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The Interaction of Benzene and Toluene with Rh Dispersed on SiO_2, Al_2O_3, and TiO_2 Carriers

THEOPHILOS IOANNIDES AND XENOPHON E. VERYKIOS

Institute of Chemical Engineering and High Temperature Processes, Department of Chemical Engineering, University of Patras, GR 26110 Patras, Greece

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The interaction of benzene and toluene with Rh dispersed on SiO_2, Al_2O_3, and TiO_2 carriers is investigated employing temperature-programmed desorption, temperature-programmed reaction and steady-state hydrogenation techniques. It is found that the aromatic molecules are weakly adsorbed on the carriers and are readily hydrogenated by spill-over hydrogen at room temperature. The surface coverage of benzene and toluene on Rh is found to be 0.39–0.42 and 0.34–0.38, respectively, following room temperature adsorption of 0.1 bar benzene or 0.03 bar toluene. Aromatic molecules adsorbed on Rh do not desorb molecularly, but dissociate at high temperatures producing hydrogen. Dehydrogenation reactivity is found to follow the order: $Rh/TiO_2 > Rh/Al_2O_3 > Rh/SiO_2$. Under hydrogen flow, only a small fraction of the adsorbed aromatic molecules is hydrogenated, and at sufficiently high temperatures the remainder is converted to CH_4. Results of benzene hydrogenation under steady-state conditions are questioned in view of carrier participation in the reaction scheme.

INTRODUCTION

Phenomena related to the interaction of aromatic molecules with transition metal surfaces are of significant fundamental and practical interest. From the fundamental point of view, the interest is primarily due to the fact that the geometric and electronic structures of these molecules are correlated with adsorptive and catalytic parameters of metallic surfaces. Thus, benzene and toluene are ideal probe molecules for the study of such interactions since they are the simplest of aromatic compounds. Furthermore, they are involved in many catalytic processes of the petrochemical industry as intermediates or final products. The interaction of benzene with Group VIII metals has been studied far more extensively than that of toluene. Studies which have been reported in the literature can be classified into two broad categories, namely, those dealing with well-defined crystallographic structures, involving spectroscopic and ultrahigh vacuum techniques (*1–14*) and those dealing with the hydrogenation of these molecules, usually on supported metal catalysts (*15–32*).

The adsorption of benzene and toluene on metallic surfaces occurs via the interaction of π-electrons of the aromatic ring with *d* orbitals of the metal. Thus, these molecules are adsorbed with the aromatic ring parallel to the surface (*1*). Both molecules are net electron donors (*2*), and the work function of the metal is reduced upon adsorption (*6*). Toluene, possessing a higher electron density in the aromatic ring, is more strongly adsorbed than benzene, as has been shown theoretically (*15*) and experimentally (*16, 17*).

The adsorption of benzene on Rh(111) has been investigated employing LEED (*1, 3, 4, 7*), HREELS (*1, 6, 7*), angle-resolved UPS (*3, 5*), work function measurements (*6*), and temperature-programmed desorption (TPD) (*1, 3, 4, 7*). The results of these studies demonstrate that benzene is adsorbed molecularly, with the aromatic ring parallel to the surface, primarily irreversibly. Only a small

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fraction, less than 20%, is desorbed molecularly with a heat of desorption of approximately 100 kJ/mol. The existence of two adsorption sites is plausible and the saturation coverage of the surface is 0.13–0.17 ML. TPD studies show that benzene decomposition is initiated at approximately 400 K at which temperature C–C bonds are broken and species of the form C–H and C_2–H are formed on the surface. Further increase in temperature leads to dehydrogenation of the species and creation of polymeric species of the form C_nH and, finally, at 800 K, a layer of graphitic carbon remains on the surface (*7*).

The hydrogenation of benzene and toluene has been investigated primarily on Ni (*22, 23*), Pd (*24, 25*), and Pt (*26, 27*) and, to a smaller extent on Rh, Ru, and Ir (*28, 29*). The kinetics of hydrogenation over the various metals present some common features. The reactions are classified as structure insensitive (*33*). The apparent activation energy is in the neighborhood of 42–58 kJ/mol. The order of the reaction with respect to the aromatic molecule is zero at low temperatures and it increases with temperature, reaching values of 0.5–0.8 at 450–550 K. With respect to H_2, the reaction order is 0.5–1.0 at low temperatures and increases with increasing temperature. Comparison of the activity of different metals is difficult since the existing literature refers to different temperatures, different partial pressures, and different carriers of the metals.

In the present study, the interaction of benzene and toluene with Rh crystallites dispersed on SiO_2, Al_2O_3, and TiO_2 carriers is investigated employing TPD and temperature-programmed reaction (TPReaction) techniques. The influence of the carrier on benzene hydrogenation activity is also investigated.

EXPERIMENTAL

(*a*) *Catalyst Preparation and Characterization*

The carriers employed in the present study are SiO_2 (Alltech Associates), γ-Al_2O_3 (Akzo Chemicals), and TiO_2 (Degussa, P-25) with surface areas >300, 100, and 50 m^2/g, respectively. Catalysts were prepared by the method of incipient wetness impregnation using $RhCl_3.3H_2O$ as the precursor compound for the metal. The Rh content was invariably 0.5 wt%. The catalysts were reduced under hydrogen flow at 250°C. Detailed information concerning the preparation of Rh catalysts has been reported in a previous publication (*34*). Their characterization, in terms of exposed metallic area, degree of dispersion, and metal crystallite size, employing selective chemisorption of hydrogen, was also described in the same publication (*34*).

