Characteristics of adsorbed intermediates in the hydrogenative ring opening of methylcyclobutane and methylcyclopentane over silica-supported Pt and Pd catalysts

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The hydrogenative ring opening of methylcyclobutane and methylcyclopentane was studied over silica-supported Pt and Pd catalysts by kinetic and infrared (IR) spectroscopic measurements. First, the temperature (473–673 K) and hydrogen pressure (3.3–73.2 kPa) dependences of the ring-opening reactions were determined. The reaction rates were determined over the initial and the working catalysts for both compounds. According to the type of product formation vs. hydrogen pressure dependence curves either dissociative or associative adsorption was suggested for methylcyclobutane and methylcyclopentane. The geometry of adsorbed intermediates was proposed on the basis of the regioselectivity of ring opening. The regioselectivity data show close to statistical ring opening for both compounds, which indicate flat-lying adsorbed intermediates. The structure of adsorbed intermediates was also studied by transmission IR spectroscopy. The H–D exchange reactions between the surface hydroxyl groups and adsorbed species in most cases confirmed the type of adsorption suggested by kinetic measurements.

Keywords: methylcyclobutane, methylcyclopentane, Pt/SiO_2 and Pd/SiO_2 catalysts, temperature and hydrogen pressure dependence, H–D exchange reactions, surface hydroxyl groups, mechanism of ring opening, IR measurements

1. Introduction

The transition metal catalyzed transformations of cycloalkanes derivatives have received much attention in theoretical and industrial catalytic hydrocarbon chemistry (see reviews [1–4]). The main reason is probably the well-established role of cyclopropane and cyclopentane-like adsorbed species in the skeletal isomerization of saturated hydrocarbons [1–3]. Additionally, cyclopropanes show exclusive ring opening under very mild conditions (low temperature and hydrogen pressure) [1] without any side reaction.

Methylcyclopentane is probably one of the most popular reactants in catalytic chemistry. Its well-characterized properties make the methylcyclopentane a suitable candidate for investigation of metal catalysts. Thus, the hydrogenative transformation of methylcyclopentane is a frequently used model reaction for characterization of metal catalysts prepared by different techniques and/or pretreated under various conditions [5–9].

In contrast with methylcyclopentane, only a few studies can be found in the literature concerning alkylcyclobutanes, probably because of the synthetic difficulties. In some of these investigations the catalytic properties of Pt and Pd catalysts were studied, such as H–D exchange and ring-opening reactions of mono- [10] and disubstituted [11,12] cyclobutanes. The main observations concerning alkylcyclobutanes and bulk or supported catalysts can be summarized briefly as follows:

The major ring-opening pathway was the scission of the sterically less hindered C–C bond. The regioselectivity data were found to be similar over the generally used metal catalysts (Pt, Pd, Rh, and Ni), however, differences are pointed out between Pt, Pd and Rh, Ni pairs [12]. Furthermore, opposite regioselectivity (the prevailance of the sterically more hindered ring opening) was detected in the Pt-, and Pd-catalyzed ring-opening reaction of propylcyclobutane [13]. The rate of the ring scission over Pd catalysts was found to be generally lower than over other widely used (Pt, Rh, Ni) transition metal catalysts, and aromatization and hydrocracking reactions also occurred at higher temperature (> 623 K) [10–12,14–16]. An important observation was that the cyclobutane ring adsorbed reversibly at low and at least partly irreversibly at higher temperatures [10–12].

In the present work, we report the effects of temperature and hydrogen pressure on the hydrogenative ring opening of methylcyclobutane and methylcyclopentane over silica-supported Pt and Pd catalysts, leading to isomeric pentanes and hexanes. The emphasis is placed on the hydrogen pressure dependence of the ring opening. This has not been studied before over Pd, although it can provide valuable information for the type of adsorption. In this respect, for example, important results were recently published for the transformations of methylcyclopentane over various Pt catalysts [7]. Further support

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for the type of adsorption will be given on the basis of regioselectivity data and surface H–D exchange reactions studied by infrared spectroscopy.

