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Transformations of Cyclohexene Oxide over Silica-Supported Cu, Pd, and Rh Catalysts in H_2/D_2 Atmosphere

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Transformations of cyclohexene oxide were studied in a recirculation reactor and a flow system over silica-supported transition and early transition metal catalysts. Hydrogen pressure dependence of the transformations was measured over Cu/SiO_2 at 403 K in the 0–98.7 kPa range. Deuterium distribution in the reactant and products were determined at 20 kPa D_2 pressure. The reactions were studied in the flow reactor under D_2 stream over Cu/SiO_2 (373 K, 403 K, 443 K, 523 K), Pd/SiO_2 (403 K), and Rh/SiO_2 (403 K) catalysts too. Deuterium distributions were determined at the commonly used 403 K. Over each catalyst, in both reactor types three main transformation pathways were found. Single C-O scission occurred via isomerization and hydrogenation. Double C-O cleavage, that is, deoxygenation was also found to be important. Product distribution varied from catalyst to catalyst and it was influenced by the conditions, as well as the reactor types. Deuterium distribution revealed significant differences in the elementary surface processes over the catalysts. Detailed mechanistic interpretation of the transformations is offered. © 1999 Academic Press

Key Words: **cyclohexene oxide; Cu/SiO_2; Pd/SiO_2; Rh/SiO_2; hydrogenative ring opening; H-D exchange; mechanism of ring opening.**

INTRODUCTION

It is well known that due to the highly strained oxirane ring epoxides may undergo easy ring opening. The ring may be opened by all sorts of nucleophiles, making these compounds versatile intermediates in organic synthesis (1). The reaction can be performed stoichiometrically as well as catalytically. For the latter method, beside applying a nucleophile with Lewis acid as activator (nucleophilic catalysis) or solid acids (electrophilic catalysis) (2), the ring may be opened using metals or supported metals in the presence of hydrogen (3). When hydrogen is replaced by deuterium, monitoring deuterium distribution in the reactant and the product(s) allows deeper insight into surface events composing the reactions. Although similar approach was tried with various epoxides (4–11), to the best of our knowledge, the cyclohexene oxide-H_2 (or D_2) system has never been the subject of detailed studies as far as the identification of transformation types and the mechanism of reactions are concerned. Closest to it were the deuterogenation of (i) 1-methyl-1,2-epoxycyclobutane over Ni (4) and Pd (5), (ii) 1-methyl-1,2-epoxycyclopentane over Pt, Pd, and Ni (7), and (iii) the conformationally rigid *cis*- and *trans*-*tert*-butylcyclohexene epoxide and their 1-methyl or 4,5-dimethyl substituted derivatives over Pd/C in the liquid phase (8). For these molecules deuterium distribution provided some information about the mode of adsorption; however, mechanistic details were only discussed for 1-methyl-1,2-epoxycyclobutane where the cyclobutane ring showed peculiar behaviour (4, 5). The stereochemistry of deuterium addition could be studied with the conformationally rigid cyclohexene epoxides and was found to be predominantly *anti*. It was considered as the proof of the rollover of the O-(mono)adsorbed species on the catalyst before the addition of the second hydrogen (or deuterium). Otherwise the reactions in various reactors were not compared and the mechanisms of other reactions than single C-O scission were not investigated. Albeit having only one metal, the Pd, common in this work and the ones previously cited, considerations discussed there may be useful here, except that direct evidences on the stereochemistry of hydrogen (deuterium) addition cannot be obtained with our model.

In this contribution we give experimental data on the single as well as the double C-O scission reactions of cyclohexene oxide with or without added hydrogen or deuterium over silica-supported Cu, Pd, and Rh catalysts. Since a reaction temperature applicable in the (closed) static recirculation reactor and the flow system for every catalyst was found, we are able to compare phenomenological features, such as the activities and selectivities of the catalysts. Moreover, deuterium distribution data obtained at this temperature allows even deeper comparisons to be made; surface events can be and are analysed in detail.

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EXPERIMENTAL

Reactants and Catalysts

Cyclohexene oxide was a Fluka product with the purity of 99.9+% by the GC-MS method.

Hydrogen was produced by a Matheson 8326 hydrogen generator equipped with a Pd membrane. Deuterium was obtained through the electrolysis of D_2O (purity was 99.8%) in a general Electric 15EHG generator. The gas was deoxygenated with a MODEL 1000 Oxygen Trap (CRS, USA) before use.

The Cu/SiO_2 catalyst was prepared by the ion-exchange method. Support was Strem large pore (120-230 mesh) silica gel. It was immersed in a tetramminecopper(II) solution at pH 11. After 24 h the blue product was washed thoroughly with double distilled water and dried at 393 K (24 h). After calcination (773 K, 3 h in air) the catalyst was reduced in a hydrogen stream (673 K, 2 h) and kept in a vacuum desiccator until use. Metal loading was 6.36%. The percentage of surface copper atoms was 14.6 by N_2O titration at 363 K. After reduction 7% of the copper atoms remained ionic, possibly as Cu^+ ions (12).

