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Transformations of Cyclohexene over Silica-Supported Copper in the Presence of Deuterium

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The transformations of cyclohexene were investigated over a silica-supported copper catalyst in a static circulation reactor in the presence of varying amount of D_2 at 443 K and in a flow system in the 323–573 K temperature range under D_2 flow. In the static system D_2 pressure significantly influenced the types of reactions taking place (distinct regions for dehydrogenation, dehydrogenation plus hydrogenation, and hydrogenation were observed). In the flow reactor benzene and cyclohexane were always formed together, due to the partial reactivation of the catalytic surface. The temperature of the reaction significantly influenced product distribution. During transformations, the deuterium content and the deuterium distribution were also monitored in both reactor types. The half-hydrogenated state, i.e., the adsorbed d_1-cyclohexyl species, was found to be the key intermediate; nevertheless, π-allyl adsorption was also significant at higher D_2 pressure and in the flow system.

INTRODUCTION

Cyclohexene is very often used as a molecular probe for studying various catalyst preparations (1–20). Despite its simple structure it can undergo various transformations over transition metal catalysts depending on the metal and experimental conditions (temperature, presence or absence of hydrogen, hydrogen pressure, etc.). The main reactions are dehydrogenation (2, 3), disproportionation (3–6), and hydrogenation (2, 3, 6 –20). With some luck, conditions can be found where these reactions can be studied separately, but on most metals these regions largely overlap. Much is known about the basic features of the transformations over Pt (8, 9), Pd (10), Rh (11), Ni (6, 12), and Ir (19) catalysts and also over stepped Pt single crystal (2, 3). However, at least to our knowledge, catalytic studies concerning the cyclohexene–copper–H_2 or D_2 systems have not been performed except for two early studies (21, 22) on related system, i.e., over $CuCr_2O_4$ and Raney Cu, respectively. One reason may be that in the past 50 years copper has rarely been considered as a hydrocarbon hydrogenation catalyst (22–26). It is true that copper is much less effective in this reaction than the commonly used Pt, Pd, Rh, or Ni, but its moderate activity and slow H−D exchange property can be advantageous in investigating concurrent reactions requiring only slightly different conditions and for mechanistic studies using D_2.

All these features provided motivation for choosing the cyclohexene–deuterium–copper system with the objectives of studying, separately if possible, the above-listed transformations, exploring the mechanisms of the reactions through the analysis of the deuterium content and distribution in the reactant as well as in the products. In addition to our experimental results, significant pieces of information are available from a very recent paper (27). In the work the cyclohexene–Cu(100)–D_2 system was studied under UHV conditions. Although transferring these results to a catalytic system requires considerable caution, some of the observations, described below, are helpful in providing a more complete interpretation of chemical events occurring on the catalytic surface.

EXPERIMENTAL

Reactants and the Catalyst

Cyclohexene was obtained *via* the dehydration of cyclohexanol. After distillation its purity was checked by GC−MS. It was found 99.9+% pure. In order to destroy possibly formed peroxides, it was passed through a column filled with freshly activated basic alumina (Camag) under inert (Ar) atmosphere before reactions in the flow system or filling it into a closed evacuated vial for further use in the static circulation reactor.

Oxygen-free hydrogen was prepared with a Matheson 8326 generator, operating with a palladium membrane.

Deuterium was prepared with a General Electric 15EHG generator (purity of D_2O was 99.8%). Deoxygenation of deuterium was carried out with a Model 1000 Oxygen Trap.

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The 6.36% Cu/silica gel (Cu/S-X) was prepared by an ion-exchange method described in the literature (28). Details are as follows: silica gel (Strem, large pore, 120–230 mesh) was immersed in a tetramminecopper(II) solution at pH 11. After 24 h the blue product was washed thoroughly with water, dried at 393 K (24 h), and decomposed at 773 K in air (3 h). The catalyst was reduced in flowing hydrogen (20 cm^3/min) at 673 K for 2 h and kept in a vacuum desiccator until use. The percentage of surface copper atoms (14.3%) was determined by N_2O decomposition by the pulse method at 363 K (29). After reduction 7% of the copper remained ionic in the form of Cu^+ determined by temperature-programmed reduction (26).

Samples (50 mg) of the stored prereduced catalyst were activated in the circulation system under 20 kPa D_2 at 573 K for 30 min or in the flow reactor under 20 cm^3/min D_2 flow for 1 h at 573 K.

Apparatus, Methodology, and Analysis

Static Circulation Reactor

The reactions were carried out in a conventional closed circulation reactor similar to that described in Ref. (30). The volume of the reactor was 69 cm^3, and the total volume of the system was 169.4 cm^3. The reactor was heated with an air thermostat. The volume of the sampling capillary was 0.05 cm^3 and the total sampling volume was 0.15 cm^3. A Hewlett–Packard (HP) Model 5890 gas chromatograph equipped with a quadrupole mass-selective detector was attached to the system. Data analysis was performed on an HP 5970 Chemstation. A 50-m-long HP-1 capillary column was used for separating the reactants and the products. The column was operated in the isothermal mode (over temperature 323 K) with helium as the carrier gas (flow rate 1.3 cm^3/min).

The reactants (2.65 kPa of cyclohexene and different amounts of D_2) were premixed in the circulation part of the system before the reaction. (Cyclohexene was subjected to several freeze–thaw–evacuate cycles before preparing the mixture.) The reaction temperature was 443 K. At a certain deuterium pressure, the product yield vs time (t) functions were always determined over a fresh sample of catalyst. Measurements were reproducible within 10%.

Flow Reactor

Reactions were carried out over 50 mg of catalyst samples in H_2 or D_2 flow (15 cm^3/min). The partial pressure of cyclohexene was 3.2 kPa. The temperature range was 323–573 K. Within this range reactions were run at temperatures in increments of 50 K. Fresh sample of catalyst (activated in 20 cm^3/min D_2 flow for 1 h at 573 K) was used at each temperature. Diffusion resistance was checked by varying the quantity of the catalysts. The chosen amount allowed investigations in the kinetic regime. Product accumulation was followed by the GC-MS technique described above, exactly like in measurements in the circulation reactor.

