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Hydrogenative transformations of methylcyclobutane over silica-supported Rh, Ni, Pt and Pd catalysts at different temperatures

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The effect of temperature on the transformations of methylcyclobutane over silica-supported Rh, Ni, Pt and Pd catalysts was studied in a wide temperature range (323–723 K) in a pulse system. The transformations taking place were cracking (hydrogenolysis), hydrogenative ring opening and ring enlargement. The reaction directions were found to depend strongly on the nature of the metal. Over Pt and Pd, hydrogenative ring opening was the main reaction at all temperatures studied. In contrast, Rh and Ni promoted hydrogenolysis at high temperature, and this reaction occurred exclusively above 573 K. The selectivity data on the ring-opening reaction were different over Pt and Pd from those over Rh and Ni. The ring-opening selectivity (ratio of isopentane to both ring-opened products) was close to statistical over Pt and Pd, while sterically less hindered bond scission was the main direction of the ring opening over Rh and Ni.

Keywords: methylcyclobutane; supported Rh, Ni, Pt and Pd catalysts; temperature dependence; ring-opening selectivity; side reactions

1. Introduction

The transition metal-catalyzed transformations of alkyl-substituted cycloalkanes and especially those of cyclopentanes, are well-known areas of catalytic research [1–4]. In contrast, the transition metal-catalyzed transformations of cyclobutane derivatives do not belong to the frequently studied reactions. We previously [5,6] surveyed most results on the transformations of cyclobutane derivatives over metal catalysts. Here, only basic conclusions and some recently published results are summarized briefly, as follows:

All authors agree that the ring opens predominantly in the sterically less hindered direction for all substituted cyclobutanes studied, and the cyclobutane ring adsorbs reversibly at low and partly irreversibly at elevated temperatures [7–9]. The selectivity of the ring opening (given as the isopentane/pentane ratio in the reference cited) of methylcyclobutane over supported Pt model catalysts increases with increasing hydrogen content of the system, while the rate of the ring opening decreases under the same conditions [10]. The metals used in the mentioned studies were supported or bulk Pt and Pd. In contrast, in the hydrogenative ring-opening reaction of propylcyclobutane, the opposite regioselectivity was recently described, and the anchoring effect of the propyl side chain was suggested [5,6]. The role of surface carbonaceous deposits contributing to this unusual selectivity was also investigated [11].

In this preliminary study, we report the effect of temperature on the transformation of methylcyclobutane over four transition metal catalysts. The emphasis is placed on hydrogenative ring opening. Side-reactions occurring at high temperature will be discussed elsewhere.

2. Experimental

Methylcyclobutane was prepared by a recently published method [12]. It was gas chromatographically pure and was used without further purification.

Silica-supported transition metal (Rh, Ni, Pt and Pd) catalysts were made by impregnation and were characterized as reported earlier [13–17]. The dispersions of the catalysts were determined by hydrogen of CO chemisorption and were checked by transmission electron microscopy. Characteristic data on the catalysts are listed in table 1.

The reactions were carried out in a conventional pulse microreactor system with 1 μl pulses (for more details, see ref. [18]). Measurements were reproducible within 10%. Oxygen-free hydrogen for surface characterization and catalytic measurements was prepared with a Matheson 8326 hydrogen generator. The hydrogen flow rate was always 30 cm^3 min^{-1}. A Carlo Erba Fractovap Mod GV gas chromatograph equipped with a thermal conductivity detector and a 1.2 m long 17% bis-

Table 1
Characteristic data on the catalysts

Catalyst	Loading (%)	Chemisorption		TEM[a]	
		D (%)[b]	d (nm)[c]	D (%)[b]	d (nm)[c]
Pt/SiO$_2$	3.0	11.8[d]	8.6	11.5	8.8
Pd/SiO$_2$	3.0	15.4[e]	6.9	16.4	6.5
Rh/SiO$_2$	3.2	27.0[d]	3.9	24.4	4.3
Ni/SiO$_2$	3.0	6.8[d]	14.9	–	–

[a] Transmission electron microscopy.

[b] Number of exposed atoms / number of total atoms.

[c] Particle size.

[d] H$_2$ chemisorption in a flow system at 298 K, assuming 1 : 1 stoichiometry.

[e] CO chemisorption in a flow system at 298 K, assuming 1 : 1 stoichiometry.

methoxyethyladipate/Chromosorb PAW column (263 K) was used for analysis. The products formed were identified by comparison with authentic compounds (Merck). Retention times (in minutes) were as follows: isopentane, 1.74; pentane, 2.22; methylcyclobutane, 3.11.

Catalysts were pretreated in flowing hydrogen (flow rate: 30 $cm^3 min^{-1}$) at appropriate temperatures for 1 h. The pretreatment temperatures were 473 K for Pt/SiO_2 and Rh/SiO_2, 523 K for Pd/SiO_2 and 673 K for Ni/SiO_2. A fresh sample of catalyst (10 ± 0.1 mg) was used at each temperature.