The Rh/SiO_2 catalyst was prepared by impregnating BDH Cab-O-Sil support with an acidic aqueous $RhCl_3$ solution. The catalyst was dried at 403 K for 16 h, washed until neutral with double distilled water, and reduced under hydrogen flow at 483 K for 3 h and then at 673 K for 4 h. Finally, it was cooled to room temperature under nitrogen flow and was stored in air in a vacuum desiccator. Rhodium loading was 3.2%. Percentage of exposed rhodium atoms was 27.0 by static hydrogen chemisorption at room temperature.

The Pd/SiO_2 catalyst was prepared similarly, but an aqueous $PdCl_2$ solution was applied. Reduction and storing conditions were the same as well. Palladium loading was 3.0%. The percentage of exposed atoms was 10.0 by static hydrogen chemisorption at 340 K.

Apparatus, Methodology, and Analysis

Static Recirculation Reactor

Reactions were carried out in a conventional closed circulation reactor. 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 25-m-long Carbowax 20M capillary column (film thickness: 0.2 mm) was used for separating the reactants and the products. The column was operated in the isothermal mode (oven temperature 323 K) with helium as the carrier gas (flow rate 1.3 cm^3/min).

The reactants (0.8 kPa of cyclohexene oxide and various amounts of H_2 or D_2) were premixed in the circulation part of the system before the reaction. Cyclohexene oxide was subjected to several freeze–evacuate–thaw cycles before preparing the reaction mixture. The reaction temperature in the hydrogen pressure-dependence measurements was 403 K. The hydrogen pressure range was 0–98.7 kPa. Temperature dependence was studied at 20 kPa hydrogen pressure in the 373 K–523 K temperature interval. Initial rates were determined from the product yield versus time (t) functions obtained at certain hydrogen pressures. These rates were converted to turnover frequency data (TOF: molecule exp.atom^{-1}s^{-1}) on the basis of exposed metal atoms. Measurements were reproducible within 10%. They were always performed over a fresh sample of catalyst (20 mg), which was activated in the reactor under 26.6 kPa hydrogen pressure at 573 K for 1 h. In the circulation reactor only Cu/SiO_2 was used.

Deuterogenation was studied at 403 K on mixture with 0.8 kPa of cyclohexene oxide and 20 kPa of D_2.

Flow Reactor

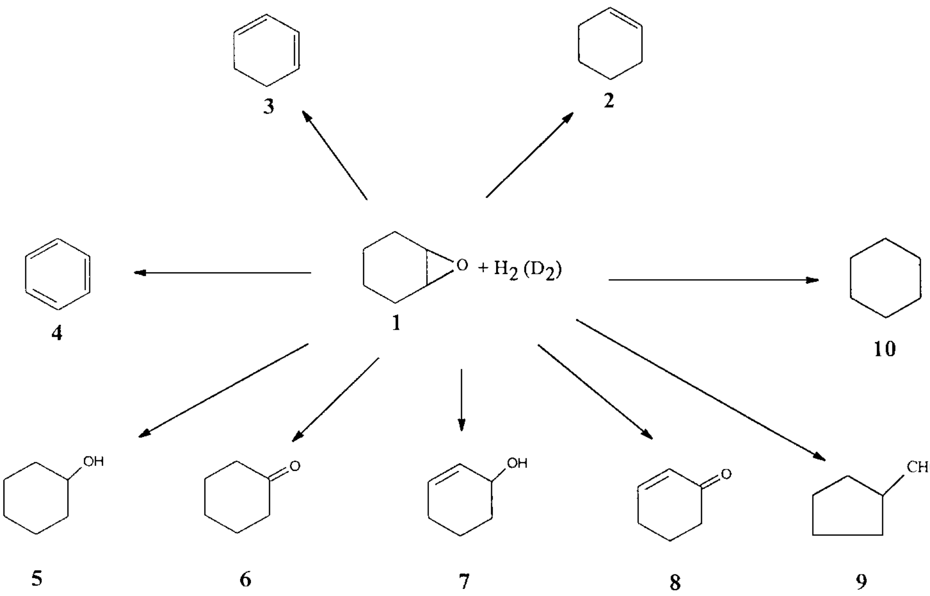
Reactions were carried out over 20 mg of Cu/SiO_2 or 10 mg of Pd/SiO_2 or 10 mg of Rh/SiO_2 sample under D_2 flow (15 cm^3/min). The partial pressure of cyclohexene oxide was 1.3 kPa. Four reaction temperatures (373 K, 403 K, 443 K, and 523 K) were used over the Cu/SiO_2. Measurements were performed at 403 K over the other two catalysts. A fresh sample of catalyst was used in each measurement. Activation conditions were as follows, Cu/SiO_2: 20 cm^3/min D_2 flow for 1 h at 573 K, Pd/SiO_2 and Rh/SiO_2: 20 cm^3/min D_2 flow for 1 h at 423 K. 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 in the previous paragraph, exactly like in measurements in the recirculation reactor.