(*b*) *Determination of Reaction Rates*

Benzene hydrogenation was investigated in a conventional flow microreactor operating at atmospheric pressure, at 30°C. Hydrogen and benzene partial pressures were kept constant at 630 and 12.5 Torr, respectively. Benzene partial pressures were established by hydrogen flow through a saturator containing the hydrocarbon, immersed in a constant temperature bath. The feed mixture was periodically analyzed before entering the reactor.

Before initiation of any reactions, the catalyst was exposed to hydrogen flow at 200°C for 2 h and then cooled under nitrogen to the reaction temperature. A similar pretreatment for 30 min was also conducted between runs on the same catalyst. Analysis of the product mixture was performed on a gas chromatograph (Hewlett–Packard, model 5890) equipped with a flame ionization detector, an automatic gas sampling valve and a reporting integrator. A capillary WCOT column, packed with Cp-Wax, separated benzene and cyclohexane. In all cases, conversion was maintained below 10%.

(*c*) *TPD and TPReaction Experiments*

The TPD apparatus consists of a flow measuring and switching system, a heated quartz tube in which the catalyst is placed, and the analysis system. The flow system is composed of high precision rotameters and needle valves, 3-, 4-, and 6-way valves and switching valves. The TPD cell is a quartz tube of 0.6 cm diameter and 15 cm length. A section at the center of the tube is expanded to 1.2 cm diameter, in which the catalyst sample, approximately 0.25 g, is placed. A 1/16″ thermocouple well runs through the center of the cell and a thermocouple is used to determine the temperature at the catalyst bed. The TPD cell is placed in a cylindrical furnace of 2.4 cm diameter which is controlled by a linear temperature programmer (Omega, CN2010). The heating rate applied in the current study was 23°C/min.

The outlet of the cell is connected to a quadrupole mass spectrometer (Sensorlab 200D-VG Quadrupole) via a heated silica capillary tube of 2 m length. The pressure in the main chamber of the mass spectrometer was less than 10^{-7} mbar. The mass spectrometer is connected to a personal computer for instrument control, data acquisition and analysis.

The gases used were supplied by L'Air Liquide and were of 99.995% purity. Helium was further purified through a heated metallic zirconium trap and H_2 through an Oxisorb and a molecular sieve 5A trap. Benzene and toluene were introduced into the TPD cell by passage of N_2 streams through two saturators, maintained at constant temperature.

Prior to any experiments it was determined that the TPD cell or the tubing were not active in the adsorption of benzene or toluene and did not contribute to the mass spectrometer signal. The procedure for each experiment was the following. The catalyst, 0.25 g, was placed in the TPD cell, supported by quartz wool, and heated at 200°C in H_2 flow for 1 h. It was then cooled under He flow. When the desired adsorption temperature was reached, the He flow was switched to benzene/N_2 or toluene/N_2 flow. Benzene and toluene concentrations in these streams were approximately 10 and 3%, respectively. After 15 min, the flow was switched to He and the lines were cleaned for 3 min. Temperature programming was then initiated and the TPD profiles were obtained. At the end of each experiment the catalyst was exposed to O_2 at 450°C for 5 min to burn off carbon deposits. This procedure was found to give reproducible TPD and TPReaction results. Blank experiments without benzene or toluene adsorption were also performed to ascertain that no hydrogen from the pretreatment procedure remained on the catalyst. For convenience, TPD and TPReaction profiles are referred to colloquially as "spectra."

RESULTS AND DISCUSSION

The supported Rh catalysts were characterized in terms of their degree of dispersion by selective equilibrium H_2 adsorption at room temperature. The volume of H_2 adsorbed at monolayer coverage was used to estimate the H/Rh ratio (atoms of hydrogen adsorbed per Rh atom in the catalyst) assuming dissociative adsorption and 1-to-1 stoichiometry. The H/Rh ratios were found to be 1.29 for Rh/SiO_2, 1.0 for Rh/Al_2O_3, and 0.70 for Rh/TiO_2, indicating that all catalysts had high dispersion of the metal. The derived mean diameter of the supported Rh crystallites, assuming that they are hemispherical, is estimated to be between 10 and 15 Å.

The interaction of Rh crystallites dispersed on SiO_2, Al_2O_3, and TiO_2 carriers with benzene and toluene was investigated with TPD experiments, TPReaction of adsorbed benzene and toluene with H_2, and benzene hydrogenation under steady-state conditions. Four kinds of experiments were conducted: (a) TPD from unmetallized carriers, (b) TPD after room temperature adsorption on the catalysts, (c) TPD after hydrogenation at three different temperatures (25, 65, and 115°C), and (d) TPReaction with hydrogen, following room-temperature adsorption of the hydrocarbons.

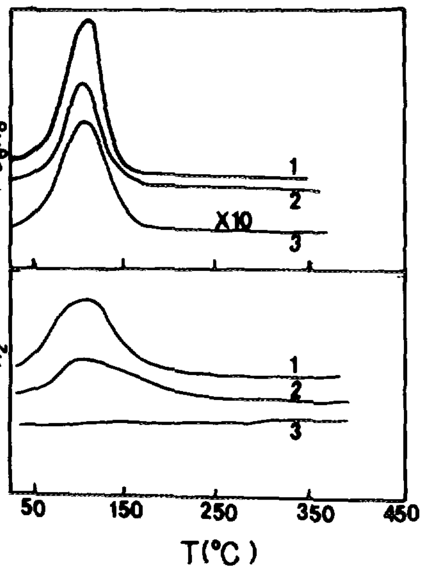

FIG. 1. TPD of benzene from unmetallized carriers. (1) SiO_2, (2) Al_2O_3, and (3) TiO_2.