2. Experimental

Methylcyclobutane was prepared by a recently published method [17]. The crude product containing 5% impurities was purified by preparative gas chromatography (Carlo Erba Fractovap Mod P, 4 m 15% squalane/kieselguhr column). The obtained methylcyclobutane was of 99.9% purity (GC-MS), *m/z* (%): 70 (11, M^+), 55 (23, $C_4H_7^+$), 42 (100) and 41 (35, $C_3H_5^+$); δ_H (ppm): 1.03 (d, *J* 6.7, 3H, CH_3), 1.54 (m, 2α H), 1.80 (m, 2β H), 2.05 (m, 2H, CH_2) and 2.37 (m, 1H, C*H*–CH_3). The methylcyclopentane (minimum purity > 99%) was obtained from Aldrich. Both hydrocarbons were used without further purification, except for a couple of freeze–evacuate–thaw cycles immediately before preparation of the reaction mixture.

3% Pt/SiO_2 and 3% Pd/SiO_2 catalysts were made by impregnation and were characterized [18] as reported earlier. The dispersion of the catalysts (number of exposed metal atoms/total number of metal atoms) was determined by H_2 and CO chemisorption. The dispersion values (11.8% for Pt/SiO_2 and 15.8% for Pd/SiO_2) obtained were checked by O_2–H_2 titration and transmission electron microscopy.

Before the kinetic measurements, the catalysts were prepared with 26.6 kPa of H_2 at 473 K (Pt/SiO_2) or 523 K (Pd/SiO_2) for 1 h. The system was then evacuated and heated to the reaction temperature.

The reactions were carried out in a conventional closed recirculation apparatus [19,20]. A Chrom 4 gas chromatograph with a flame ionization detector and a 4 m long glass column filled with 15% squalane/Chromosorb PAW was used for analysis.

Always, 1.33 kPa hydrocarbon and various amounts of hydrogen were premixed before the reaction, except for the temperature dependence measurements, when the hydrogen pressure was 19.9 kPa at each temperature.

At the hydrogen pressures studied, the product accumulation vs. time curves were always determined over a fresh sample of catalyst (10 mg). 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 metal atoms, determined by H_2 or CO chemisorption.

The transmission infrared spectroscopic (IR) measurements were performed with a Specord 71 IR spectrometer. A static IR cell was attached to a vacuum system. A self-supporting wafer pressed from 24 ± 0.5 mg of catalyst was used for the IR investigations. The catalyst samples were pretreated with 26.6 kPa D_2 for 2 h and evacuated for 2 h at the temperature of pretreatment used in the kinetic measurements as mentioned above, then it was treated with 1.33 kPa methylcyclobutane or methylcyclopentane at various temperatures. The IR spectra were taken after evacuation at room temperature.

3. Results

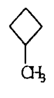
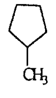
3.1. Temperature dependence of the hydrogenative transformations

The collected activity and selectivity data for both reactants determined over the initial Pd/SiO_2 catalyst as an example for temperature dependence at a constant hydrogen pressure (19.9 kPa) are given in table 1.

The results show that the conversions pass through a maximum as a function of temperature for both compounds. In the temperature range studied (473–673 K)

Table 1

Temperature dependence of the hydrogenative transformation of methylcyclobutane and methylcyclopentane over Pd/SiO_2 catalyst (10 mg catalyst, 1.33 kPa hydrocarbon, 19.9 kPa H_2 for methylcyclobutane and 66.5 kPa for methylcyclopentane) [a]

Reactant	*T* (K)	Conversion (%)	Selectivity				
			cracking (%)	ring opening (%)	S	S_1	S_2
	473	3	–	100	0.52		
	523	12	–	100	0.56	–	–
	573	37	–	100	0.57	–	–
	623	21	–	100	0.52	–	–
	673	4	–	100	0.42	–	–
	543	0	–	–	–	–	–
	573	[b]	–	100	–	–	–
	623	13	–	100	–	2.22	1.72
	673	5	6	94	–	0.96	3.01

[a] $S = r_{\text{initial,isopentane}}/r_{\text{initial,total}}$, $S_1 = r_{\text{initial,2-Me-pentane}}/r_{\text{initial},n\text{-hexane}}$, $S_2 = r_{\text{initial,2-Me-pentane}}/r_{\text{initial,3-Me-pentane}}$.