Deuterium Distribution

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

Cyclohexene oxide reacts over the catalysts with and without added hydrogen. Two reaction types are observed: single and double C-O cleavage. The main products are carbonyl compounds, alcohols, and cyclic hydrocarbons, depending on the catalyst, reactor type as well as reaction conditions (Scheme 1).



SCHEME 1. Products from the metal-catalyzed transformations of cyclohexene oxide.

Transformations of Cyclohexene Oxide over Cu/SiO_2 in the Recirculation Reactor

Without added hydrogen the reaction started with a long induction period at 403 K. After 20 min cyclohexene (**2**) and 1,3-cyclohexadiene (**3**) emerged. The reaction is deoxygenation (double C-O scission), followed by further hydrogen losses. When there was added hydrogen the induction period disappeared. Deoxygenation and dehydrogenation remained major transformation routes but further reaction pathways also opened. The hydrogenative ring opening of the epoxide ring gave cyclohexanol (**5**) and its isomerization resulted in cyclohexanone (**6**) and 2-cyclohexane-1-ol (**7**). Due to the limited hydrogenation ability of copper, the main product was cyclohexene even with added hydrogen. Under these conditions the adsorbed olefin precursor was not hydrogenated but dehydrogenated over the surface and desorbed as 1,3-cyclohexadiene (**3**). On elevation of the temperature further dehydrogenation may occur over the surface of the catalyst, and in line with this benzene (**4**) formation could be detected. Temperature dependence measurements allowed the calculation of apparent activation energies for products appearing at each temperature. They are given in Table 1.

Turnover frequency data of initial product formation rates at 403 K are listed in Table 2.

At this temperature benzene was not found, even at the lowest hydrogen pressure applied, and above 33.3 kPa there was no 1,3-cyclohexadiene formation either. The oxirane ring opened via isomerization in the entire hydrogen pressure range, but it was suppressed at high hydrogen pressures. The formation of the allyl alcohol analogue 2-cyclohexene-1-ol ceased above 53.3 kPa hydrogen pressure. The hydrogenative ring opening route increased its share on increasing hydrogen pressure, just like deoxygenation. This latter process, resulting from double C-O scission, was a major transformation pathway from low hydrogen pressures and it became predominant over 53.3 kPa.

Despite replacing hydrogen by deuterium the reactant was free of deuterium, making it clear that the epoxide ring is destroyed on touching the catalyst surface; that is, there is no cyclohexene oxide desorption. There was no deuterium in the cyclohexene product either after the 5-min sampling. Later, deuterium appeared in cyclohexene as the result of secondary H-D exchange of the cyclic olefin.

The isomerization pathway of single C-O cleavage produced cyclohexanone-d_1 and cyclohexanone-d_2 in nearly 2 : 1 initial ratio. The products of the hydrogenative route were cyclohexanol-d_2 and cyclohexanol-d_3 in 3 : 1 initial

TABLE 1

Apparent Activation Energies for the Overall Transformation of Cyclohexene Oxide and the Formation of Major Products

Compounds	E_a/kJmol^{-1}
Reactant	
1	39.6
Products	
2	38.4
3	38.8
5	30.2
6	36.5

Note. 373 K–523 K temperature range, 0.8 kPa cyclohexene oxide, 20 kPa H_2.

TABLE 2

Initial Product Formation Rates (Turnover Frequencies/10^{-4} Molecule exp.atom^{-1}s^{-1}) in the Function of H_2 Pressure over Cu/SiO_2 Catalyst at 403 K in the Recirculation Reactor (0.8 kPa Cyclohexene Oxide, 20 mg Catalyst)

	H_2 pressure/kPa								
Products	1.3	6.7	13.3	20.0	33.3	46.7	53.3	69.3	98.7
2	6.0	10.9	15.5	19.5	24.0	25.7	26.5	28.7	30.3
3	1.2	1.5	1.7	1.2	0.5	0	0	0	0
5	0	0.5	3.2	4.3	6.1	7.5	7.9	9.0	10.1
6	9.3	16.5	20.9	25.6	26.8	24.0	20.6	18.0	15.5
7	0	0	2.8	3.2	3.3	3.2	2.8	0	0

ratio. In both cases these ratios approached 1 : 1 on increasing the residence time. Data are listed in Table 3.

Transformations of Cyclohexene Oxide over Cu/SiO_2 Catalyst in the Flow Reactor

Similarly to the recirculation reactor, cyclohexene oxide transformed in the flow system without added hydrogen (under He stream). The products at 403 K were cyclohexanol, cyclohexanone, and 2-cyclohexene-1-ol. Contrary to observations made in the recirculation reactor, neither cyclohexene nor 1,3-cyclohexadiene (product of deoxygenation and further dehydrogenation) were formed. The conversion was low, 1.2–1.5%, over the steady-state surface. Isomerization and the hydrogenative ways of single C-O scission were equally important transformation routes. When the temperature was raised to 523 K the conversion increased to 47%. Products of deoxygenation and further dehydrogenation appeared but the isomerization pathway of C-O bond scission was overwhelming ($r_{\mathrm{iso}}/r_{\mathrm{deox}} = 6.7$). It is to be noted that benzene was not formed, even at this temperature. No sign of the hydrogenative ring opening was found either.