3. Results and discussion

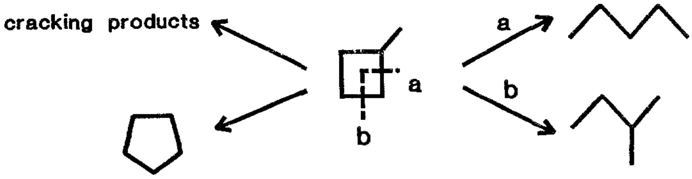
As it is known various transformations can be observed in the transition metal-catalyzed reactions of cyclic hydrocarbons. The transformations generally described were observed in the present study too, such as hydrogenative ring opening (products are saturated aliphatic hydrocarbons with unchanged number of carbon atoms), cracking (products are hydrocarbons with shorter chain than ring-opened products) and isomerization (ring enlargement, which produces saturated hydrocarbon ring with more carbon atoms than was the original). Aromatization was not observed neither did homologization occur under these mild conditions (scheme 1).

Experimental results are given in table 2. When reaction occurs at all, ring opening is the main transformation pathway, over each catalyst, in a wide temperature range.

However, at relatively high temperature (623 K) ring enlargement also takes place over Pt and Pd, leading to cyclopentane as the sole ring-enlargement product. Cracking too occurs to some extent at higher temperatures, except for Rh/SiO_2, where exclusively hydrocracking proceeds even at 573 K. It is important to note that the formation of isomeric C_5-olefins cannot be observed at all.

The results show that there is a temperature optimum for the formation of ring-opened products over each catalyst.

In agreement with earlier results on the metal-catalyzed ring opening of methylcyclobutane [7–10], cleavage of the sterically less hindered C–C bond (formation of isopentane) is the major ring-opening route. However, there are significant dif-



Scheme 1. Reaction pathways in the transformation of methylcyclobutane over silica-supported Pt, Pd, Rh and Ni catalysts.

Table 2
Temperature dependence of conversion and selectivities in the transformation of methylcyclobutane over transition metal catalysts in a pulse system [a]

Catalyst	T (K)	Conversion (%)	Selectivity			S [c]
			cracking [b] (%)	ring opening (%)	ring enlargement (%)	
Pt/SiO_2	423	3	–	100	–	0.54
	473	8	–	100	–	0.58
	523	62	1	99	–	0.56
	573	74	2	98	–	0.55
	623	73	3	95	2	0.54
	673	54	3	92	5	0.53
	723	31	6	84	10	0.50
Pd/SiO_2	573	6	1	99	–	0.55
	623	50	2	91	7	0.52
	673	52	5	87	8	0.50
	723	22	5	88	7	0.44
Rh/SiO_2	323	3	–	100	–	0.60
	373	21	–	100	–	0.75
	423	75	3	97	–	0.71
	473	82	12	88	–	0.70
	523	76	60	40	–	0.64
	573	100	100	–	–	–
	623	97	100	–	–	–
Ni/SiO_2	423	19	–	100	–	0.74
	473	54	2	98	–	0.71
	523	86	34	66	–	0.64
	573	93	88	12	–	0.67
	623	83	97	3	–	0.66
	673	71	100	–	–	–

[a] 10 ± 0.1 mg of catalyst, flowing hydrogen (flow rate: 30 cm^3 min^{-1}).
[b] Mainly methane (at least 85%).
[c] Selectivity of the ring-opening reactions. $S = b/(a+b)$.

ferences between the catalysts used. The selectivity is reasonably good over Rh/SiO_2 and Ni/SiO_2, while Pt/SiO_2 and Pd/SiO_2 bring about close to statistical product distribution, as can be seen in fig. 1.

Rh/SiO_2 and Ni/SiO_2 exhibited increasing cracking activity with increasing temperature, with the concomitant decrease of hydrogenative ring opening (table 2). This is in accordance with earlier results [19].

As it is shown in table 2 cracking is negligible over Pt/SiO_2 and Pd/SiO_2 catalysts at each temperature. In contrast, it is an important side-reaction over