Deuterium distribution was qualitatively characterized by ^{13}C-NMR (Bruker 400-MHz spectrometer) spectrometry concentrating on the positions of the deuterium in cyclohexene. Measurements were done on samples collected for 60 min in a trap cooled with liquid N_2 at the outlet of the flow reactor. Similar measurements could not be done in the static system because of the insufficient amount of material in the reactor for NMR measurements.

Deuterium Distributions

Deuterium distribution was calculated on the basis and vicinity of the parent peaks. In the calculations the natural abundance for ^{13}C and D, the C−H and C−D fragmentation reactions were taken into account.

RESULTS

Transformations of Cyclohexene Depending on D_2 Pressure in the Static Reactor

Product Formation and Distribution

Reactions depending on D_2 pressure were investigated in the static circulation reactor at 443 K (Table 1).

There was no detectable transformation without deuterium. Only dehydrogenation occurred, producing benzene at low D_2 pressure (2.7 kPa). Dehydrogenation and hydrogenation giving benzene and cyclohexane, respectively, were observed at somewhat higher D_2 pressure (9.1 kPa). At 20.0 kPa and above only hydrogenation proceeded. Reactions below 46.7 kPa D_2 pressure started after an induction period, which disappeared when a fresh reaction

TABLE 1

Product Accumulation in the Transformations of Cyclohexene (2.65 kPa) over Cu/SiO_2 (50 mg) in the Function of D_2 Pressure at 443 K in a Closed Circulation Reactor

D_2 pressure (kPa)	Products	Concentration (mol%)			
		5 min	15 min	30 min	35 min
2.7	Benzene	0	0	0.5	1.4
	Cyclohexane	0	0	0	0
9.1	Benzene	0	0	4.1	11.4
	Cyclohexane	0	0	3.9	8.9
20.0	Benzene	0	0	0	0
	Cyclohexane	0	0	7.3	14.1
33.3	Benzene	0	0	0	0
	Cyclohexane	0	2.9	39.6	57.6
40.0	Benzene	0	0	0	0
	Cyclohexane	0	0	11.9	24.4
46.7	Benzene	0	0	0	0
	Cyclohexane	0.3	1.1	5.5	10.5
54.4	Benzene	0	0	0	0
	Cyclohexane	0.2	0.5	0.6	0.9

mixture (e.g., 2.6 kPa of D_2 and 20.0 kPa of D_2) was contacted with the used catalyst. At high enough D_2 pressure (at 46.7 kPa), cyclohexane (only hydrogenation occurred) could already be detected at the first sampling (5 min).

Deuterium Content and Deuterium Distribution in the Reactant and in the Products in the Static Reactor

During transformations, the deuterium content and the deuterium distribution were monitored. Before details are given it is important to point out that “alone” neither benzene nor cyclohexane underwent deuterium exchange up to 673 or 473 K, respectively; thus deuterium-exchanged benzene and cyclohexane were originated from cyclohexene through surface reactions.

Cyclohexene (relevant data are in Table 2). During the induction period, only single H–D exchange in the cyclohexene took place at each D_2 pressure.

At the lowest D_2 pressure applied (2.7 kPa), i.e., in the dehydrogenation region, among the exchanged molecules, this d_1-cyclohexene remained predominant; d_2-cyclohexene appeared only at the 35-min sampling with an intensity of almost two magnitudes less than that of d_1-cyclohexene. (The position of the exchanged deuterium could not be determined here, for the reason given in the last paragraph under Experimental).

TABLE 2

Deuterium Distribution in Cyclohexene during Its Reactions (2.65 kPa of Cyclohexene) over Cu/SiO_2 (50 mg) in the Function of D_2 Pressure at 443 K in a Closed Circulation Reactor

D_2 pressure (kPa)	Number of deuterium atoms	Deuterium distribution (%)			
		5 min	15 min	30 min	35 min
2.7	d_0	93.8	93.7	93.6	93.1
	d_1	6.2	6.3	6.4	6.8
	d_2	—	—	—	0.1
9.1	d_0	94.1	93.8	88.8	82.9
	d_1	5.9	6.2	7.7	9.8
	d_2	—	—	1.1	1.3
	d_3	—	—	0.6	1.6
	d_4	—	—	0.9	1.9
	d_5	—	—	0.8	1.8
	d_6	—	—	0.1	0.6
	d_7	—	—	—	0.1
20.0	d_0	93.9	93.8	93.2	92.9
	d_1	6.1	6.2	6.8	7.1
33.3	d_0	93.8	91.3	81.2	79.1
	d_1	6.2	8.3	8.4	8.1
	d_2	—	0.2	0.9	1.1
	d_3	—	0.1	0.9	0.4
	d_4	—	—	1.0	1.2
	d_5	—	0.1	1.1	1.0
	d_6	—	—	0.9	1.6
	d_7	—	—	1.7	1.6
	d_8	—	—	2.2	2.9
	d_9	—	—	1.7	2.3
	d_{10}	—	—	—	0.7

At 9.1 kPa D_2 pressure, at the sampling when product desorption actually started, polydeuterated cyclohexene molecules could also be detected (d_2-d_6-cyclohexene molecules in decreasing amounts); however, d_1-cyclohexene remained predominant. This remained so as the reaction proceeded.

At the starting point of the hydrogenation region (20.0 kPa), only d_1-cyclohexene was found throughout the reaction. At higher D_2 pressure (33.3 kPa) the deuterium distribution changed. Although d_1-cyclohexene remained the most abundant exchanged product throughout the reaction, later (35-min sampling), every type of deuterated cyclohexene was detected with a local maximum of d_8-cyclohexene.

