no benzene desorption was seen during TPD measurements at any coverages of carbon.

The dehydrogenation of MCH can proceed in two possible channels: either by the stepwise breaking of C–H bonds in the ring to form toluene or by cleaving off the methyl group accompanied by C–H bond cleavage from the ring to form benzene. Since toluene is a likely product, its absence in our TPD studies is at least partly due to the nearly complete decomposition of adsorbed toluene on Pt(111) during heating.<sup>12</sup> One of the C–H bonds in the methyl group of toluene breaks below room temperature when toluene is bonded on Pt(111) surfaces.<sup>11,15</sup> Toluene desorption from the surface requires the very unlikely recovery of this bond, and thus only 5% of the toluene desorbs at monolayer coverage in TPD experiments after toluene adsorption, compared to 50% for the same situation with benzene.<sup>12</sup> Since benzene dehydrogenates completely for less than half-monolayer benzene adsorption on clean Pt(111),<sup>12</sup> any benzene converted from adsorbed MCH on clean Pt(111) is also subjected to further dehydrogenation all the way to carbon. Preadsorbed K reduces the dehydrogenation activity of Pt and destabilizes adsorbed benzene,<sup>11,13</sup> promoting its desorption as a product. The data in inset a of Figure 4 for  $\theta_K = 0.19$  show that benzene desorption occurs at 230 K, and thus conversion from MCH to benzene must occur below 230 K. To our knowledge, this is the first direct observation of C–C bond breaking on Pt(111) at such a low temperature, and it suggests that potassium acts as a promoter for the cleavage of the MCH C–C bond between the methyl group and the ring. The ratio of the areas below the  $H_2$  desorption-rate-limited peak at 450 K and the reaction-rate-limited region between 500 and 700 K shown in inset b of Figure 4 for  $\theta_K = 0.19$  is about 3:1 (this ratio is also obtained for  $\theta_K = 0.15$  and is more clearly seen if we expand the  $H_2$  desorption curves). These observations are consistent with the following MCH dehydrogenation pathway over this K-promoted Pt(111) surface:  $C_7H_{14,a} \rightarrow C_6H_{6,a} + CH_{2,a} + 6H_a$  below 230 K,  $C_6H_{6,a} \rightarrow C_6H_{6,gas} + 230 K$ ,  $6H_a \rightarrow 3H_{2,gas}$  at 450 K, and  $CH_{2,a} \rightarrow C_a + H_{2,gas}$  between 500 and 700 K. The application of vibrational spectroscopy will be helpful to confirm this proposed mechanism and other possible reaction channels.

Since no products other than  $H_2$  were observed in a similar study<sup>13</sup> of cyclohexane/Cs/Pt(111) at any coverages of cyclohexane and Cs, the electronic effects exerted by the adsorbed alkali are not sufficient to cause benzene desorption from the surface. This clearly demonstrates the important role of the methyl group in MCH for the formation and particularly the desorption of benzene from MCH/K/Pt(111) surfaces. Benzene was also absent during TPD of cyclohexane on Pt(111) precovered by various amounts of a typical site blocker, Bi,<sup>6</sup> but it did desorb as a product during TPD of cyclohexane on Pt(111) with postdosed Bi.<sup>16</sup> The hydrocarbons species produced from the methyl fragment creates a locally high coverage and acts more like postdosed than preadsorbed carbon. Therefore, the combined local postdosing effect of  $CH_x$  from the methyl group and the electronic effect of preadsorbed alkali are the keys for MCH  $\rightarrow$  benzene conversion and our observation of benzene desorption from the surface under UHV conditions.

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**Conclusions**

About 35% of the MCH monolayer on Pt(111) decomposes to carbon and hydrogen upon heating while the rest of the layer desorbs intact. The benzyl species is an important intermediate in the decomposition. The coadsorption of carbon or low coverages of potassium ( $\theta_K \leq 0.1$ ) with MCH on Pt(111) surfaces reduced the MCH dehydrogenation probability in favor of molecular desorption. Benzene formation and subsequent desorption into the gas phase was observed during TPD over K-precovered Pt(111) surfaces with  $0.1 < \theta_K < 0.25$ . This suggests that potassium acts as a promoter for the cleavage of the C–C bond between the

methyl group and the ring in MCH. The desorption of the benzene product from MCH decomposition occurs due to the strong destabilization of adsorbed benzene by potassium in addition to the local postdosing effect of adsorbed  $\text{CH}_x$  from the methyl fragment.

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