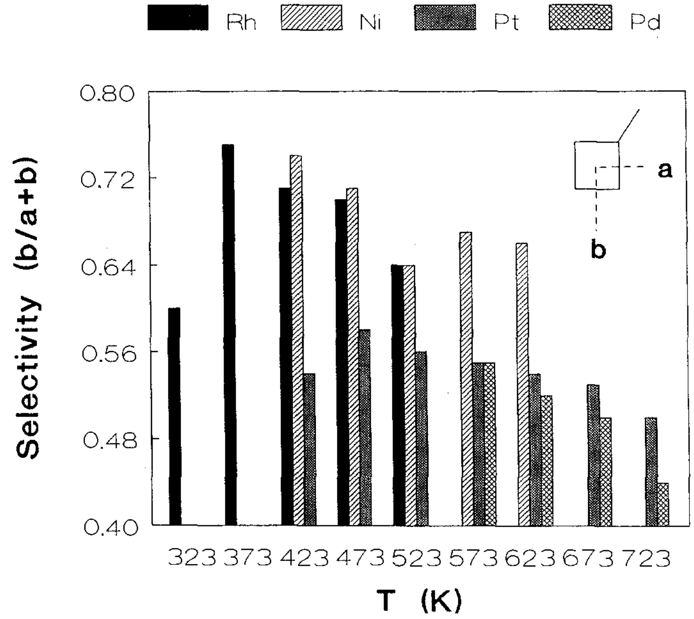
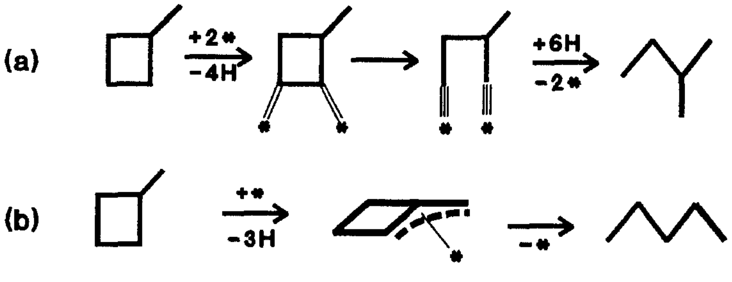


Fig. 1. The effect of temperature on the selectivity of ring-opening reaction of methylcyclobutane over supported Rh, Ni, Pt and Pd catalysts.

Rh/SiO_2 and Ni/SiO_2 catalysts at higher temperatures, producing overwhelmingly methane. The finding coincides with results of Matsumoto and coworkers [20], however.

It is well known that the temperature has a significant effect on the rate of ring-opening reactions through regulation of both the hydrogen coverage of the surface and the extent of coking. As the temperature is raised, the catalyst surface becomes very quickly quite complex, to such an extent that the actual reaction slows down and new reaction paths may open. In light of this it is not surprising that the catalyst activity in terms of conversion passes through a maximum as a function of temperature, especially since it is well known that a clean metal surface is needed for ring-opening reactions. Thus, elevation of temperature does not necessarily result in a monotonous acceleration of the reaction as is usual for transformations in the homogeneous phase.

The selectivity data relating to ring-opening directions show that the sterically less hindered C–C bond scission (formation of isopentane) predominates for each catalyst. The only exception is Pd/SiO_2 at 723 K, where the selectivity is lower than 0.5, which means that the sterically more hindered C–C-bond rupture (formation of pentane) prevails to some extent. These observations are in accordance with earlier findings on methylcyclobutane [7–10], but in contrast with recent results observed on the hydrogenative ring opening of propylcyclobutane [5,6]. The ring-opening selectivities increase in the sequence Pd, Pt<Ni, Rh. This is surprising,



Scheme 2. Mechanisms of the ring-opening reaction of methylcyclobutane: (a) over Rh/SiO_2 and Ni/SiO_2 catalysts, (b) over Pt/SiO_2 and Pd/SiO_2 catalysts.

because in the case of substituted cyclopropanes nearby equal selectivities were observed over the above-mentioned catalysts [15–17]. This phenomenon may be interpreted on the basis of the results of Gault and coworkers [2,7,9]. We propose that a *selective* mechanism (selective ring opening in the less hindered direction), which requires an α, α, β, β-tetraadsorbed edge-on species as the adsorbed intermediate [2], is predominantly operative over Rh/SiO_2 and Ni/SiO_2. In contrast, a *non-selective* mechanism (statistical ring scission), taking place through a side-chain-bonded flat-lying adsorbed species, is more characteristic over Pt and Pd. This is in agreement with the results of Zimmerman and Hayek [10]. Moreover, the bond strength of the possible π-allyl-type adsorbed intermediate changes in the sequence $Rh < Ni < Pt < Pd$ [7,21], which is opposite to the sequence of selectivity increase. In support of the above reasoning let us cite the following papers: (i) Kemball described that the hydrogenative transformations of hydrocarbons took place through α, β-di, α, α, β-tri, α, α, β, β-tetraadsorbed species over Rh catalysts, (ii) Pt and especially Pd preferred the formation of π-bonded intermediates [22–24]. Thus we may conclude that the formation of pentane (via scission of the more hindered C–C bond) probably takes place via a π-allyl adsorbed flat-lying intermediate bonded on the methyl group. This surface species gives nearby equal chances to ring scission in directions a and b. The above findings can be summarized in a reaction scheme, in which the adsorbed structures used have already been described in the literature (scheme 2).

We propose that the formation of cyclopentane over Pt/SiO_2 and Pd/SiO_2 catalysts may be interpreted in terms of the formation of a five-membered adsorbed intermediate as the primary reaction. The lack of secondary transformations may be accounted for by the short contact time in the pulse method applied here.

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