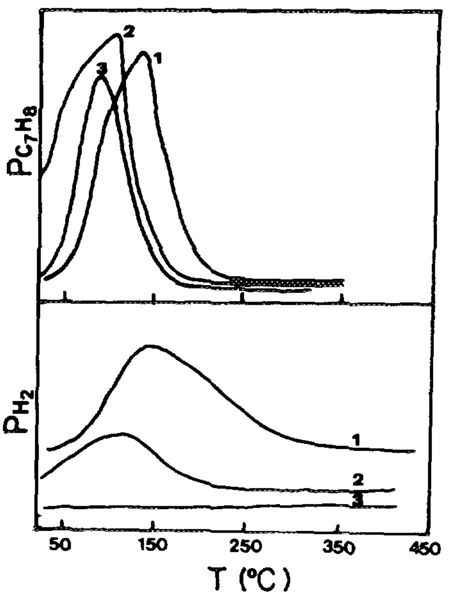

FIG. 2. TPD of toluene from unmetallized carriers: (1) SiO_2, (2) Al_2O_3, and (3) TiO_2.

(*a*) *TPD of Benzene and Toluene from Unmetallized Carriers*

It is well known (*19–21*) that oxide carriers are active in benzene and toluene adsorption; thus, it is necessary to investigate the adsorption/desorption characteristics of the carriers so as to be able to differentiate between molecules adsorbed on the carrier and molecules adsorbed on the metal. TPD spectra of benzene desorbing from the three carriers after room temperature adsorption are shown in Fig. 1, while corresponding spectra of toluene desorption are shown in Fig. 2. Benzene desorbs at low temperatures with a symmetric peak whose maximum is at a temperature of 80–93°C. The quantity of benzene desorbing appears to be proportional to the specific surface area of the carriers, which is >300 m^2/g for SiO_2, 100 m^2/g for Al_2O_3, and 50 m^2/g for TiO_2. Toluene also desorbs at low temperatures, but at somewhat higher values than for benzene, as illustrated in Table 1, in which peak temperatures of benzene and toluene desorption from the carriers are reported. Similar results have been reported by other investigators (*19, 20*) for benzene and toluene adsorption on TiO_2. These results may imply that toluene is more strongly adsorbed on the oxide surfaces, because it is a better π-electron donor than benzene. On the other hand, the desorption of benzene from the carriers may occur at lower temperatures than toluene because of its lower boiling point, if it is assumed that adsorption of the hydrocarbons occurs mostly as physical adsorption.

As illustrated in Figs. 1 and 2, benzene and toluene desorption from SiO_2 and Al_2O_3 carriers is accompanied by H_2 desorption,

TABLE 1

TPD Peak Temperatures, T_M, of Benzene and Toluene Desorption from the Carriers

	T_M (°C)	
Carrier	Benzene	Toluene
SiO_2	93	130
Al_2O_3	72	110
TiO_2	80	95

at somewhat higher temperatures. This implies that the molecules go through a partial dehydrogenation on these surfaces. The possibility of H_2 detection being an experimental artifact, i.e., the m/z = 2 signal arising from toluene or benzene mass fragments was investigated experimentally by addition of these molecules in the mass spectrometer stream. The signal corresponding to m/z = 2 was not measurably altered, indicating that the H_2 detected does indeed originate from dehydrogenation of the aromatic molecules on the carrier surface. The H_2 detected corresponds to only 1–2% of adsorbed benzene and 5–8% of adsorbed toluene. Dissociative adsorption of benzene and toluene over active SiO_2 has been reported in the literature (*21*). It must also be noted that SiO_2 and Al_2O_3 are active catalysts for cracking and rearranging of hydrocarbon chains, albeit at higher temperatures. As illustrated in Figs. 1 and 2, dehydrogenation of benzene or toluene does not occur, to any measurable extent, on the surface of TiO_2.

Finally, it was also examined whether the carriers are active in the hydrogenation of benzene and toluene by exposing them, with aromatics adsorbed on their surfaces, to H_2. The result was negative, indicating that the carriers, in the absence of metal, do not adsorb H_2 dissociatively, since atomic hydrogen is required to attack the aromatic molecules.

(*b*) *TPD of Benzene and Toluene from Supported Rh*

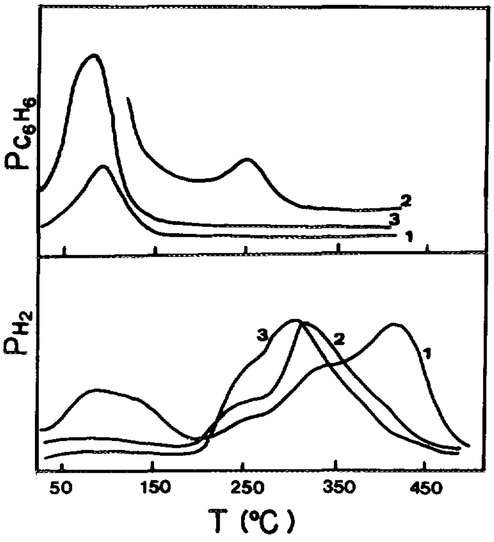

FIG. 3. TPD spectra following room-temperature adsorption of benzene on (1) Rh/SiO_2, (2) Rh/Al_2O_3, and (3) Rh/TiO_2.

