Temperature and hydrogen pressure dependences in the ring opening of methylcyclobutane over Pt/SiO_2 catalyst

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The temperature and hydrogen pressure dependences in the ring-opening reactions of methylcyclobutane were studied over Pt/SiO_2 catalyst. The temperature dependence of the ring opening revealed that the reaction rate vs. temperature curves passed through a maximum. On the basis of this information two temperatures were selected for hydrogen pressure studies: 573 K, close to the lowest temperature at which any reaction took place at all, and 623 K, where the ring opening of methylcyclobutane exhibited the highest rate. The initial formation rate vs. hydrogen pressure dependence curves are of bimodal type at 573 K, but they increase monotonously at 623 K. Over the working catalyst, no significant changes were observed at 573 K, but the curve for pentane formation changed to a large extent at 623 K. At 573 K, the selectivity of ring opening was close to statistical, with little excess of isopentane (sterically less hindered direction) over both the clean and the working catalyst. This was also observed at 623 K, however, over the working catalyst as the hydrogen pressure increased the selectivity of the ring opening increased as well. Moreover, at the highest hydrogen pressures studied excellent selectivity for the formation of isopentane was observed. The mechanisms over the initial and the working catalysts are discussed on the basis of these experimental findings.

Keywords: methylcyclobutane; Pt/SiO_2 catalyst; effects of temperature and hydrogen pressure; initial and working catalysts; mechanisms of ring opening

1. Introduction

The transition metal-catalyzed transformations of alkyl-substituted cyclopropanes and especially cyclopentanes have received much attention in catalytic research [1–4]. The main reason is probably the well-established role of adsorbed species of these compounds in the isomerization reactions of saturated hydrocarbons [1–3]. In contrast, only a few studies relate to cyclobutane derivatives. They

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include the investigations of H–D exchange and ring-opening reactions in hydrogen atmosphere. In our previous papers, this topic has been treated extensively [5], and here only basic conclusions concerning methylcyclobutane and some recently published results are summarized briefly, as follows:

(i) Gault and co-workers studied the regioselectivity and the kinetics of the ring opening [6], and also those of the H–D exchange reactions [7].

(ii) Zimmermann and Hayek studied the hydrogenative ring-opening reactions of methylcyclobutane over supported platinum model catalysts [8].

Both groups concluded that the ring opened mostly in the sterically less hindered direction and that the cyclobutane ring adsorbed reversibly at low temperatures and partly irreversibly at elevated temperatures.

Recently, new results have been published on ring enlargement and aromatization [9,10], and the role of surface carbonaceous deposits in the ring opening of propylcyclobutane has also been investigated [11]. Nowadays, in a preliminary communication results concerning the hydrogenative transformations of methylcyclobutane over silica supported Pt, Pd, Rh, and Ni/SiO_2 catalysts were published [12].

In this study, we report the effects of temperature and hydrogen pressure on the hydrogenative ring opening of methylcyclobutane over Pt/SiO_2 catalyst, leading to isomeric pentanes. The emphasis is placed on the hydrogen pressure dependence of the ring opening, which is indicative of the type of adsorption. In a wide temperature range, only hydrogenative ring opening occurs, and thus our investigations are simplified to a large extent. However, two ring-opening routes appear, which allows the study of ring-opening selectivity too.

2. Experimental

Methylcyclobutane was prepared by a recently published method [13]. It was gas chromatographically pure and was used without further purification, except for a couple of freeze–evacuate–thaw cycles immediately before preparation of the reaction mixture.

A 3% Pt/SiO_2 catalyst was made by impregnation [14] and was characterized [15] as reported earlier. The dispersion value of the catalyst (11.8%) was determined by hydrogen chemisorption and was checked by O_2-H_2 titration and transmission electron microscopy.

Before the kinetic measurements, the catalyst was activated in 26.6 kPa of H_2 at 473 K for 0.5 h. The system was then heated to the reaction temperature.

The reactions were carried out in a conventional closed recirculation apparatus (for more details, see refs. [16,17]). A Carlo Erba Fractovap 2150 gas chromatograph with a flame ionization detector was attached to the system. A 4 m long 15% squalane/Chromosorb PAW column was used for analysis.