Benzene. Benzene resulting from dehydrogenation was not exchanged initially, but at 9.1 kPa D_2 pressure d_1-benzene was formed too. Moreover, as the reaction proceeded multiple exchange also occurred, d_1-d_4-benzene molecules were detected in decreasing amounts.

Cyclohexane (relevant data are in Table 3). Cyclohexane appeared first at 9.1 kPa D_2 pressure, after 30 min. Here d_2-cyclohexane was predominant; however, molecules with varying deuterium content (d_3-d_6-cyclohexane molecules) were also found in significant amounts. As the reaction proceeded further, d_1-d_8-cyclohexane species could be detected and their quantities did not differ appreciably. This fact may be taken as an indication of flat-lying intermediate.

At 20 kPa D_2 pressure (the starting point of the hydrogenation reaction) d_2-cyclohexane was also predominant at the earliest possible sampling (30 min) and d_6-cyclohexane was also detected in significant amount. Noteworthy is the lack of d_1-, d_3-, and d_4-cyclohexane molecules. d_1-, d_3-Cyclohexane molecules were not formed at later stages of the reaction either, while otherwise cyclohexane molecules with almost every kind of deuterium content was detected. Significant exchange also occurred on the other side of the molecule. The distribution of deuterated products was different again at 33.3 kPa D_2 pressure (well in the hydrogenation region). Here, at the 15-min sampling time d_2- and d_3-cyclohexane were formed nearly in equal amounts (there was no d_1-product just as in the other cases), while later d_1-d_{12}-cyclohexane molecules were all found.

Transformations of Cyclohexene in the Flow Reactor

In this reactor cyclohexene started to react at considerably lower temperatures than in the circulation reactor. There was no transformation in He flow, but in deuterium atmosphere both benzene and cyclohexane were formed at each temperature studied. A temperature where exclusive dehydrogenation or hydrogenation occurred was not

TABLE 3

Deuterium Distribution in Cyclohexane during the Reactions of Cyclohexene (2.65 kPa) over Cu/SiO_2 (50 mg) in the Function of D_2 Pressure at 443 K in a Closed Circulation Reactor

D_2 pressure (kPa)	Time (min)	Deuterium distribution (%)											
		d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}
9.1	5	—	—	—	—	—	—	—	—	—	—	—	—
	15	—	—	—	—	—	—	—	—	—	—	—	—
	30	—	36.4	19.5	16.7	7.9	19.5	—	—	—	—	—	—
	35	3.0	13.3	13.8	16.5	17.7	18.1	12.4	5.2	—	—	—	—
20.0	5	—	—	—	—	—	—	—	—	—	—	—	—
	15	—	—	—	—	—	—	—	—	—	—	—	—
	30	—	45.3	—	—	—	37.9	16.8	—	—	—	—	—
	35	—	6.2	—	1.9	5.1	4.8	17.7	28.3	22.6	11.6	1.8	—
33.3	5	—	—	—	—	—	—	—	—	—	—	—	—
	15	—	38.1	44.6	—	8.2	—	9.1	—	—	—	—	—
	30	0.4	5.9	6.4	6.1	7.2	8.7	10.6	14.1	14.8	14.4	9.4	2.0
	35	0.9	4.7	5.1	5.5	6.5	7.7	10.9	13.2	15.3	15.9	11.3	3.0

found. From 323 to 473 K cyclohexane was predominant (Fig. 1), at 523 K nearly equal amounts of the two products were formed, and at 573 K benzene clearly overwhelmed cyclohexane (Fig. 2).

Steady-state activity for benzene formation was attained at each temperature; of course the specific value increased considerably with temperature (Table 4).

Cyclohexane formation reached steady state only at 523 and 573 K (Table 4). At other temperatures exponential-type deactivation was observed with time on stream (Fig. 3).

Deuterium Content and Deuterium Distribution in the Reactant and in the Products in the Flow Reactor

The deuterium content and the deuterium distribution were also monitored here at two temperatures (423 and 523 K; Tables 5 and 6, respectively).

Cyclohexene. First, let us point out that about half of the cyclohexene molecules did not undergo deuterium exchange. Of those molecules which did, single H–D exchange was predominant at both temperatures and over the steady-state surface at 523 K. However, the formation of d_2-cyclohexene was also significant. At the lower temperature, exchange was mainly constrained on one side of the molecule, while at 523 K the other side became increasingly involved. ^{13}C-NMR measurements revealed that the first deuterium goes into allylic position mainly, but it also can be found at the double bond in appreciable amount. (Although accurate quantitative data cannot be given for the ratio of deuterium in the vinyl to deuterium in the allylic positions due to the technique of sample collecting, a rough estimation may be attempted and it puts the ratio at 1 : 2.)

Benzene. The always forming benzene did not contain deuterium at 423 K; however, more forcing conditions resulted in the formation of d_1-benzene in significant amounts.