TPD spectra obtained after benzene adsorption on Rh/SiO_2, Rh/Al_2O_3, and Rh/TiO_2 catalysts are shown in Fig. 3. The spectra consist of C_6H_6 and H_2 only, in agreement with other studies (*1, 3, 4, 7*). Only benzene desorbing from the carrier is apparent in the spectra obtained over Rh/SiO_2 and Rh/TiO_2. The quantities of benzene that desorb molecularly from the catalysts are similar to the quantities of benzene that desorb from the unmetallized supports. Although one cannot exclude the possibility that small quantities of benzene are also physisorbed on Rh, the benzene peak in the TPD spectra can be safely attributed to benzene adsorbed on the support. In the case of Rh/Al_2O_3, however, a peak, significantly smaller in intensity appears at approximately 250°C. This peak must be attributed to benzene desorbing from Rh surfaces since it was not observed in the spectra from the carriers. The H_2 which is observed at temperatures higher than 200°C originates from dehydrogenation of benzene strongly adsorbed on Rh, since H_2 desorption from Rh occurs at significantly lower temperatures (*34*). Dehydrogenation is initiated at approximately 200°C, in all cases. Hydrogen desorbing at lower temperatures has already been attributed to benzene dehydrogenation on carrier surfaces. The H_2 spectrum after benzene adsorption over Rh/SiO_2 seems to consist of three overlapping peaks, the most intense of which is at approximately 440°C. The spectra over Rh/Al_2O_3 and Rh/TiO_2 seem to consist of two overlapping peaks with maxima at 320 and 280–300°C, respectively. This observation implies that the dissociation/dehydrogenation activity of Rh/

TABLE 2

Amount of Benzene Adsorbed on Rh and on the Support Following Exposure at 25°C

Catalyst	Adsorbed benzene (μmol/g) On Rh	Adsorbed benzene (μmol/g) On support
Rh/SiO_2	18.9	400
Rh/Al_2O_3	17.9–21.8	70
Rh/TiO_2	17.1	30

SiO_2 is lower than that of Rh/Al_2O_3 and Rh/TiO_2.

The area under the H_2 desorption curve is proportional to the quantity of H_2 desorbing. If it is assumed that benzene adsorbs on the bare Rh surface without any C–H bond rupture and that H_2 originates from complete dehydrogenation of benzene adsorbed on Rh, according to,

$$C_6H_6(ads) \rightarrow 6C(ads) + 3H_2(g), \quad (1)$$

so that only hydrogen-free carbon remains on the surface, then one-third of the molar quantity of H_2 desorbed at temperatures above 200°C corresponds to the molar quantity of benzene adsorbed on the metal. The former assumption can be justified by the following arguments: (a) benzene adsorbs nondissociatively on Rh crystals under UHV conditions (*1–7*) and (b) if a C–H bond rupture occurs, the resulting adsorbed H atoms would produce a TPD spectrum similar to that after H_2 adsorption, which exhibits a peak around 100°C (*34*). The latter assumption was checked experimentally by extending a few TPD runs to temperatures up to 600°C, in which no additional hydrogen was observed to desorb.

The quantities of benzene adsorbed on Rh and on the support were calculated from the TPD spectra. The low-temperature benzene peak corresponds to desorption from the support while the high-temperature hydrogen peak corresponds to dehydrogenation of benzene adsorbed on the metal. The results are shown in Table 2. For the support with the highest surface area, i.e., SiO_2, the ratio of the two benzene adspecies is approximately 20, while for the support with the lowest surface area, i.e., TiO_2, the ratio is about 2. It should be noted, however, that because benzene is weakly held on the support a certain amount desorbs prior to initiation of the TPD run and is not accounted for. Knowing the dispersion of each catalyst (1.0 for Rh/SiO_2 and Rh/Al_2O_3 and 0.7 for Rh/TiO_2), the benzene surface coverage can be estimated. The values computed are 0.39 for Rh/SiO_2, 0.41 for Rh/Al_2O_3, and 0.42 for Rh/TiO_2. In all cases, the benzene surface coverage of Rh is approximately the same and corresponds to a stoichiometry of 1 molecule of benzene per 2.5 surface atoms of Rh. The saturation coverage which has been reported for benzene adsorbed on Rh(111) is 0.13–0.17 (*1, 7*). Thus, small (<10 nm) Rh crystallites can adsorb approximately twice as much benzene as Rh single crystals. Indications that small metallic crystallites can adsorb more benzene than corresponding crystallographic planes have previously appeared in the literature. Palazov *et al.* (*27*) have reported 27.3 mg of benzene adsorbed per g of Pt in a 5%Pt/Al_2O_3 catalyst of 22% dispersion. This corresponds to a saturation coverage of 0.31. From the study of Candy *et al.* (*35*) an adsorption stoichiometry of 1 molecule of benzene per 2.3 atoms of Ni can be estimated (*36*) which corresponds to a saturation coverage of 0.43.

These results are contradictory to the notion that benzene is adsorbed parallel to the metallic surface under high surface coverages. The van der Waals area of a benzene molecule is 35 $Å^2$ (*12*), while the area corresponding to a Rh atom is 7.2 $Å^2$. Thus, the expected maximum surface coverage is approximately 0.2. It has been reported, however, that the C–H bonds form an angle with the surface upon adsorption (*1, 2*). Therefore, the effective area of an adsorbed benzene molecule is smaller. If, further, the C–C and C–H bond lengths are considered (1.4 and 0.8 Å, respectively), a minimum