Transformations of cyclohexene oxide were studied under deuterium flow as well, at various temperatures. Data corresponding to 403 K (to allow comparison with product distribution in the recirculation reactor) and 523 K (the highest temperature applied) are shown as examples in Table 4. However, observations made at the other two temperatures (373 K and 443 K) are also described in the following.

The catalyst stabilized after about half an hour, that is, steady-state activity was attained at 373 K and 403 K. The steady-state conversion levels were in the range of 5–7% and 42–49%, respectively. At 443 K, although nearly full conversion was achieved initially, the catalysts gradually deactivated. At still higher temperature (523 K) a similar phenomenon was observed. Products differed, depending on temperature. At 373 K cyclohexene, cyclohexanol, cyclohexanone, and 2-cyclohexene-1-ol were found. At 403 K another product, 2-cyclohexene-1-one (**8**), could be detected in small, but not negligible quantities. Although initially, cyclohexene was the most significant product, its formation rate decreased over the steady-state catalyst at both temperatures. The significance of 2-cyclohexene-1-ol changed in the opposite way. It was either not observed over the initial catalyst (373 K) or its quantity was low (403 K). Later on, its formation rate increased and surpassed that of the cyclohexene. The initial cyclohexanol formation was significantly faster than that of cyclohexanone both at 373 K and 403 K. However, once again, the tendency of formation rate change of these two molecules was the opposite over the steady-state catalyst. At the 120-min sampling they were about the same at 373 K, while at 403 K cyclohexanone was formed faster than cyclohexanol.

At higher temperatures the tendency of changes in the formation rates of cyclohexene, cyclohexanone, cyclohexanol was the same. However, products not seen at lower temperatures appeared from 443 K: they are 1,3-cyclohexadiene and cyclopentane carbaldehyde (**9**). Cyclopentane carbaldehyde was formed with a low rate at 443 K but it became an important product at 523 K (210-min sampling). Further dehydrogenation of the adsorbed cyclohexene precursor and desorption as 1,3-cyclohexadiene started at 443 K and went to benzene at 523 K.

Deuterium distribution in the reactant and the products was determined in the reaction at 403 K (Table 5).

There was no deuterium in cyclohexene oxide and it was negligible in cyclohexene. Cyclohexanone-d_1 was overwhelming over the initial catalyst and there was not any

TABLE 3

Deuterium Distribution in the Ring-Opening Products of Cyclohexene Oxide over Cu/SiO_2 Catalyst at 403 K in the Recirculation Reactor

		Deuterium distribution/%											
		Cyclohexene (**2**)			Cyclohexanol (**5**)				Cyclohexanone (**6**)				
t/min	Conv/%	d_0	d_1	d_2	d_2	d_3	d_4	d_5	d_0	d_1	d_2	d_3	d_4
5	8.3	100	0	0	66.2	22.1	11.7	0	11.2	56.5	31.0	1.3	0
20	42.0	98.0	2.0	0	46.4	33.3	20.3	0	3.4	43.3	40.6	12.7	0
35	66.0	93.2	5.1	1.7	31.9	40.3	24.9	2.9	1.7	31.6	41.1	22.4	3.2

Note. 20 mg catalyst, 0.8 kPa cyclohexene oxide, 20.0 kPa D_2.

TABLE 4

Product Distribution in the Flow Reactor over Cu/SiO_2 at 443 K and 523 K

	Product distribution/mol%						
Products	5 min	20 min	35 min	50 min	65 min	120 min	210 min
403 K							
2	32.2	20.0	10.3	9.6	9.5	8.2	5.8
5	21.1	35.6	37.0	29.3	26.5	10.6	8.2
6	0.5	0.6	0.8	1.5	2.7	16.8	18.9
7	0.3	0.6	1.0	1.7	2.6	8.0	11.1
8	0.3	0.6	0.7	0.5	0.5	0.4	1.3
Conv./%	54.4	57.4	49.8	42.6	41.8	44.4	45.3
523 K							
2	31.7	24.3	22.7	20.2	19.9	17.7	11.0
3	0	0	0	0	0	0	5.0
4	0.5	1.1	1.2	1.2	1.0	1.1	0
5	56.4	61.2	61.8	61.7	62.0	59.5	27.0
6	4.7	5.7	5.7	6.8	6.5	9.4	36.0
8	0	0	0	0	0	0	0.4
9	0	0	0	0	0	0.4	6.0
Conv./%	93.3	92.3	91.4	89.9	89.4	88.1	85.4

Note. 20 mg catalyst, 1.3 kPa cyclohexene oxide, 15 cm^3/min D_2 flow.

cyclohexanone molecule without deuterium. The steady-state catalyst exhibited peculiar behaviour. Increasing amounts of cyclohexane-d_0 were detected. The proportion of cyclohexane-d_1 dropped to close to half of the value on the initial catalyst, but hardly changed any further. The percentage of cyclohexanone-d_2 increased to about 40% from the initial 11.5%, but dropped again as results of later samplings attest. There was no cyclohexanol-d_1 over the initial surface, while cyclohexanol-d_2, d_3, and d_4 were detected in similar amounts. Over the steady-state surface, however, cyclohexanol-d_1 was found in increasing proportions, just as cyclohexanol-d_2, while the percentage of cyclohexanol-d_3 and d_4 decreased on further samplings. Note, that cyclohexanol-d_5, d_6, and d_7 became less significant in this order.