In each case, 1.33 kPa methylcyclobutane and various amounts of hydrogen were premixed before the reaction, except for the temperature dependence measurements, when the hydrogen pressure was always 19.9 kPa.

At each hydrogen presssure, the product accumulation vs. time curves were always determined over a fresh sample of catalyst (10 mg). Measurements were reproducible within 10%. Both initial and steady-state rates were measured and converted to turnover frequency (TOF: molecule exposed atom^{-1} s^{-1}) data on the basis of the number of exposed Pt atoms, determined by H_2 chemisorption.

3. Results and discussion

3.1. TEMPERATURE DEPENDENCE OF THE HYDROGENATIVE TRANSFORMATION

As already mentioned, only hydrogenative ring opening occurs in a wide temperature range (473–623 K). However, at relatively high temperature (673 K) ring enlargement also takes place, which leads to cyclopentane as the sole ring-enlargement product. Naturally, hydrogenolysis (cracking) too occurs at this temperature to some extent. It is important to note that the formation of isomeric C_5-olefins cannot be observed at all. Thus, hydrogenative ring opening is the main reaction at each temperature (fig. 1a). Our experimental results show that the product formation rate vs. temperature curves belonging to the ring-opening reactions pass through a maximum (fig. 1b).

It is well known that the temperature has a significant effect on the rate of ring-opening reactions, by regulating both the hydrogen coverage of the surface and the extent of coking. As the temperature is raised, the catalyst surface can become quite complex very quickly, to such an extent that the actual reaction slows down and new reaction paths may open up. In light of this, the maximum curve observed for the temperature dependence is not surprising. An elevation of temperature does not necessarily result in a monotonous acceleration of the reaction as is usual for transformation in the homogeneous phase.

On the basis of the experimental findings, two temperatures were selected for hydrogen pressure studies: 573 K, close to the lowest temperature at which any reaction took place at all, and 623 K, where the ring opening of methylcyclobutane exhibited the highest rate.

3.2. HYDROGEN PRESSURE DEPENDENCE OF HYDROGENATIVE RING-OPENING REACTIONS

The effects of hydrogen pressure on the ring-opening reactions were studied at two different temperatures: 573 and 623 K. As reported recently in similar investigations with propylcyclobutane [5], the typical product yield vs. time curves clearly show significant differences in their shapes as a function of temperature. At the lower temperature (573 K), the curves are almost linear, i.e. the initial and steady-