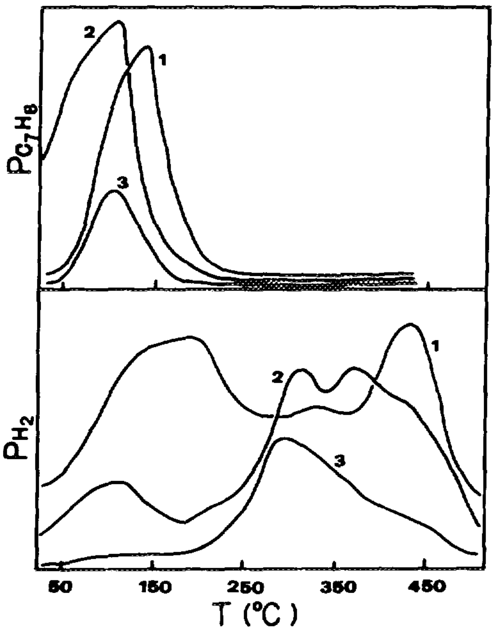

FIG. 4. TPD spectra following room-temperature adsorption of toluene on (1) Rh/SiO_2, (2) Rh/Al_2O_3, and (3) Rh/TiO_2.

area of 15 Å^2 can be estimated. With this value for the area of the benzene molecule, a maximum surface coverage of 0.47 can be computed. Other possible explanations are that a fraction of the adsorbed benzene forms a σ-bond with the surface or that new adsorption sites are created at the metal-support interfacial area in which benzene is bonded partly on the metal and partly on the carrier.

TPD spectra obtained from Rh/SiO_2, Al_2O_3, and TiO_2 catalysts following room-temperature toluene adsorption are shown in Fig. 4. The spectra of molecularly desorbing toluene are essentially identical to the spectra obtained from the unmetallized carriers (Fig. 2). No molecularly desorbing toluene which could be attributed to originate from Rh was detected in any case. Significant quantities of H_2 were detected, however, which can be attributed to dehydrogenation of toluene. H_2 appearing at low temperatures (50–200°C) originates from the carrier, as Fig. 2 indicates. The H_2 spectra of Rh/SiO_2 and Rh/Al_2O_3 are relatively complicated and are characterized by a major peak at approximately 450°C (Rh/SiO_2) and two overlapping peaks at 320 and 380°C (Rh/Al_2O_3). This shape of the spectra could be attributed to different adsorbed states of toluene or stage-wise dehydrogenation of the adsorbed molecules. The H_2 spectrum after toluene adsorption over Rh/TiO_2 is simpler and is characterized by a single peak with maximum at approximately 300°C. As in the case of benzene, these spectra imply that toluene dissociation/dehydrogenation occurs more readily on Rh/TiO_2 than on Rh/SiO_2.

Since no other products, besides H_2, were detected during the TPD experiments, the quantity of H_2 detected to desorb can be used to estimate the quantity of adsorbed toluene, assuming that toluene decomposes according to

$$C_7H_8(\text{ads.}) \rightarrow 7\ C(\text{ads.}) + 4\ H_2\ (\text{g}). \quad (2)$$

The surface coverages thus obtained are 0.34–0.38 for Rh/SiO_2, 0.37 for Rh/Al_2O_3, and 0.36 for Rh/TiO_2. These surface coverages are somewhat smaller than those estimated with benzene which could be due to the larger size of the toluene molecule and to stereochemical hindrance of the methyl group of toluene (*38*).

(*c*) *Reactivity of Adsorbed Benzene and Toluene towards Hydrogenation*

The reactivity of adsorbed benzene was investigated by saturating the Rh surface with benzene, then exposing it to H_2 flow for 15 min at temperatures of 25, 65, and 115°C, and then obtaining the TPD spectrum. The spectra thus obtained correspond to benzene which has not reacted at the particular temperature and decomposes to H_2 and surface carbon during temperature programming. The TPD spectra obtained over Rh/SiO_2, Rh/Al_2O_3, and Rh/TiO_2 for benzene with the methodology described above are shown in Figs. 5a–5c. A common feature of all catalysts is that exposure to H_2, even at 25°C, resulted in hydrogenation of the

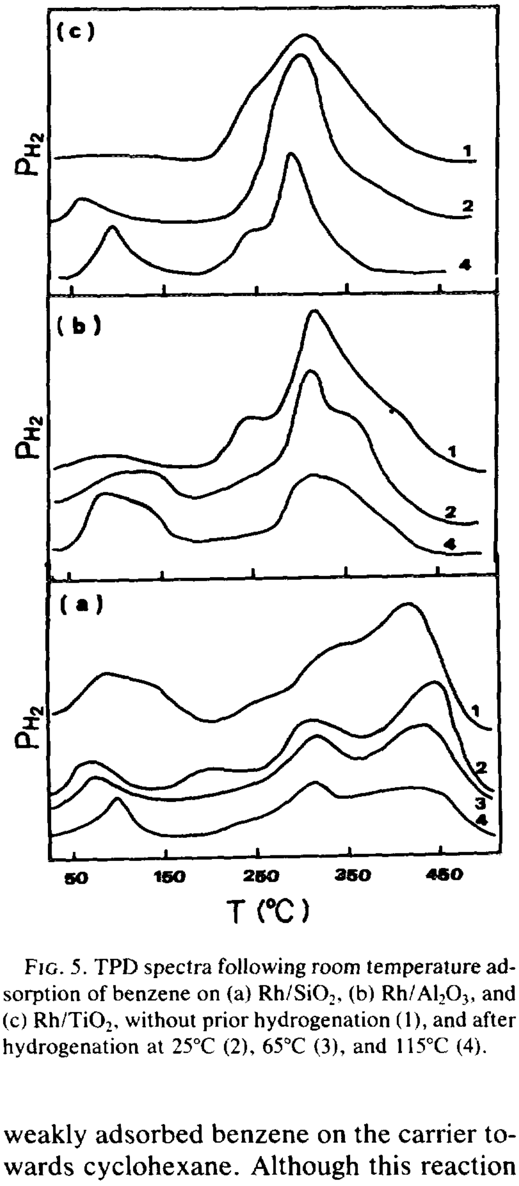

FIG. 5. TPD spectra following room temperature adsorption of benzene on (a) Rh/SiO_2, (b) Rh/Al_2O_3, and (c) Rh/TiO_2, without prior hydrogenation (1), and after hydrogenation at 25°C (2), 65°C (3), and 115°C (4).