Transformations of Cyclohexene Oxide over Rh/SiO_2 and Pd/SiO_2 Catalysts in the Flow Reactor

The reactions and the parallel analysis of deuterium distribution in the reactants and the products were performed at 403 K allowing certain comparisons to be made with observations over Cu/SiO_2 under the same conditions.

As it was expected cyclohexene oxide reacted significantly faster over Pd/SiO_2 and Rh/SiO_2 than over Cu/SiO_2 (Table 6).

Conversions were close to 100% or even reached this value over both transition metals. Three products were only detected. They were cyclohexane (**10**), cyclohexanone, and cyclohexanol. Cyclohexane could be derived from deoxygenation (double C-O scission), cyclohexanone was the product of the isomerization route and cyclohexanol was that of the hydrogenative pathway of single C-O cleavage. The hydrogenative route was found to be the overwhelming transformation pathway on both metals. The isomerization route was more significant over Pd/SiO_2, while deoxygenation was the more important transformation pathway over Rh/SiO_2. Deoxygenation was faster than isomerization over the initial Pd/SiO_2. However, after the initial stage the rate of cyclohexane formation decreased, finally, it was even ceased.

Data concerning deuterium distribution in the reactant and the product molecules are summarised in Table 7.

Deuterium in cyclohexene oxide was not found over any of the catalyst, however, it could be observed in cyclohexane in every possible position (cyclohexene-d_1 is not one of them) with about the same abundance. Cyclohexanone-d_1 is more abundant than cyclohexanone-d_2 over the initial catalysts and remains so over Rh/SiO_2, albeit its relative abundance decreases on continuous reactant flow. Cyclohexanone-d_3 is unimportant over Rh/SiO_2, while cyclohexanone-d_y ($y = 1$–7) appears over Pd/SiO_2 catalyst with approximately equal probability at the 65-min sampling. The relative importance of cyclohexanone-d_4 was found to be the highest among these species. Although

TABLE 5

Deuterium Distribution in the Ring-Opening Products of Cyclohexene Oxide over Cu/SiO_2 Catalyst at 403 K in the Flow Reactor

	Deuterium distribution/%													
	Cyclohexene (**2**)			Cyclohexanol (**5**)							Cyclohexanone (**6**)			
t/min	d_0	d_1	d_2	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_0	d_1	d_2	d_3
5	96.5	3.2	0.3	0	25.3	33.3	25.4	11.6	4.3	0.1	0	88.5	11.5	0
20	96.9	3.0	0.1	0	26.8	34.9	25.1	9.8	3.2	0.2	0	100	0	0
35	98.0	2.0	0	0	27.5	33.8	25.7	9.7	3.1	0.2	10.6	49.3	40.1	0
50	98.8	1.2	0	0	32.2	32.4	23.8	8.9	2.6	0.1	9.7	47.7	36.4	6.2
65	98.2	1.8	0	0.4	32.9	32.7	22.9	8.3	2.7	0.1	15.3	42.6	33.4	8.7
120	99.2	0.8	0	6.6	51.6	25.5	12.5	3.8	0	0	35.9	45.8	16.3	2.0
210	99.7	0.3	0	15.2	62.4	16.4	5.3	0.7	0	0	47.9	43.0	8.9	0.2

Note. 20 mg catalyst, 1.3 kPa cyclohexene oxide, 15 cm^3/min D_2 flow.

TABLE 6

Product Distribution in the Flow Reactor over Pd/SiO_2 and Rh/SiO_2 at 403 K

	Product distribution/mol%				
Products	5 min	20 min	35 min	50 min	65 min
Pd/SiO_2					
10	3.4	1.0	0.5	0.3	0.1
5	88.6	96.1	97.3	97.7	98.0
6	2.7	2.2	2.2	2.0	1.9
Conv./%	94.7	99.3	100	100	100
Rh/SiO_2					
10	26.4	19.3	14.4	10.7	10.3
5	71.6	77.5	83.5	88.7	89.1
6	0.6	0.5	0.7	0.4	0.5
Conv./%	98.6	97.3	98.6	99.8	99.9

Note. 10 mg catalyst, 1.3 kPa cyclohexene oxide, 15 cm^3/min D_2 flow.

multiply exchanged cyclohexanol molecules were observed over both catalysts, cyclohexanol-d_2 is absolutely overwhelming over Pd/SiO_2. Its abundance is the highest over Rh/SiO_2, nevertheless, significant amount of cyclohexanol-d_3 was also formed over this metal.