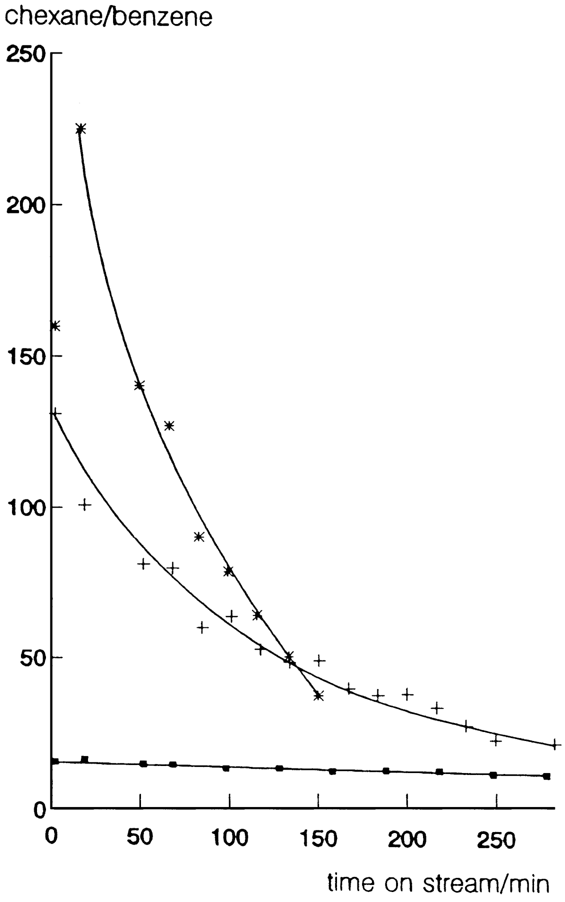


FIG. 1. Cyclohexane to benzene ratio (chexane/benzene) vs time on stream relations in flow reactor at 323 K (+), 373 K (∗), and 473 K (■) (50 mg catalyst, partial pressure of cyclohexene: 3.2 kPa, D_2 flow: 15 cm^3/min).

TABLE 4

Steady-State Cyclohexane and Benzene Yields at Various Temperatures in the Reactions of Cyclohexene over Cu/SiO$_2$ in Flow System

	Steady-state yield (mol%)					
Temperature (K):	323	373	423	473	523	573
Cyclohexane	—	—	—	—	40.74 ± 0.86	11.07 ± 0.43
Benzene	0.029 ± 0.002	0.071 ± 0.003	0.077 ± 0.012	3.98 ± 0.41	44.39 ± 0.70	86.64 ± 1.13

Note. 50 mg catalyst; partial pressure of cyclohexene, 3.2 kPa; D$_2$ flow, 15 cm^3/min.

Since about half the amount of benzene did not undergo deuterium exchange even at 523 K over the initial surface and about one third also remained deuterium free over the steady-state surface, it is safe to say that exchange in benzene was due to secondary surface transformations. It is important to mention that over the steady-state surface among the exchanged molecules d$_1$-d$_6$-benzene were found in decreasing amounts.

Cyclohexane. Deuterated cyclohexane was formed in a manner similar to how it was formed in the circulation reactor. d$_2$-Cyclohexane was predominant and d$_3$-cyclohexane was appreciable. Molecules with varying deuterium content (d$_4$-d$_9$-cyclohexane molecules at 423 K and d$_4$-d$_{12}$-cyclohexane in decreasing amounts over the steady-state surface) were also found. It is important to mention that d$_1$-cyclohexane formation was always very small.

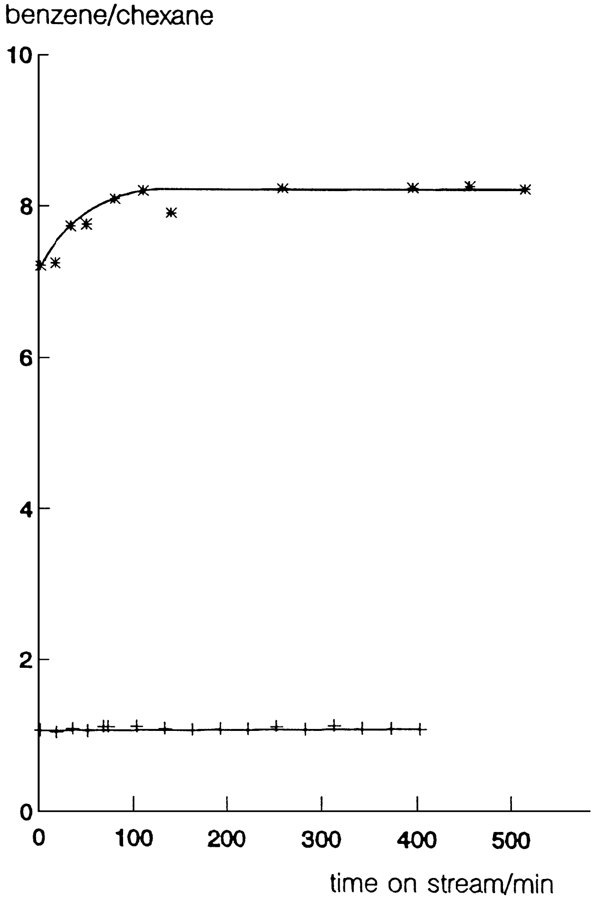


FIG. 2. Benzene to cyclohexane ratio (benzene/chexane) vs time on stream relations in flow reactor at 523 K (+) and 573 K (∗) (50 mg catalyst, partial pressure of cyclohexene: 3.2 kPa, D$_2$ flow: 15 cm^3/min).

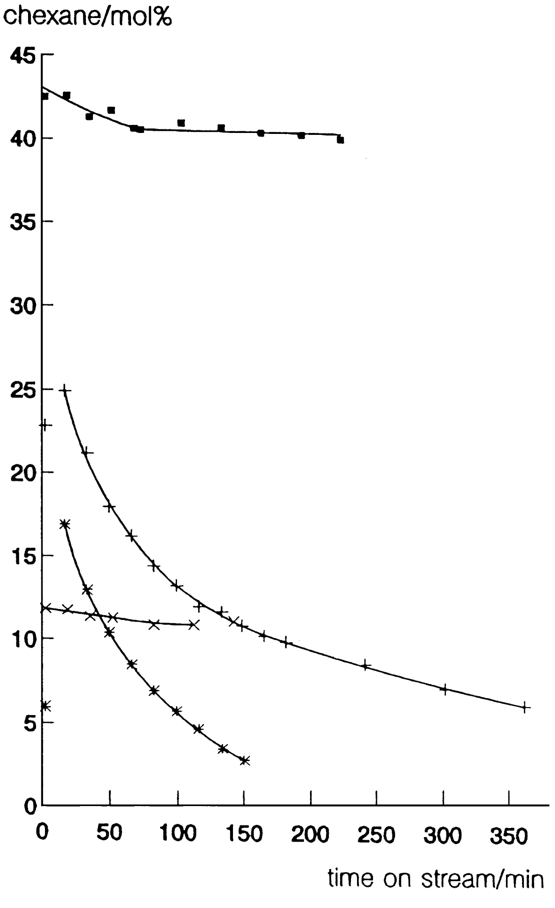


FIG. 3. Cyclohexane (chexane) yield vs time on stream functions in flow reactor at 373 K (∗), 423 K (+), 523 K (■), and 573 K (×) (50 mg catalyst, partial pressure of cyclohexene: 3.2 kPa, D$_2$ flow: 15 cm^3/min).