weakly adsorbed benzene on the carrier towards cyclohexane. Although this reaction was not investigated in detail, the fact that cyclohexane appeared immediately upon introduction of hydrogen to the reactor implies that benzene hydrogenation on the carrier by spillover hydrogen is very fast at temperatures as low as 25°C. Only in the case of Rh/SiO_2 were small quantities of benzene detected to desorb at low temperatures (benzene originating from the carrier) after hydrogenation at 25 and 65°C, but none after hydrogenation at 115°C. In contrast, the strongly adsorbed benzene on Rh is rather inactive, as the H_2 spectra indicate. The quantity of H_2 detected or, alternatively, the quantity of unreacted benzene, decreases with increasing temperature of hydrogenation, as expected.

The H_2 TPD spectrum obtained from benzene adsorption over the Rh/SiO_2 catalyst without prior hydrogenation and after hydrogenation at 25, 65, and 115°C is shown in Fig. 5a. Referring to the runs after hydrogenation, hydrogen detected at low temperatures (<200°C) originates from dehydrogenation of benzene weakly adsorbed on the surface of SiO_2 and from H_2 desorbing from Rh. Hydrogen detected at higher temperatures (>200°C) originates from dehydrogenation of benzene strongly adsorbed on Rh. The quantity of H_2 detected in the high temperature region decreases with increasing temperature of hydrogenation, prior to conducting the TPD experiment, as would be expected. It is interesting to note, however, that even after hydrogenation at 115°C, significant quantities of H_2 are detected, which implies that a fraction of benzene adsorbed on Rh is inactive even at 115°C in the presence of H_2. It should also be stated that cyclohexane was detected to desorb at low temperatures (peak temperature of ~80°C) but none was detected at high temperatures.

Over Rh/Al_2O_3 catalysts, no molecular benzene was detected to desorb after hydrogenation at 25°C. Hydrogen spectra from this catalyst are shown in Fig. 5b. The H_2 spectrum remains intense even after hydrogenation at 115°C, implying that strongly adsorbed benzene on Rh is not easily hydrogenated under these conditions. The quantity of H_2 desorbing at low temperatures (50–150°C) increases after the hydrogenation cycles. Apparently, H_2 is adsorbed on Rh during hydrogenation and subsequently desorbs in this temperature region, as has been illustrated by H_2 TPD experiments, the results of which have been reported earlier (*34*). This is more clearly illustrated in the Rh/TiO_2 spectra (Fig. 5c). Prior to hydrogenation no low-temperature H_2 desorption is observed. After hydrogenation, however,

TABLE 3

Influence of the Carrier on the Activity of Rh towards Benzene Hydrogenation

	Adsorbed benzene (µmol/g)		
Catalyst	Initially	After hydrog. at 115°C	R_B
Rh/SiO_2	18.9	11.1	0.59
Rh/Al_2O_3	19.8	10.9	0.55
Rh/TiO_2	17.1	8.9	0.52

the spectra contain the H_2 peak which corresponds to H_2 desorption from Rh (*34*). This result implies that H_2 can be adsorbed on Rh surfaces highly saturated with strongly adsorbed benzene. It was also observed that during benzene adsorption on H_2-covered Rh surfaces, the benzene molecule does not dispose of all of the adsorbed hydrogen. Similar phenomena have been observed over Ni (*23*) and Pt (*37*) catalysts.

The quantity of benzene remaining on the Rh surface after 15 min hydrogenation at 115°C was estimated from the H_2 spectra following the method described earlier. The quantity of benzene adsorbed on the Rh particles at 25°C was also determined and the ratio of the amount of benzene remaining on the Rh surface after hydrogenation at 115°C to the amount of benzene initially adsorbed on Rh, R_B, was also estimated. These quantities are reported in Table 3. It is apparent that the dehydrogenation reactivity of strongly adsorbed benzene, as described by the parameter R_B, is weakly affected by the carrier employed to disperse the Rh crystallites. However, reactivity increases in the order Rh/SiO_2 < Rh/Al_2O_3 < Rh/TiO_2. The same conclusion is drawn by examination of the H_2 TPD spectra of Figs. 5a–5c since these correspond to benzene dehydrogenation and not H_2 desorption. It is apparent that over Rh/TiO_2, H_2 evolution occurs at the lowest temperatures, followed by Rh/Al_2O_3 and Rh/SiO_2.

The reactivity of adsorbed toluene was also investigated by conducting TPD experiments after exposure of the catalysts to H_2 at temperatures of 25, 65, or 115°C. TPD spectra obtained over Rh/SiO_2, Rh/Al_2O_3 and Rh/TiO_2 catalysts are shown in Figs. 6a–6c, respectively. The hydrogenation of adsorbed toluene has many features in common with the hydrogenation of adsorbed benzene (Fig. 5). Toluene weakly adsorbed on the surface of the carriers is hydrogenated to methylcyclohexane even at room temperature. However, the rate of its hydrogenation is lower than that of benzene. The H_2 spectra observed over Rh/SiO_2 (Fig. 6a)