[b] Products only in traces.

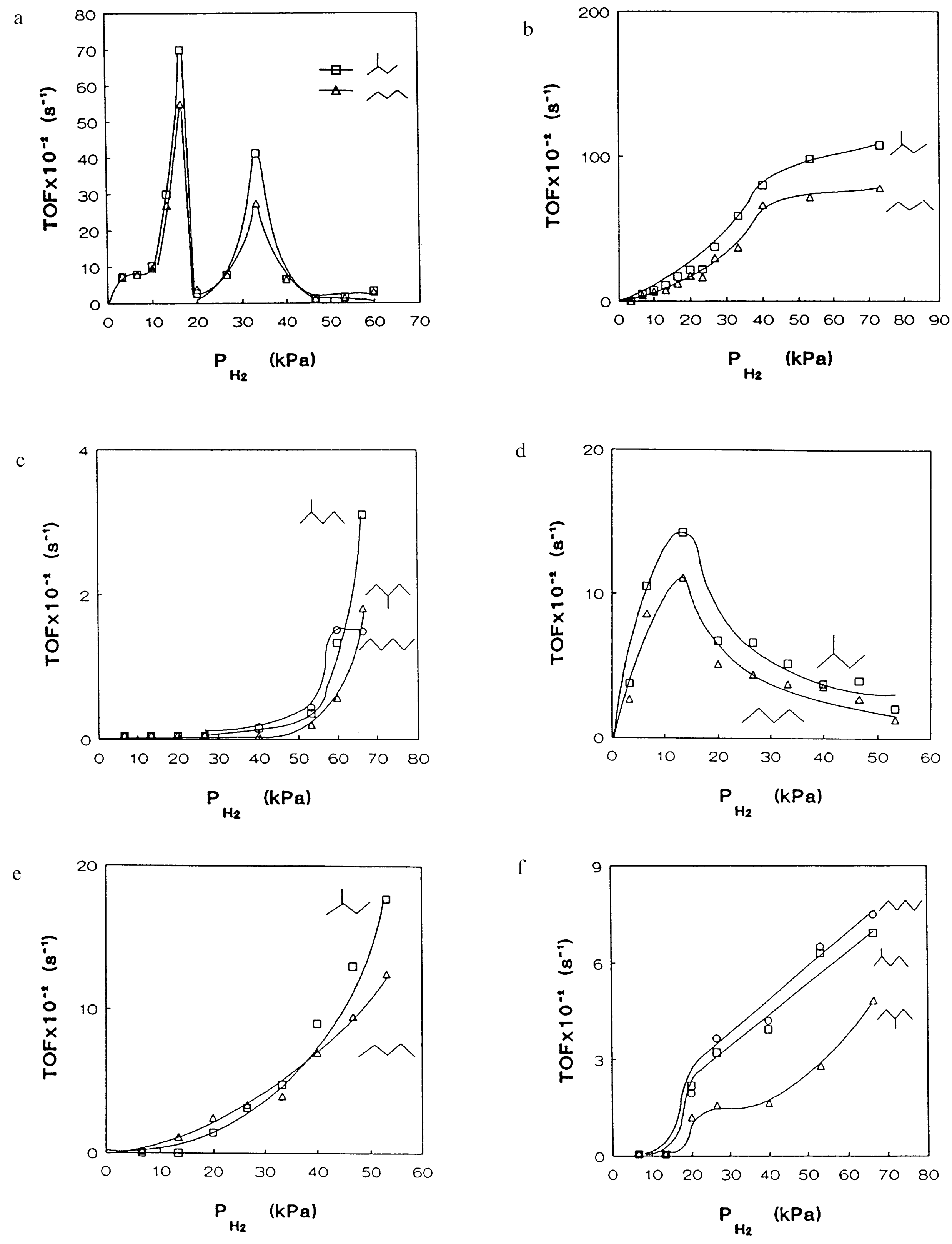


Figure 1. Initial turnover frequency of product formation vs. hydrogen pressure curves of the ring-opening reaction of methylcyclobutane and methylcyclopentane over Pt/SiO_2 and Pd/SiO_2 catalysts at various temperatures. (a) MECB, 573 K, Pt/SiO_2; (b) MeCB, 623 K, Pt/SiO_2; (c) MECP, 623 K, Pt/SiO_2; (d) MECB, 523 K, Pd/SiO_2; (e) MECB, 673 K, Pd/SiO_2; (f) MECP, 623 K, Pd/SiO_2.