DISCUSSION

Cyclohexene oxide reacts over silica-supported Cu, Pd as well as Rh catalysts under relatively mild conditions. Overall, the picture is similar over each catalyst. In the presence of H_2/D_2 three main reaction types take place. Each reaction leads to the disappearance of the oxirane ring. This occurs either via deoxygenation or the cleavage of one C-O bond either through isomerization or hydrogenation. Details are different, however.

As it may be expected, significant differences arise on changing the catalysts. Perhaps, it is more surprising that change in the reactor type also influences reaction characteristics.

At the beginning, let us note that added hydrogen/deuterium is needed for the reactions to occur over Rh/SiO_2 and Pd/SiO_2. However, there are reactions over Cu/SiO_2 when there is no added hydrogen/deuterium. The reactions are slow and they are different in the static and the flow reactors. In the first one, an induction period indicates that surface transformation is needed for the exclusive reaction, the deoxygenation to occur. In the latter C-O bond scission via isomerization route and even hydrogenation took place. For this reaction hydrogen is possibly obtained from hydrogen-rich weakly adsorbed carbonaceous residues resembling the reactant. Deoxygenation products were not found in the flow reactor, nevertheless, 2-cyclohexene-1-ol may very well be the intermediate not desorbing in the static system on the way to cyclohexene.

Now, let us compare the main features of the three main reaction pathways in the presence of deuterium at the commonly used 403 K in the flow system. The activities of the catalysts largely differ. The transition metal catalysts are very much more active than Cu/SiO_2. Their hydrogenation ability also differs significantly. The deoxygenated product is an olefin over Cu/SiO_2, while it desorbs hydrogenated from Rh/SiO_2 and Pd/SiO_2. The deoxygenation pathway is significant over Cu/SiO_2 and Rh/SiO_2, but it is negligible over Pd/SiO_2. The hydrogenative C-O bond scission is the

TABLE 7

Deuterium Distribution in Cyclohexanol and Cyclohexanone Derived from the Hydrogenative Ring Opening of Cyclohexene Oxide[a] over Pd/SiO_2 and Rh/SiO_2 at 403 K in the Flow Reactor

	Deuterium distribution/%																
	Cyclohexanol (**5**)										Cyclohexanone (**6**)						
t/min	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_1	d_2	d_3	d_4	d_5	d_6	d_7
Pd/SiO_2																	
5	88.4	8.0	2.1	1.4	0.1	0	0	0	0	0	37.1	18.3	13.7	14.2	11.9	4.8	0
20	88.4	8.0	2.1	1.4	0.1	0	0	0	0	0	18.5	10.8	18.9	23.1	14.6	12.0	2.1
35	88.4	8.0	2.2	1.4	0.1	0	0	0	0	0	6.5	12.7	18.8	24.3	19.2	11.6	6.9
50	88.4	7.8	2.3	1.5	0.1	0.1	0	0	0	0	3.4	7.6	17.6	25.5	22.0	15.9	8.0
65	88.4	8.0	2.2	1.4	0.1	0.1	0	0	0	0	2.8	11.3	19.6	23.3	20.4	14.8	7.8
Rh/SiO_2																	
5	47.3	17.5	10.9	8.3	5.9	4.1	2.7	1.9	1.1	0.3	86.6	13.4	0	0	0	0	0
20	45.5	19.1	11.8	8.6	6.0	3.9	2.5	1.6	0.9	0.1	100	0	0	0	0	0	0
35	47.8	20.6	11.8	8.1	5.3	2.9	1.8	1.1	0.6	0	60.6	27.5	11.9	0	0	0	0
50	54.6	20.4	10.4	6.5	4.0	2.0	1.1	0.7	0.3	0	69.2	24.2	6.6	0	0	0	0
65	60.0	19.3	8.8	5.6	3.2	1.6	0.9	0.5	0.1	0	48.4	38.5	13.1	0	0	0	0

Note. 10 mg catalyst, 1.3 kPa cyclohexene oxide, 15 cm^3/min D_2 flow.

[a] For deuterium distribution in cyclohexane, see text.

major transformation pathway over Rh/SiO_2 and Pd/SiO_2 throughout the measurements and it is more important than the isomerization route in the initial stages of the run over Cu/SiO_2 as well. On this catalyst the relationship between the two ways of single C-O bond scission turns to the reverse later. Deoxygenation transforms the surface of the Cu/SiO_2 catalyst dramatically. Further deoxygenation and hydrogenative C-O scission are diminished gradually over the working surface and the isomerization ability of the catalyst increases dramatically. Deoxygenation promotes the formation of surface oxides; that is, ionic centres become abundant. Therefore, isomerization is favoured to hydrogenation over Cu/SiO_2. It is to be noted that the ionic surface becomes active in rearrangement reactions at high enough, but still moderate (443 K), temperatures. This reaction, leading to cyclopentane carbaldehyde, is a typical ionic ring contraction. The noble metals are much less prone to surface oxidation. Here hydrogenation remains overwhelming. Since the activity towards direct deoxygenation over Cu/SiO_2 decreases there is more chance for the formation of the intermediate on the deoxygenation pathway, consequently, 2-cyclohexene-1-ol and at higher temperature 2-cyclohexene-1-one formation rates gradually increase.