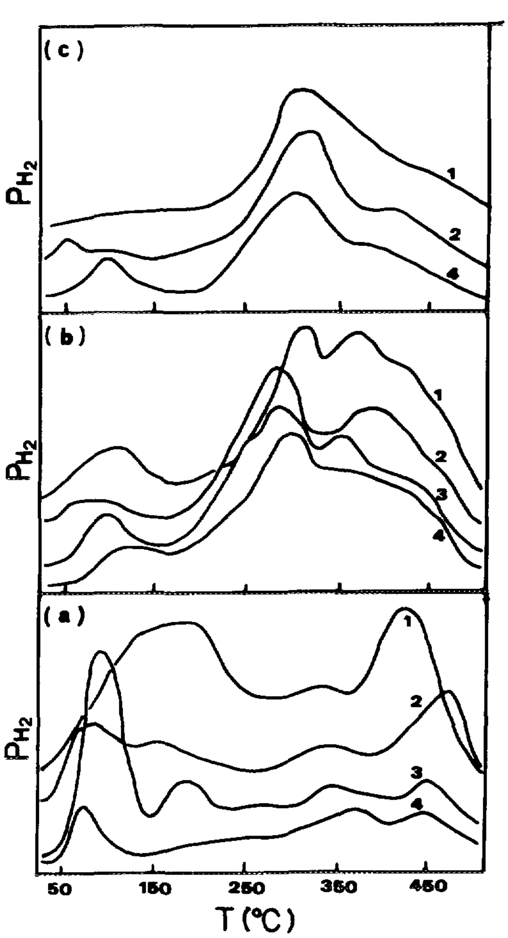

FIG. 6. TPD spectra following room temperature adsorption of toluene on (a) Rh/SiO_2, (b) Rh/Al_2O_3, and (c) Rh/TiO_2, without prior hydrogenation (1), and after hydrogenation at 25°C (2), 65°C (3), and 115°C (4).

are rather complicated since H_2 originates from three different sources: (a) from toluene decomposition on SiO_2, (b) from desorption of H_2 adsorbed on Rh during hydrogenation, and (c) from the decomposition of toluene adsorbed on Rh particles. Based on the H_2 spectra of the unmetallized carriers (Fig. 2) and TPD spectra of H_2 desorbing from Rh (*34*), it can be concluded that the first two sources contribute to the spectrum at temperatures less than 200–250°C. The quantity of H_2 appearing at higher temperatures decreases with increasing hydrogenation temperature, especially between 25 and 65°C. The spectra obtained under similar conditions over Rh/Al_2O_3 (Fig. 6b) and Rh/TiO_2 (Fig. 6c) indicate that hydrogenation even at 115°C alters very little the position and the intensity of the H_2 peaks which originate from the decomposition of toluene adsorbed on Rh. Thus, toluene strongly adsorbed on the metal is not active towards hydrogenation. This is not due to inability of H_2 to adsorb on the toluene-covered Rh surface, as is indicated in Fig. 6c in which the peak of H_2 desorbing from the metal at approximately 90°C is readily discernible. The adsorbed hydrogen does not seem to interact strongly with the adsorbed toluene since the H_2 peak in the spectrum (Fig. 6c) is identical with the one obtained during H_2 TPD from a clean Rh surface (*34*). The parameter R_T, the ratio of the amount of toluene remaining on the surface after hydrogenation at 115°C to the amount of toluene initially adsorbed at 25°C, was determined in an identical manner as for R_B, for the Rh/Al_2O_3 and Rh/TiO_2 catalysts. For Rh/SiO_2 it was not determined due to the complexity of the spectra obtained. For Rh/Al_2O_3 the value of R_T is 0.93 and for Rh/TiO_2 0.79. These values are significantly higher than the values of R_B (Table 3), indicating that toluene hydrogenation activity of the Rh surfaces is less than their benzene hydrogenation activity.

(*d*) *TPReaction of Benzene and Toluene on Supported Rh*

The reactivity of benzene adsorbed on Rh/SiO_2, Al_2O_3, TiO_2 was also investigated by TPReaction experiments. Benzene was adsorbed on the catalysts at room temperature, the flow was then switched to H_2 and when cyclohexane production at room temperature ceased, temperature programming was initiated under H_2 flow. The weakly adsorbed benzene is hydrogenated at room temperature. As temperature increases, a fraction of strongly adsorbed benzene is hydrogenated or desorbs and, at higher temperatures the remaining benzene decomposes on the surface in fragments of the form C_xH_y which, at even higher temperatures are hydrogenated to CH_4. Thus, the temperature of CH_4 evolution as well as the quantity of CH_4 produced are indicators of the strength of benzene adsorption on the Rh surface. In all cases, CH_4 was found to desorb at a peak temperature of approximately 330°C. The quantity of CH_4 produced, however, was found to depend on the carrier of the Rh crystallites. Quantities of CH_4 desorbed, normalized with respect to the quantity observed to desorb over Rh/SiO_2 and with respect to the benzene adsorption capacity of the metal in each case are 1 for Rh/SiO_2, 0.44 for Rh/Al_2O_3, and 0.39 for Rh/TiO_2. This result, which is in accordance with the results in Table 3, implies that the benzene on Rh/TiO_2 is less strongly held and more active towards hydrogenation to cyclohexane. On the other hand, benzene on Rh/SiO_2 appears to be the most strongly held and the least active towards hydrogenation.