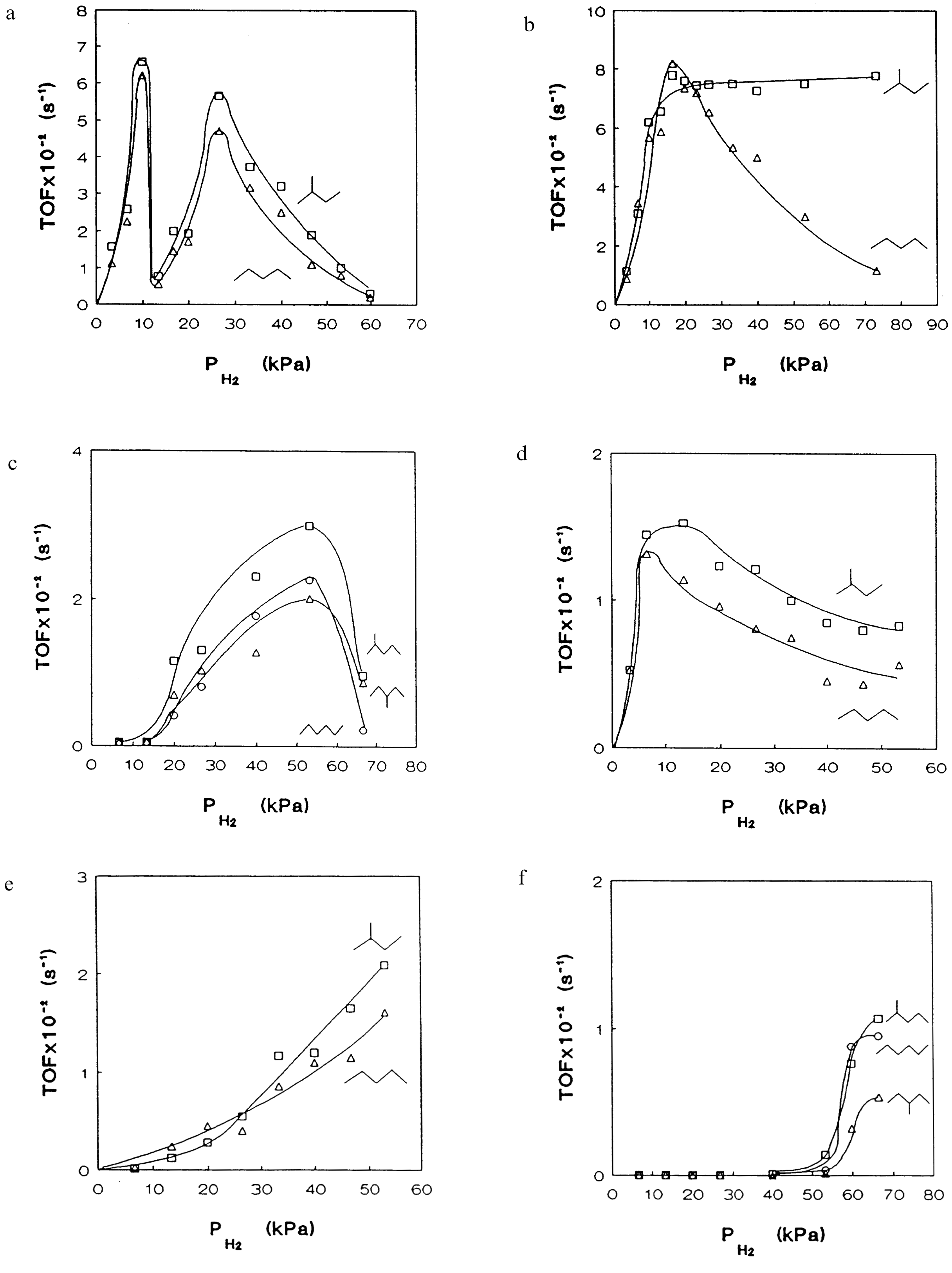


Figure 2. Turnover frequency of product formation vs. hydrogen pressure curves of the ring-opening reaction of methylcyclobutane and methylcyclopentane over the working Pt/SiO_2 and Pd/SiO_2 catalysts at various temperatures. (a) MECB, 573 K, Pt/SiO_2; (b) MeCB, 623 K, Pt/SiO_2; (c) MECP, 623 K, Pt/SiO_2; (d) MECB, 523 K, Pd/SiO_2; (e) MECB, 673 K, Pd/SiO_2; (f) MECP, 623 K, Pd/SiO_2.

practically exclusive hydrogenative ring opening occurs. Other expected hydrocarbon reactions, such as cracking, ring enlargement or aromatization, take place to a small extent. It is worth noting that the formation of isomeric olefins cannot be observed either.

On the basis of the temperature dependence studies, the following temperatures were selected for hydrogen pressure measurements: 573 and 623 K for methylcyclobutane, 623 K for methylcyclopentane over Pt/SiO_2; while 523 and 673 K for methylcyclobutane, 623 K for methylcyclopentane over Pd/SiO_2. These temperatures were convenient for kinetic studies, the only exception is 673 K for methylcyclobutane, where the selectivity was opposite to that observed at 523 K (table 3, see below).

3.2. *Hydrogen pressure dependence of hydrogenative ring-opening reactions*

The effects of hydrogen pressure on the ring-opening reactions were studied at the temperatures mentioned above. As reported recently in similar investigations with propylcyclobutane [13], significant differences were observed in the shape of the typical product yield vs. time functions. On the basis of these product accumulation curves two types of product formation rate (TOF) vs. hydrogen pressure functions were calculated. The first from the initial rates and the other from the second linear part of the product accumulation curves, thought to be characteristic of the initial and the working catalysts, respectively.