TABLE 5

Deuterium Distribution in Cyclohexene, Cyclohexane, and Benzene during the Reactions of Cyclohexene over Cu/SiO_2 under D_2 Flow at 423 K in a Flow Reactor

Compound[a]	Time (min)	Deuterium distribution (%)						
		d_1	d_2	d_3	d_4	d_5	d_6	d_7
Cyclohexene[b]	5	58.4	25.6	10.3	4.2	1.4	0.1	—
	15	59.0	24.2	10.4	4.3	1.5	0.1	—
	35	67.1	22.9	6.9	2.4	0.7	—	—
	45	76.7	17.7	4.2	1.1	0.3	—	—
Cyclohexane	5	2.8	46.3	29.6	13.1	5.3	2.2	0.7
	15	2.9	46.6	28.9	12.6	5.9	2.5	0.6
	35	3.2	56.2	28.4	9.1	2.9	0.2	—
	45	3.4	62.8	26.2	7.3	0.4	0.0	—

Note. 50 mg catalyst; partial pressure of cyclohexene, 3.2 kPa; D_2 flow, 15 cm^3/min.

[a] Benzene was not exchanged.

[b] Percentage of unexchanged cyclohexene at 5 min, 52.0; 15 min, 50.5; 30 min, 60.2; 45 min, 69.7.

DISCUSSION

In order to give a proper background before we attempt to rationalize the above observations, first, the main features of transition metal-catalyzed cyclohexene reactions are reviewed briefly.

Basically three types of transformation pathways are observed. Over Pt(223) single crystal dehydrogenation is overwhelming under UHV conditions and it is sensitive to the structure of the carbonaceous overlayer (2, 3). Disproportionation occurs over Pt, Pd, and Ni in He stream (4). This reaction is inhibited by hydrogen (3, 6). It is not observed over silica- or alumina-supported Pt (7, 8), Pd (10), Rh (11), Ir/MgO (19), and Pt black (9), but proceeds over Ni/SiO_2 in the gas and in the liquid phase leading to deactivation of the catalyst (6, 12). The reaction is structure sensitive, occurring readily over large metal particles (6). Under catalytic conditions (from, e.g., 10 kPa H_2 pressure in the gas phase and at 101.3 kPa hydrogen pressure in the liquid phase) over the Pt (223) single crystal (2, 3), Pt black (9), supported Pt (7, 8), Pd (10), Rh (11), and Ir (19) only hydrogenation proceeds. The reaction over these metals (7–11) and also over Ni/SiO_2 (12) is found to be completely structure insensitive or just mildly structure sensitive (16, 17). Partial reaction orders are zero for cyclohexene and between 0.5 and 1 for H_2 (depending on temperature, H_2 pressure, and whether the reactions are run in the gas or the liquid phase) (7–12, 16, 17). Activation energies over the supported catalysts are as follows: 28.8 kJ/mol (Pt (8)), 38.9 kJ/mol (Pd (10)), 20.9 kJ/mol (Rh (11)), and 22.8 kJ/mol (Ni (12)).

This survey shows that the behavior of Ni/SiO_2 catalyst resembles that of our Cu/SiO_2 best. We also found simultaneous benzene and cyclohexane formation at low hydrogen (deuterium) pressure and benzene formation was suppressed by its rising. Carbonaceous residues resulting most probably from benzene poisoned direct cyclohexene hydrogenation in the flow system. However, substantial differences do exist; e.g., conditions for dehydrogenation and dehydrogenation plus hydrogenation could be set and they could be studied separately. Flow conditions allowed the partial regeneration of the catalysts; therefore, benzene and

TABLE 6

Deuterium Distribution in Cyclohexene, Cyclohexane, and Benzene during the Reactions of Cyclohexene over Cu/SiO_2 under D_2 Flow at 523 K in a Flow Reactor

Compound	Time (min)	Deuterium distribution (%)											
		d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}
Cyclohexene[a]	5	50.2	25.5	9.4	6.4	4.1	2.5	2.0	—	—	—	nr	nr
	15	46.2	24.2	10.9	7.0	4.5	3.5	2.2	1.5	—	—	nr	nr
	35	43.5	23.0	12.4	8.0	5.4	3.6	2.2	1.4	0.5	—	nr	nr
	190[b]	32.2	19.4	13.2	10.2	9.0	6.1	4.9	2.9	1.6	0.5	nr	nr
Cyclohexene	5	1.1	53.1	26.5	10.4	4.1	2.7	2.1	—	—	—	—	—
	15	1.2	49.3	26.5	10.9	5.1	3.1	2.4	1.5	—	—	—	—
	35	1.1	45.5	26.4	11.3	6.0	4.1	3.2	2.3	0.1	—	—	—
	190[b]	0.8	34.0	24.8	13.6	7.8	5.9	5.0	4.0	2.8	0.5	0.5	0.3
Benzene[c]	5	53.1	32.6	14.2	0.1	—	—	nr	nr	nr	nr	nr	nr
	15	46.7	30.8	18.2	4.3	—	—	nr	nr	nr	nr	nr	nr
	35	42.3	28.8	17.3	9.8	2.6	—	nr	nr	nr	nr	nr	nr
	190[b]	35.1	25.3	18.2	12.1	6.0	3.3	nr	nr	nr	nr	nr	nr

Note. nr, not relevant. 50 mg catalyst; partial pressure of cyclohexene, 3.2 kPa; D_2 flow, 15 cm^3/min.