TPReaction studies of toluene adsorbed on Rh/SiO_2, Al_2O_3, and TiO_2 catalysts with H_2 were also carried out following the methodology which was described earlier for benzene. The TPReaction spectra obtained are shown in Fig. 7. An essential difference between these spectra and those obtained with benzene is the appearance of methylcyclohexane and toluene at low temperatures. This is due to the lower reactivity of toluene on the carriers, as compared to that of benzene. In the case of benzene, the aromatic molecule adsorbed on the carrier reacted completely prior to the initiation of the

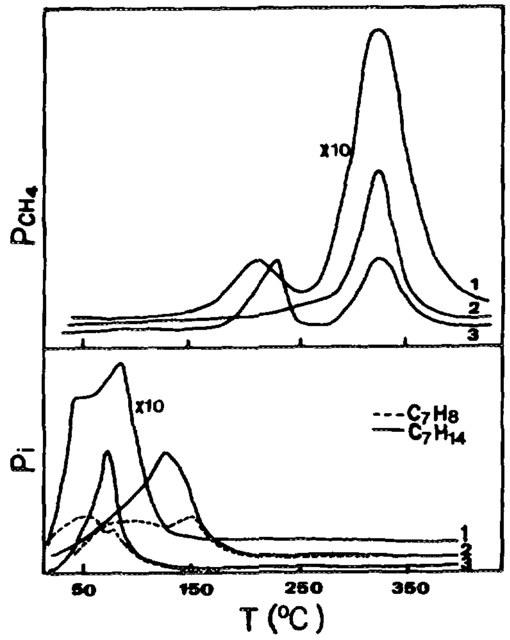

FIG. 7. TPReaction of adsorbed toluene under H_2 flow over (1) Rh/TiO$_2$, (2) Rh/SiO$_2$, and (3) Rh/Al$_2$O$_3$.

TPReaction experiment. The CH_4 spectra consist of a major peak at 322–326°C, while in Rh/Al$_2$O$_3$ and to a smaller extent in Rh/TiO$_2$ a smaller CH_4 peak appears at 210–225°C. The position of the CH_4 peaks does not seem to depend on the carrier nor on the aromatic molecule, since similar spectra were also obtained with benzene, indicating that CH_4 production takes place through the same intermediates in both cases. The normalized quantities of CH_4 produced, with respect to the toluene adsorption capacity of the metal in each case are 1.0 for Rh/SiO$_2$, 0.74 for Rh/Al$_2$O$_3$, and 0.43 for Rh/TiO$_2$. This is the same order as that observed with benzene.

(*e*) *Steady-State Benzene Hydrogenation*

Benzene hydrogenation over Rh/SiO$_2$, Al$_2$O$_3$, and TiO$_2$ was also investigated at steady state conditions at 30°C. In these experiments the partial pressures of H_2 and benzene were maintained constant at 630 and 12.5 Torr, respectively. Turnover frequencies obtained are the following: $57 \times 10^{-3}\ s^{-1}$ for Rh/SiO$_2$, $90 \times 10^{-3}\ s^{-1}$ for Rh/Al$_2$O$_3$, and $43 \times 10^{-3}\ s^{-1}$ for Rh/TiO$_2$. Thus, at steady-state conditions, the reactivity of Rh for benzene hydrogenation increases in the order Rh/TiO$_2$ < Rh/SiO$_2$ < Rh/Al$_2$O$_3$. However, the observed differences in the activity of Rh with respect to the carrier are very small. This order of reactivity is different from that obtained with the TPD and TPR experiments. The TPR study showed that even at 115°C, a significant fraction (~50%) of benzene strongly adsorbed on the Rh surfaces does not react with H_2. In contrast, benzene adsorbed on the carrier is readily hydrogenated at room temperature by spill-over hydrogen. Furthermore, at this low temperature, significant quantities of benzene are adsorbed on the carrier, as indicated by the TPD experiments on unmetallized carriers (Fig. 1). Based on this observation, the rates of benzene hydrogenation observed on supported Rh crystallites must be significantly influenced or even controlled by reaction occurring on the carrier surface. In that case, estimation of turnover frequencies based on the observed rates and the metal dispersion, are meaningless. Many studies have appeared in the literature which report alteration in aromatics hydrogenation activity of metals dispersed on different high-surface-area carriers. In view of the results obtained in the present study, their conclusions must be questioned with respect to participation of the carriers in the measured rates of hydrogenation.

CONCLUSIONS

TPD and TPReaction studies of benzene and toluene adsorbed on Rh/SiO$_2$, Rh/Al$_2$O$_3$, and Rh/TiO$_2$ catalysts were carried out to investigate the interaction of these molecules with Rh crystallites and to identify any influence of the carrier on the nature and magnitude of these interactions. It was found that both aromatic molecules adsorb on the surface of the carrier and are readily hydrogenated at room temperature by spillover hydrogen atoms originating from the metal. Hydrogenation on the carriers does not occur in the absence of metal.

Benzene and toluene strongly adsorbed on Rh dissociate at high temperatures producing H_2. Thus, the TPD spectra correspond to dehydrogenation kinetics and not to benzene/toluene desorption kinetics. TPReaction studies of benzene and toluene adsorbed on supported Rh under H_2 flow have shown that the aromatic molecules adsorbed on Rh, especially toluene, are not easily hydrogenated. However, at sufficiently high temperatures, a fraction is hydrogenolyzed towards CH_4. The TPReaction spectra of benzene and toluene are very similar, indicating that CH_4 originates from transformations of the same surface species. The strength of adsorption and the reactivity of adsorbed benzene and toluene with hydrogen were found to be affected by the carrier employed to disperse the metal. The dehydrogenation reactivity, in the absence of H_2, was found to follow the order $Rh/TiO_2 > Rh/Al_2O_3 > Rh/SiO_2$.

Rates of benzene hydrogenation under steady state conditions indicate that the reactivity of catalysts decreases in the order $Rh/Al_2O_3 > Rh/SiO_2 > Rh/TiO_2$, but differences are small. However, this result is questioned in view of support participation in the benzene hydrogenation reaction.

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