A comparison of the transformation properties over Cu/SiO_2 in the flow system and the static recirculation reactor reveals that increased residence time and moderate hydrogen availability facilitates further dehydrogenation during deoxygenation. In the static, recirculation system cyclohexadiene is also formed, while cyclohexene is the sole product not having oxygen in the flow reactor. Hydrogen availability is crucial in determining cyclohexanone formation rates relative to the hydrogenative way of single C-O scission. Cyclohexanone formation, that is, the isomerization route of ring opening, is faster in the recirculation reactor than the hydrogenative route of C-O cleavage. It is the reverse in the flow system until deoxygenation transforms the catalyst to an oxidic surface with abundant ionic centres. Then, isomerization becomes faster than hydrogenation.

Before analyzing H-D exchange results let us summarize those pieces of information from earlier works which concern the Pd-catalyzed deuterogenation of 1-methyl-1,2-epoxycyclobutane (5) and 1-methyl-1,2-epoxycyclopentane (7). Isomerization of both compounds occurred over Pd and the hydrogenative route of C-O scission was not detected. It is to be remarked that during this transformation the bridge C-C bond was cleaved first. The oxo compound from this molecule in the deuterium stream was mostly cyclopentanone-d_2. Nearly 60% of the oxo compound from 1-methyl-1,2-epoxycyclopentane was deuterium-free. The most abundant of those containing deuterium was 2-methylcyclopentanone-d_2 (11.2%).

As another preliminary, let us give a brief and necessarily simplified picture about the possible geometrical arrangements of our reactant, the cyclohexene oxide. For making considerations visual molecules are placed on a flat surface (first simplification). The geometry of the molecule is optimized as an isolated entity without added hydrogen/deuterium (second simplification), with the AM1 semiempirical method (13) (third simplification) in minimum conformation but without concentrating on finding the global minimum (fourth simplification). The possible arrangements are depicted in Fig. 1.

Adsorption form **A** represents edgewise attachment, **B** depicts flat adsorption, and **C** is adsorption on the tip of the epoxide ring. All those arrangements are discarded where the oxygen atom is not in close vicinity of the surface, since it is known that (irreversible) adsorption starts at the oxygen atom. In form **A** the hydrogen atom on the pillar carbon and another on the neighbouring carbon are in easy exchange positions. The two hydrogens on the next carbon are not too far from the surface, therefore, they might participate in H-D exchange. Adsorption form **B** may allow the exchange of hydrogens on the C-C bridge. Seemingly, form **C** should be discarded at once, since none of the C-O bonds are in contact with the surface. Nevertheless, we decided to keep this form because of a mechanism described by Teplyakov and Bent recently (14). It is a type of the Eley–Rideal mechanism, where the H_2/D_2 molecule is loosely attached to the surface at one end of the molecule and the hydrogen/deuterium on top attacks. Thus, a ring opening of this type might be a viable form of transformation route and can be an alternative explanation for the *anti* addition in

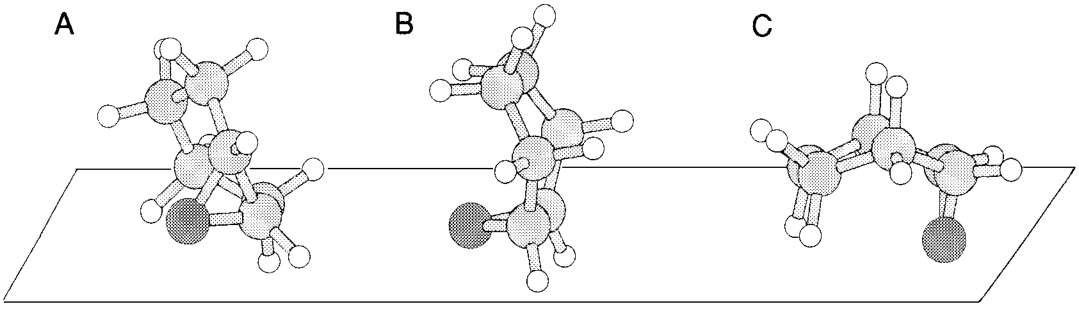


FIG. 1. Adsorption geometries of cyclohexene oxide over a flat surface: **A**, edgewise; **B**, flat; **C** on tip.