[a] Percentage of unexchanged cyclohexene at 5 min, 46.5; 15 min, 43.0; 35 min, 39.7; 190 min, 29.9.

[b] Steady-state surface.

[c] Percentage of unexchanged benzene at 5 min, 44.4; 15 min, 40.2; 35 min, 35.2; 190 min, 26.1.

cyclohexane formation could be followed in a wide temperature range.

Transformations in the Circulation and the Flow System

Experimental results show some common features in the two types of reactors: (i) there is no reaction without hydrogen (or deuterium), (ii) the products are benzene and cyclohexane, and (iii) fragmentation does not occur. Otherwise, details are different, but results are complementary.

Recirculation of products in the static system afforded conditions where three distinct reaction regions can be distinguished and studied:

(a) under hydrogen (deuterium) poor conditions only dehydrogenation occurs,
(b) somewhat higher hydrogen (deuterium) coverage creates conditions for concomitant benzene and cyclohexane formation, and
(c) under hydrogen (deuterium)-rich conditions only hydrogenation prevails; the other reaction is suppressed.

Continuous hydrogen flow in the flow reactor results in partial regeneration of the catalysts; thus both products (benzene and cyclohexane) are always formed. Here, temperature is expected to be the crucial factor, and indeed activity and selectivity are substantially influenced by its variation. High temperature promotes the formation of carbonaceous residues, which do contribute to the formation of a steady-state surface appropriate for a lasting and high activity of benzene and cyclohexane production. Although a steady-state (low) activity for benzene formation is attained at low temperature, the surface must be different; it should contain benzene-like hydrocarbon residues, which effectively retard cyclohexane formation. Between 473 and 523 K a dramatic change in product distribution is found (the initial cyclohexane/benzene ratio is decreased from around 17 to about 0.9), reflecting a major change in transformation mechanism.

Transformation Mechanisms

Deuterium distribution with direct information on the location of exchanged deuterium in cyclohexene (423 K, flow system) allows some insight into the chemistry of surface events. Furthermore, papers on related systems. (cyclohexene–D_2–Pt or Pd (31), cycloalkenes–D_2–Pd (32), cyclopentene–D_2–Pt, Pd, Ir, Rh, Ni, or Ru (33)) provide considerable help in rationalizing transformation mechanisms.

Generally, the presence of d_1-cyclohexene throughout the induction period at every D_2 pressure and in the flow system indicates the abundance of adsorbed half-hydrogenated and π-allylic cyclohexyl species over the surface. H–D exchange during the induction period in the static system means that it is a more facile process than either dehydrogenation or hydrogenation (Scheme 1a).

Monodeuterated cyclohexene was also found over the Cu(100) surface under UHV conditions (27). The authors proved that deuterium added to the top face of the double bond (cyclohexene lies flat on the surface) and a hydrogen atom was eliminated from the bottom (β elimination) with 100% selectivity from the bottom, giving d_1-cyclohexene as a desorption product. This formation mechanism has been borrowed, because it may fit our results as well.

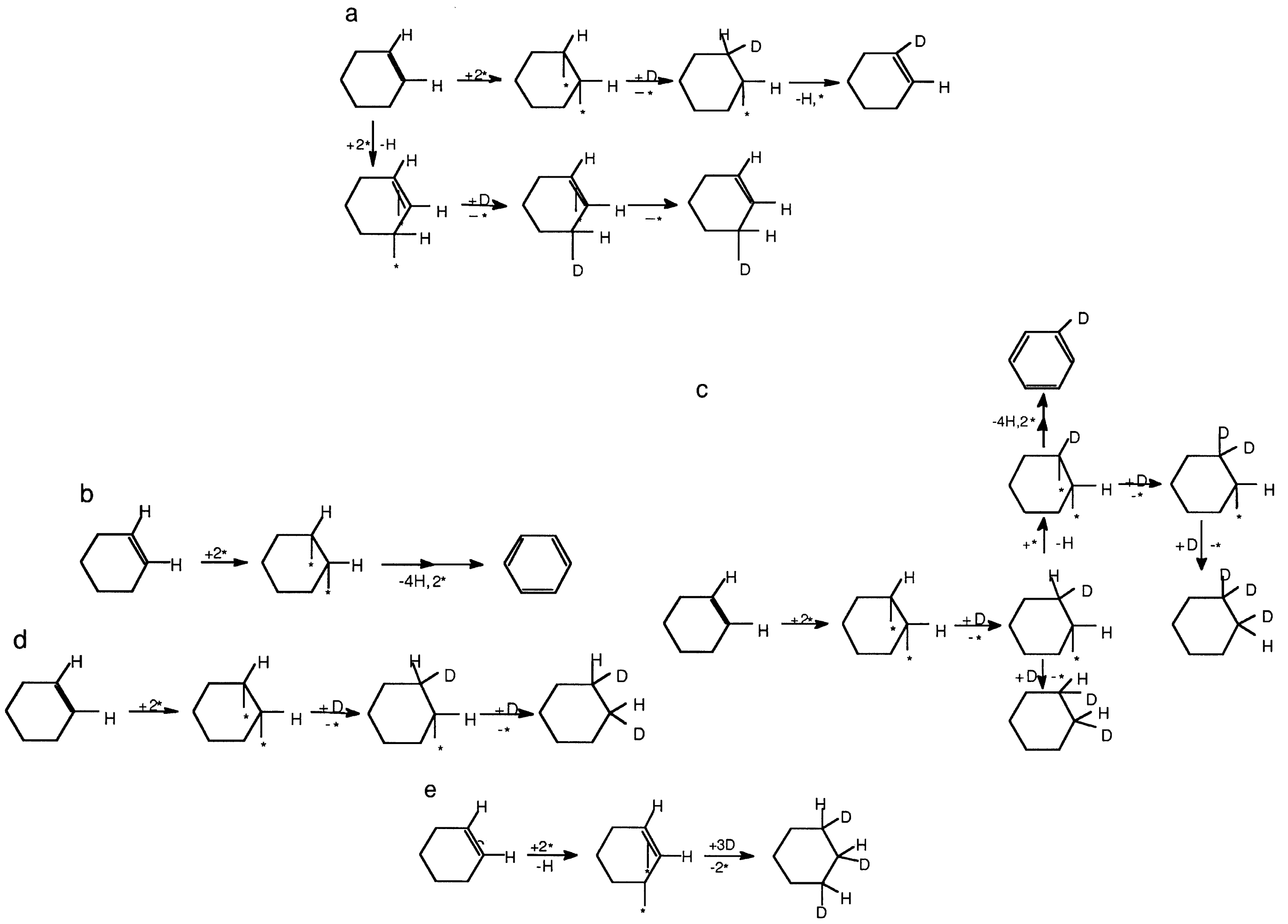
In the dehydrogenation region in the static reactor and at 423 K in the flow reactor, the lack of exchanged benzene reveals that diadsorbed light cyclohexene is the only source of its initial formation. This means that benzene-like species are formed quickly over the surface. However, their desorption is slow and added deuterium does not participate in dehydrogenation as reactant except helping desorption to some extent (Scheme 1b).