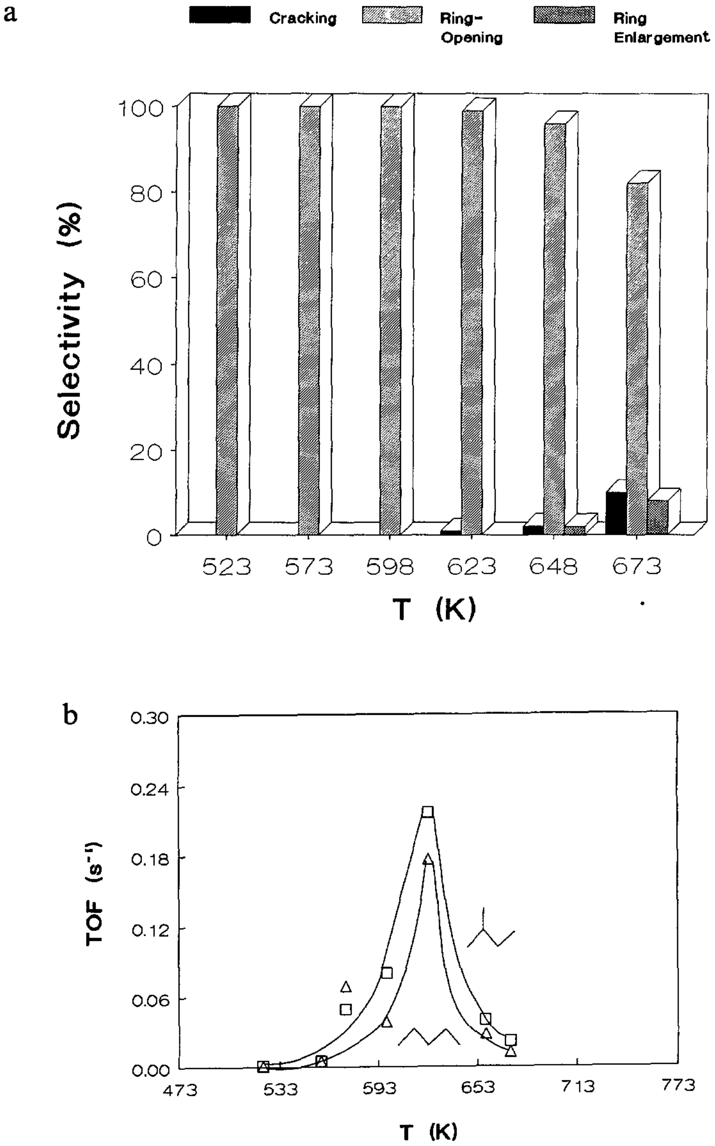


Fig. 1. (a) Selectivity of reaction pathways in hydrogenative transformations of methylcyclobutane over Pt/SiO_2 catalyst. (b) Turnover frequency of product formation vs. temperature curves of the ring-opening reactions over the initial surface at 20.0 kPa hydrogen pressure.

state parts can hardly be distinguished; at higher temperature (623 K), however, the two parts can easily be separated, as illustrated in fig. 2.

From these product yield vs. time curves, therefore two types of product formation rate vs. hydrogen pressure functions were constructed: one from the initial rates considered to be characteristic of the clean (or initial) catalyst, and the other from the second linear part, thought to be characteristic of the working catalyst.

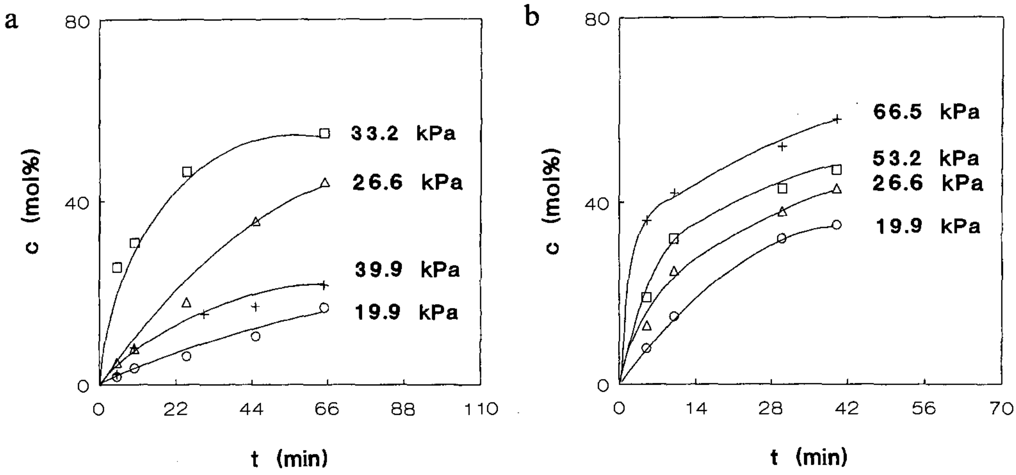


Fig. 2. Product yield vs. time curves of isopentane in the ring-opening reactions of methylcyclobutane over Pt/SiO_2 catalyst at (a) 573 K, (b) 623 K.

First we consider the initial formation rate vs. hydrogen pressure dependence curves (fig. 3).

As a function of temperature, two types of hydrogen pressure dependence curves are observed. At 573 K, the curve is of bimodal type; at 623 K, the curve increases monotonously.

The main problem is whether any information concerning the structure of the initially formed adsorbed species can be deduced from the shapes of these curves. In earlier papers [5,18,19] and also in a recent book [20], this topic is discussed in some depth. Before the actual considerations, the brief conclusions are as follows:

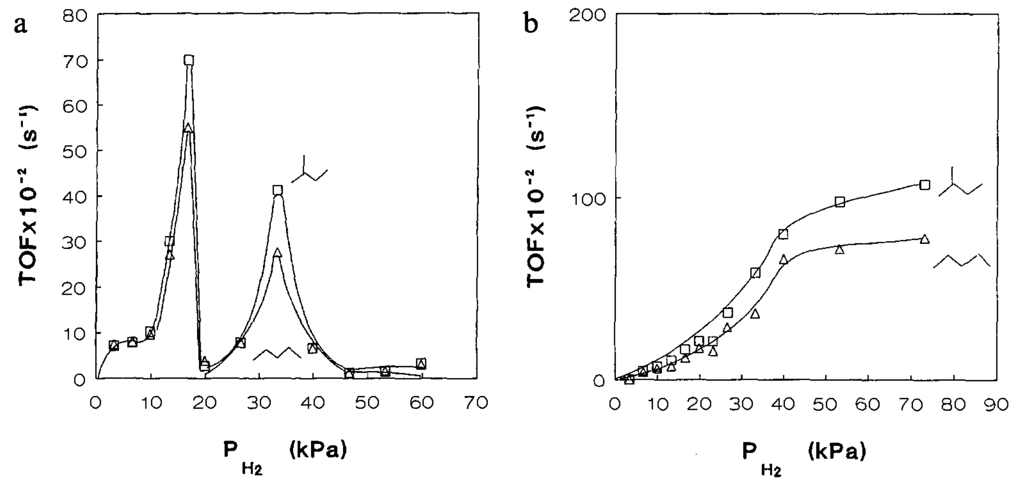


Fig. 3. Turnover frequency of product formation vs. hydrogen pressure curves over the initial catalyst at (a) 573 K, (b) 623 K.

– When the compound is adsorbed equally as strongly as or more weakly than the adsorption of hydrogen, there is an optimal hydrogen pressure for the reaction and the high excess of hydrogen sweeps the reacting intermediates off the surface; a maximum curve is observed (Langmuir–Hinshelwood mechanism).

– When the adsorption becomes partly or largely irreversible, the competition between hydrogen and the reactant is lost, and thus the hydrogen now only regulates the hydrogen content of the adsorbed species: (i) When the compound adsorbs dissociatively (C–H bond rupture), a maximum curve can be expected, since the hydrogen excess inhibits C–H bond scission by suppressing the dissociation equilibrium,

$$C_nH_{2n}(g) \longrightarrow C_nH_{2n-m}(a) + mH(a)$$

(ii) If associative adsorption takes place (only C–C bond rupture occurs), hydrogen does not affect the formation of the adsorbed species, i.e. monotonously increasing or saturation-type curves are observed,

$$C_nH_{2n}(g) \longrightarrow CnH_{2n}(a)$$

The bimodal hydrogen pressure dependence curves determined at 573 K clearly show that a simple Langmuir–Hinshelwood mechanism does not operate. The two maxima in the hydrogen pressure curve suggest that the adsorption changes in the hydrogen pressure range applied. Similar reactions with propylcyclobutane over Pt/SiO_2 produced a curve of the same type at the lowest temperature at which the reaction occurred [5]. The main reasons for this shape were discussed there, and only the basic conclusions which seem to be valid here too are repeated now. For the first maximum, adsorption of dissociative type can be proposed, while a further increase in hydrogen pressure results in the formation of new types of reaction intermediates. The other maximum may reflect the inhibition of a C–H rupture in another, less unsaturated surface species, or the hydrogen excess is now simply large enough to remove any kind of reacting intermediates from the surface.

It may also be clear that associative adsorption occurs at 623 K, since a monotonous increase in the ring-opening rate can be observed in the hydrogen pressure range applied.

After the initial catalyst, let us analyze the hydrogen pressure dependence curves observed over the working catalyst (fig. 4).

As already mentioned, these curves were constructed from the steady-state part of the product yield vs. time functions.

The formation of a surface carbonaceous overlayer in catalytic reactions, and especially in hydrocarbon transformations, is a well-known fact. The literature contains many data on this topic, and especially on the formation and effects of such carbonaceous deposits [21]. The types of surface carbonaceous deposits formed in the hydrogenative transformations of propylcyclobutane have also been investigated [11].