Over the initial catalysts, three types of hydrogen pressure dependence curves are observed in the hydrogen pressure range studied as a function of temperature. A special type with two maxima was detected with methylcyclobutane at 573 K over Pt/SiO_2 (figure 1a [21]). In other cases, the reaction rate increases monotonically (methylcyclobutane: Pt/SiO_2, 623 K (figure 1b [21]) and Pd/SiO_2, 673 K (figure 1e); methylcyclopentane: both catalysts at 623 K (figures 1c and 1f)) or shows a maximum in character (methylcyclobutane: Pd/SiO_2, 523 K, (figure 1d)).

Hydrogen pressure dependence curves observed over the working catalysts can be seen on figure 2. The shapes of these TOF vs. hydrogen pressure functions, are similar to those determined over the initial catalysts except for both compounds over platinum at 623 K. In both cases the monotonic increase levels off (figures 2b and 2c). In addition, an approximately one order of magnitude decrease in the ring-opening rate was also observed relative to the initial rates.

Data concerning the regioselectivities of the ring opening are summarized in tables 2 and 3. Selectivity data observed over the initial catalysts are, in general, in agreement with the results mentioned in the introduction. Regioselectivity of methylcyclobutane ring opening is close to statistical at most hydrogen pressures at both temperatures, with a small excess in isopentane (the product of the sterically less hindered ring scission). At 673 K over palladium ring opening is similarly near statistical, but now with a slight excess of pentane at low hydrogen pressures.