Under forcing conditions (523 K, flow system) this remains the predominant transformation pathway since initially more than 40% of benzene is not exchanged. However, even over the initial surface the quantity of d_1-benzene is significant, exhibiting that benzene can also form through the allyl-adsorbed cyclohexene precursor state. Over the steady-state surface d_1-d_6-benzene molecules also indicate multiple exchange due to dynamic exchange of benzene precursors forming part of the working surface (i.e., the working surface is decorated by carbonaceous benzene-like residues). They have a longer residence time over the surface and thus are able to undergo multiple and even full H–D exchange.

In the region where benzene and cyclohexane are detected in the static system, d_0-benzene formation can be accounted by the route in Scheme 1b. The predominantly formed d_1-benzene and d_2-cyclohexane are originated from the monoexchanged adsorbed cyclohexyl intermediate. Diadsorbed monoexchanged intermediate coming from the half-hydrogenated form can lead to d_1-benzene; it can also be responsible for d_3-cyclohexane (Scheme 1c).

At 20.0 kPa, d_2-cyclohexane is the product of a simple Horiuti–Polanyi mechanism (Scheme 1d); again, adsorbed d_1-cyclohexyl is the key intermediate. the high relative intensity for d_6-cyclohexane clearly shows that exchange occurs through flat-lying species.

When deuterium pressure is raised further, d_3-cyclohexane becomes abundant (it was not present at all at 20.0 kPa), as does d_2-cyclohexane. The latter may be interpreted with the Horiuti–Polanyi mechanism, but the other cannot be the result of the pathway depicted in Scheme 1c (readsorption forming the d_1-diadsorbed intermediate and then the addition of two deuterium atoms), because high D_2 pressure does not favor hydrogen loss, which would be a necessary prerequisite for readsorption. It is more plausible to assume a new route, which is the formation of a π-allyl intermediate and then the addition of three D atoms. (Scheme 1e).



SCHEME 1. (a) Formation pathway for d_1-cyclohexene at every D_2 pressure in the static system and in the flow reactor. (b) Formation pathway for d_0-benzene under dehydrogenation conditions in the static system and in the flow reactor at 423 K. (c) Formation pathways for d_1-benzene, d_2-cyclohexane, and d_3-cyclohexane *via* the half-hydrogenated state when both dehydrogenation and hydrogenation take place. (d) Hydrogenation, i.e., formation of d_2-cyclohexane *via* the Horiuti–Polanyi mechanism. (e) Formation of d_3-cyclohexane *via* π-allyl adsorption.

As far as cyclohexane formation is concerned in the flow system at 423 and 523 K, Scheme 1e adequately describes the situation. The Horiuti–Polanyi mechanism is predominant; however, hydrogenation *via* a π-allylic intermediate is also a significant transformation route.

The above reaction pathways operate together in proportions depending on reaction conditions and they give a reasonable picture about the chemistry of surface events. This scheme is about initial transformations, since multiple exchange (which, though slow, still occurs) complicates the picture considerably. Multiple exchange probably occurs through an α,β process, and rollover mechanism also operates under hydrogenation conditions.

The Nature of the Active Surface

Although a detailed analysis of the active surface will be given in a follow-up paper (34), a short summary of the most important findings may also be well placed here. We found that the metal surface was covered by carbonaceous residues, both hydrogen-rich and coke-like species. Obviously, coking deactivates the catalyst; nonetheless, its accumulation was slow. The hydrogen-rich residues were product- and reactant-like, relatively strongly held species. They do contribute significantly to the formation of the active surface; that is, they are part of the active sites. Their formation needs time, and under hydrogen-poor conditions this formation is slow and takes up the introduced reactant molecules. Consequently, an induction period was found in the static system. In restart reactions over the used catalysts this induction period disappeared. While the reaction proceeds, the metal surface is largely covered by carbonaceous residues and large enough metal ensembles are not available to hydrogenate, e.g., the cyclopropane molecule (known to require clean metal surface (35)) either in a competitive reaction or in using the catalyst sample, which have already seen cyclohexene–deuterium reaction mixture.

CONCLUSIONS

Conditions for cyclohexene transformations in D_2 are substantially different but complementary in the recirculation static system and the flow reactor. In the first one distinct regions of dehydrogenation, dehydrogenation plus hydrogenation, and hydrogenation can be studied. Concomitant benzene and cyclohexane formations are always observed in the flow reactor, due to the partial rejuvenation of the surface.