This phenomenon can be observed in the hydrogenative ring opening of methyl-

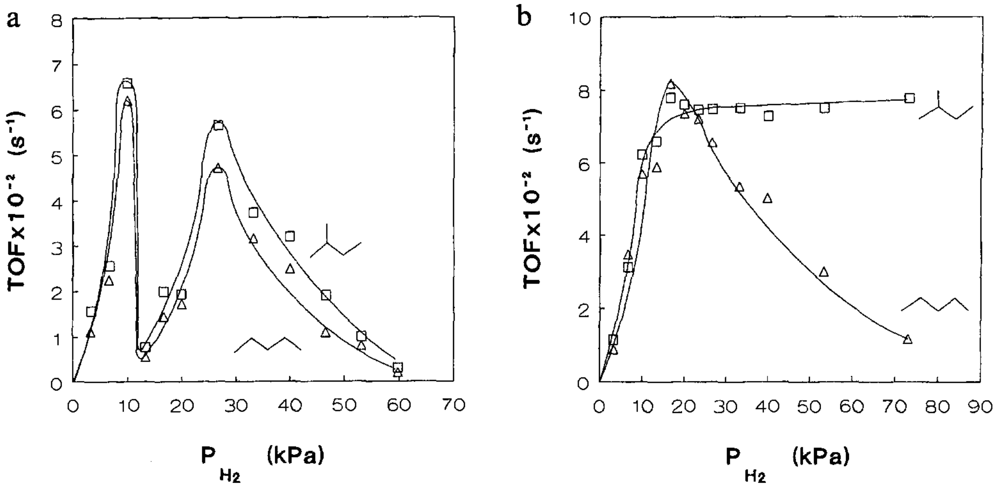


Fig. 4. Turnover frequency of product formation vs. hydrogen pressure curves over working catalyst at (a) 573 K, (b) 623 K.

cyclobutane too. However, the working surface can hardly be distinguished from the initial clean catalyst at 573 K. As far as the hydrogen pressure dependence curves are concerned, they show that the initial surface is not very different from the working one at this temperature, as the shapes of the curves are very similar. In contrast, the shapes of the curves change significantly at 623 K. Moreover, the shapes of the hydrogen pressure functions relating to the individual products are different, which supports our suggestion that TOF vs. H_2 pressure curves can be used for mechanistic considerations. A saturation-type curve instead of a monotonous increase can be observed for isopentane, showing that the initially formed intermediates react further. In contrast, a large maximum is now observed for pentane. This indicates that the reacting species differ from those initially formed, i.e. the associative adsorption turns to dissociative. A probable reason is that the anchoring effect [5] of the short side-chain is too weak to compensate the effect of increasing hydrogen pressure.

These significant changes reveal that the initial and working catalysts can be quite different at 623 K. Regioselectivity data lend further support to this conclusion.

3.3. RING-OPENING SELECTIVITIES OVER THE INITIAL AND WORKING CATALYSTS

Data concerning ring-opening selectivities are summarized in table 1. These selectivity data are in agreement with the results mentioned in the introduction, while they differ from our experimental findings concerning the ring opening of propylcyclobutane [5]. Selective ring opening in the sterically more hindered direc-

Table 1
Selectivity of the ring-opening reaction [a]

p_{H_2} (kPa)	573 K		623 K	
	a	*b*	*a*	*b*
3.3	0.50	0.53	[b]	0.56
6.7	0.50	0.52	0.55	0.47
9.9	0.52	0.53	0.53	0.52
13.3	0.52	0.53	0.59	0.52
16.6	0.56	0.58	0.58	0.48
19.9	0.49	0.51	0.55	0.54
23.2	–	–	0.54	0.51
26.6	0.52	0.55	0.55	0.53
33.9	0.60	0.55	0.63	0.57
39.9	0.51	0.56	0.57	0.64
46.6	0.50	0.55	–	–
53.2	0.51	0.52	0.58	0.68
59.8	0.50	0.51	–	–
73.2	–	–	0.57	0.86