conformationally rigid cyclohexene epoxides to the rollover mechanism (8). The rollover of such bulky adsorbed molecules is difficult to envisage anyway. In form **C** two hydrogen atoms of the C-C bond in the cyclohexane ring opposite to the oxirane ring get close to the surface. Before going into detail let us nail down once again that the lack of exchanged cyclohexene oxide shows that the oxirane ring is destroyed on landing on the metal surface. Furthermore, let us distinguish two main adsorption types, depending on what bond(s) is (are) broken in the first step of surface transformations. The cleavage of the O-C bond leads the associatively adsorbed species (associative adsorption), while the concomitant scission of the O-C bond and one or more C-H bonds results in dissociatively adsorbed moieties (dissociative adsorption). Cyclohexanone can only form through dissociatively adsorbed species, whatever adsorption geometries are assumed. Form **A** would facilitate the cleavage of the O-C bond on the surface, providing the possibility for cyclohexanol formation only. (Cyclohexanone formation would need the dissociation of a hydrogen from the carbon atom far from the surface.) If there is associative adsorption, two deuterium atoms will be in the cyclohexanol. If it is dissociative, then the number will be three, but it also can be four (and it is more probable) as the neigbouring carbon has a hydrogen close to the surface, which may take part in the primary adsorption process. In a secondary exchange two more hydrogens may take place. When form **B** is assumed dissociative adsorption seems to be the most probable. Beside the O-C bond two hydrogens (on the C-C bridge) have the possibility of taking part in the primary process. Here, cyclohexanone would contain two and cyclohexanol four deuterium atoms. The products may form via π-allyl adsorbed species too. This means dissociative adsorption (thus, cyclohexanone may also form), which would lead to one new deuterium in cyclohexanone or three new deuterium atoms on alcohol formation. The other hydrogen on the C-C bridge then can take part in secondary H-D exchange. Perhaps, associative adsorption may take place for **B** as well. Then d_2 alcohol may form (and, of course, there is no cyclohexanone). Although form **C** was not discarded at once, but it is taken as not very possible since a rational explanation for O-C bond scission on adsorption is not found. If it happens, it is an associative adsorption giving two new deuterium atoms in cyclohexanol. However, on adsorption H-D exchange may occur parallel to the ring opening. Then two hydrogens on the C-C bond opposite to the bridge C-C bond may take part in the process. The overall result will then be four new deuterium atoms in the molecule. The above described possibilities are summarized in Table 8.

TABLE 8

Deuterium Distribution to Be Expected from Primary H-D Exchange of Adsorbed Species Based on the Model in Fig. 1

Geometry of adsorption	Mode of adsorption	Cyclohexanone	Cyclohexanol
A (edgewise)	Associative	—	d_2
	Dissociative	—	d_3 and/or d_4
	π-Allyl	—	—
B (flat)	Associative	—	Perhaps, d_2
	Dissociative	d_2	d_4
	π-Allyl	d_1	d_3
C (on tip)	Associative	—	d_4
	Dissociative	—	—
	π-Allyl	—	—

A comparison of the experimental findings and considerations summarized above and in Table 8 results in the following:

(1) Cyclohexanone is formed mainly via π-allyl adsorbed species over the initial Cu/SiO_2 catalyst in the recirculation system; i.e., the adsorption is dissociative. In the flow system this is the main adsorption type over the fresh Pd/SiO_2 and clearly overwhelming over the fresh Cu/SiO_2 and Rh/SiO_2 catalysts as well. When the catalysts are oxidized in the course of transformation, other adsorption type, dissociative through flat-lying species, becomes competitive in both reactor types over Cu/SiO_2 and over Rh/SiO_2 in the flow system. After the initial stages Pd/SiO_2 displays close to even distribution in the d_1-d_7 region. An explanation has not been found yet and it is clearly beyond the capabilities of our simplified model.

(2) Cyclohexanol-d_2 is predominant in the recirculation reactor over the initial Cu/SiO_2 and over Rh/SiO_2 in the flow system throughout the run. It is overwhelming over Pd/SiO_2 at each sampling. This molecule indicates the hydrogenative ring opening via edgewise associatively adsorbed species. Ring opening through either edgewise or flat-lying, but certainly dissociatively adsorbed species becomes competitive over the used/transformed Cu/SiO_2 surface.

(3) Cyclohexene coming from double C-O scission is practically not exchanged, indicating that the cyclohexane ring is not in contact with the surface. Over the hydrogenating catalyst cyclohexane with every possible deuterium position shows that H-D exchange is faster than hydrogenation followed by desorption.

The above described simplified model performed satisfactorily in rationalization of adsorption leading to single C-O scission. Characteristic adsorption types are depicted in Fig. 2.

CONCLUSIONS

It has been demonstrated through the metal-catalyzed transformations of cyclohexene oxide that if a common temperature can be found, analysis and comparison of product distribution and deuterium distribution in the products in different reactor types, over various metals can lead to a deeper understanding of surface transformations. It

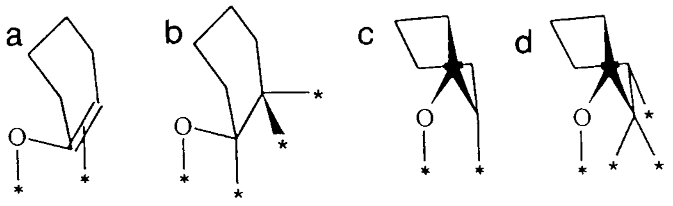


FIG. 2. Adsorbed intermediates on the way to cyclohexanone and/or cyclohexanol: (a) flat-lying, π-allyl; (b) flat-lying, dissociative; (c) edgewise, associative; and (d) edgewise, dissociative.

has also been shown that the possibilities are enhanced if models of realistic background can be used.

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