Reactions in D_2 revealed that adsorbed d_1-cyclohexyl species are the most abundant intermediates over the copper surface. They are the key species on the way to both benzene and cyclohexane formation. Hydrogenation through adsorbed π-allyl intermediate becomes competitive at high D_2 pressure and in the flow reactor (this also means D_2 abundant circumstances).

Since with time on stream the relative quantities of d_1-cyclohexene and d_2-cyclohexane, a synthetic method for the preparation of these deuterated species may be based on this system. Of course conditions should be optimized and effective separation techniques should be found.

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REFERENCES

1. Bartók, M., and Molnár, Á., "Stereochemistry of Heterogeneous Metal Catalysis," Chapter III, p. 53. Wiley, Chichester/Brisbane/New York/Toronto/Singapore, 1985.
2. Blakely, D. W., and Somorjai, G. A., *J. Catal.* **42**, 181 (1976).
3. Davis, S. M., and Somorjai, G. A., *J. Catal.* **65**, 78 (1980).
4. Rebhan, D. V., and Haensel, V., *J. Catal.* **111**, 397 (1988).
5. Cogen, J. M., Ezaz-Nikpay, K., Fleming, R. H., Baumann, S. M., and Maier, W. F., *Angew. Chem.* **99**, 1222 (1987).
6. McConica, C. M., and Boudart, M., *J. Catal.* **117**, 33 (1989).
7. Segal, E., Madon, R. J., and Boudart, M., *J. Catal.* **52**, 45 (1978).
8. Madon, R. J., O'Connell, J. P., and Boudart, M., *J. AIChE* **24**, 904 (1978).
9. O'Rear, O. J., Löffler, D. G., and Boudart, M., *J. Catal.* **94**, 225 (1985).
10. Gonzo, E. E., and Boudart, M., *J. Catal.* **52**, 462 (1978).
11. Boudart, M., and Sajkowski, D. J., *Faraday Discuss.* **92**, 57 (1991).
12. Boudart, M., and Cheng, W.-C., *J. Catal.* **106**, 134 (1987).
13. Chen, Y.-W., and Li, C., *Catal. Lett.* **13**, 359 (1992).
14. Anderson, J. R., and Kemball, C., *Proc. Roy. Soc. (London)* **226**, 472 (1954).
15. Jannes, G., Kerckx, P., Lenoble, B., Vanderwegen, P., Verlinden, C., and Puttemans, J. P., *in* "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L Guczi, F. Solymosi, and P. Tetenyi, Eds.), Akadémiai Kiadó, Budapest, 1993.
16. Pálinkó, I., *Stud. Surf. Sci. Catal.* **88**, 603 (1994).
17. Pálinkó, I., *Appl. Catal. A: Gen.* **126**, 39 (1995).
18. Notheisz, F., Mastalir, Á., and Bartók, M., *J. Catal.* **134**, 608 (1992); Mastalir, Á., Notheisz, F., Bartók, M., Király, Z., and Dékány, I., *J. Mol. Catal.* **99**, 115 (1995).
19. Xu, Z., and Gates, B. C., *J. Catal.* **154**, 335 (1995).
20. Matyjaszczyk, M. S., *Chem. Scripta* **23**, 224 (1984).
21. Adkins, H., and Connor, R., *J. Am. Chem. Soc.* **53**, 1091 (1931).
22. Stanfield, J. A., and Robbins, P. E., *2nd ICC, Paris*, 2579 (1961).
23. Gajardo, P. S., Lartiga, M. C., and Droquett, S. C., *J. Phys. Chem.* **82**, 2323 (1978); Schachter, M. C., Gajardo, P. S., and Droquett, S. C., *J. Phys. Chem.* **79**, 1698 (1975); Thagavi, M. B., Pajonk, G., and Teichner, S. J., *Bull. Soc. Chim. France*, 180 (1978); Thagavi, M. B., Pajonk, G., and Teichner, S. J., *J. Coll. Interface Chem.* **71**, 451 (1979).
24. Hirota, K., Yoshida, N., Teratani, S., and Kitayama, T., *J. Catal.* **13**, 306 (1969); Hirota, K., Yasuda, Y., Teratani, S., and Yoshida, N., *Z. Phys. Chem. N. F.* **71**, 195 (1970).
25. Bartók, M., Pálinkó, I., and Molnár, Á., *J. Chem. Soc. Chem. Commun.* 953 (1987).
26. Molnár, Á., Pálinkó, I., and Bartók, M., *J. Catal.* **114**, 478 (1988); Pálinkó, I., Molnár, Á., Kiss, J. T., and Bartók, M., *J. Catal.* **121**, 396 (1990).
27. Teplyakov, A. V., and Bent, B. E., *J. Chem. Soc., Faraday Trans.* **91**, 3645 (1995).
28. Kobayashi, H., Takezawa, N. C., Minochi, C., and Takahashi, K., *Chem. Lett.*, 1197 (1980).
29. Evans, J. W., Wainwright, M. S., Bridgewater, A. J., and Young, D. J., *Appl. Catal.* **7**, 75 (1983); Denise, B., Sneeden, R. P. A., Beguin, B., and Cherifi, O., *Appl. Catal.* **30**, 353 (1987).
30. Bartók, M., Notheisz, F., Zsigmond, Á. G., and Smith, G. V., *J. Catal.* **100**, 39 (1986).
31. Smith, G. V., and Swoap, J. R., *J. Org. Chem.* **31**, 3904 (1966).
32. Hilaire, L., and Gault, F. G., *J. Catal.* **20**, 267 (1971).
33. Brown, R., Dolan, A. S., Kemball, C., and McDougall, G. S., *J. Chem. Soc., Faraday Trans.* **89**, 1095 (1993); and references therein.
34. Fási, A., Pálinkó, I., and Bartók, M., submitted for publication.
35. Pálinkó, I., Notheisz, F., and Bartók, M., *Catal. Lett.* **1**, 127 (1988); Pálinkó, I., Notheisz, F., and Bartók, M., *Stud, Surf. Sci. Catal.* **48**, 729 (1989).