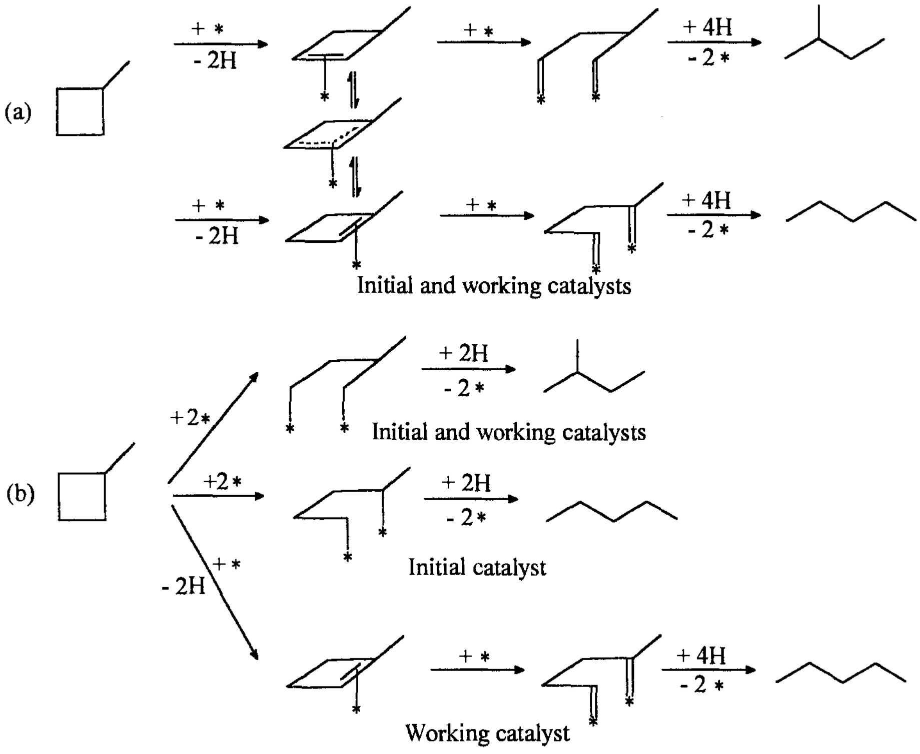
[a] $a = r_{\text{initial,isopentane}}/(r_{\text{initial,isopentane}} + r_{\text{initial,pentane}})$.
$b = r_{\text{working,isopentane}}/(r_{\text{working,isopentane}} + r_{\text{working,pentane}})$.
[b] There are no products.

tion was found in the transformation of propylcyclobutane, while the ring opened selectively in the sterically less hindered direction at most temperatures and hydrogen pressures in the transformation of methylcyclobutane. The selectivity was close to statistical at lower hydrogen pressures at both temperatures, while it increased in parallel with the increase of hydrogen pressure. A comparison of the ring-opening selectivities over the clean and working catalysts showed that there was only a slight difference between the two states of the catalyst at 573 K. However, significant differences could be observed at 623 K, mainly at higher hydrogen pressures.

3.4. MECHANISMS OF THE RING-OPENING REACTIONS

It is clear that the results observed cannot be explained by a single mechanism. The mechanism changes both with the rise of temperature, and with the elevation of hydrogen pressure.

At 573 K (scheme 1 (a)), dissociatively adsorbed species predominate at low hydrogen pressures. However, at elevated hydrogen pressures, the type of the adsorbed intermediates changes. Since the selectivity values are close to statistical, a flat-lying species is suggested for the ring-opening reaction initially. Since the working catalyst is quite similar to the initial one at this temperature, the same mechanism is proposed over the working catalyst (scheme 1 (a)).



Scheme 1. Mechanisms of the ring-opening reactions at (a) 573 K, (b) 623 K.

In contrast, at 623 K (scheme 1 (b)), the initial adsorption differs from that typical for the working catalyst. Initially, associative adsorption takes place in both directions through a flat-lying intermediate suggested by near-statistical ring opening. However, this picture changes significantly over the working catalyst. The formation of pentane occurs via a dissociatively adsorbed intermediate standing on atoms C(1) and C(2), while isopentane is formed through an adsorbed species similar to the one initially formed. The most striking feature of our observations is the opposite ring-opening selectivities of methylcyclobutane and propylcyclobutane. The selective ring opening in the sterically less hindered direction may be attributed in part to the weak anchoring effect of the short methyl side-chain in the transformation of methylcyclobutane, as opposed to propylcyclobutane [5]. As a result, it is known that the sterically more hindered C–C bond opens to a large extent over the metal–support interface [22]. Extensive coking, however, results in a decrease in the available metal surface, and the relative increase in the metal–carbonaceous interface does not result in a selectivity shift towards C(1)–C(2) bond scission, since the anchoring effect is negligible. Adsorbed surface intermediates yielding pentane, become less abundant, therefore contributing eventually to a decrease in the rate of pentane formation.

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