2-methylpentane, 3-methylpentane and *n*-hexane are the main products of methylcyclopentane ring opening, in agreement with the literature [2,4,7]. The product dis-

Table 2

Regioselectivity data on the ring-opening reaction of methylcyclobutane at 573 and 623 K and methylcyclopentane at 623 K catalyzed by Pt/SiO_2 catalyst (10 mg catalyst, 1.33 kPa hydrocarbon) [a]

P_{H_2} (kPa)	MECB				MECP			
	573 K		623 K		623 K			
	S_i	S_w	S_i	S_w	S_{i1}	S_{i2}	S_{w1}	S_{w2}
3.3	0.50	0.53	[b]	0.56	–	–	–	–
6.7	0.50	0.52	0.55	0.47	[b]	[b]	[b]	[b]
9.9	0.52	0.53	0.53	0.52	–	–	–	–
13.3	0.52	0.51	0.59	0.48	[b]	[b]	[b]	[b]
16.6	0.56	0.58	0.58	0.54	–	–	–	–
19.9	0.49	0.51	0.55	0.51	1.12	1.80	2.20	1.66
23.2	–	–	0.54	0.53	–	–	–	–
26.6	0.52	0.55	0.55	0.57	0.88	2.05	1.63	1.35
33.9	0.60	0.55	0.63	0.57	–	–	–	–
39.9	0.51	0.56	0.57	0.64	0.93	2.39	–	–
46.6	0.50	0.55	–	–	–	–	–	–
53.2	0.51	0.52	0.58	0.68	0.98	2.01	1.32	1.48
59.8	0.50	0.51	–	–	–	–	–	–
66.5	–	–	–	–	0.92	1.42	3.35	1.10
73.2	–	–	0.57	0.86	–	–	–	–

[a] $S_i = r_{initial,isopentane}/r_{initial,total}$, $S_w = r_{working,isopentane}/r_{working,total}$, $S_{i1} = r_{initial,2\text{-Me-pentane}}/r_{initial,n\text{-hexane}}$, $S_{i2} = r_{initial,2\text{-Me-pentane}}/r_{initial,3\text{-Me-pentane}}$, $S_{w1} = r_{working,2\text{-Me-pentane}}/r_{working,n\text{-hexane}}$, $S_{w2} = r_{working,2\text{-Me-pentane}}/r_{working,3\text{-Me-pentane}}$.

[b] Ring opening does not take place.

Table 3
Regioselectivity data on the ring-opening reaction of methylcyclobutane at 523 and 673 K and methylcyclopentane at 623 K catalyzed by Pd/SiO$_2$ catalyst (10 mg catalyst, 1.33 kPa hydrocarbon) [a]

P_{H_2} (kPa)	MECB				MECP			
	523 K		673 K		623 K			
	S_i	S_w	S_i	S_w	S_{i1}	S_{i2}	S_{w1}	S_{w2}
3.3	0.58	0.50	–	–	–	–	–	–
6.7	0.54	0.52	0.45	0.47	–	–	–	–
13.3	0.56	0.57	0.40	0.42	–	–	–	–
19.9	0.56	0.56	0.42	0.48	–	–	–	–
26.6	0.59	0.59	0.48	0.53	–	–	–	–
33.2	0.57	0.57	0.54	0.56	–	–	–	–
39.9	0.54	0.70	0.55	0.51	1.01	[b]	0.98	[b]
46.6	0.59	0.71	0.57	0.58	–	–	–	–
53.2	0.61	0.59	0.58	0.56	0.98	1.74	2.96	4.32
59.8	–	–	–	–	0.97	2.33	0.96	2.51
66.5	–	–	–	–	2.22	1.72	1.21	2.03

[a] $S_i = r_{\mathrm{initial,isopentane}}/r_{\mathrm{initial,total}}$, $S_w = r_{\mathrm{working,isopentane}}/r_{\mathrm{working,total}}$, $S_{i1} = r_{\mathrm{initial,2\text{-}Me\text{-}pentane}}/r_{\mathrm{initial},n\text{-}\mathrm{hexane}}$, $S_{i2} = r_{\mathrm{initial,2\text{-}Me\text{-}pentane}}/r_{\mathrm{initial,3\text{-}Me\text{-}pentane}}$, $S_{w1} = r_{\mathrm{working,2\text{-}Me\text{-}pentane}}/r_{\mathrm{working},n\text{-}\mathrm{hexane}}$, $S_{w2} = r_{\mathrm{working,2\text{-}Me\text{-}pentane}}/r_{\mathrm{working,3\text{-}Me\text{-}pentane}}$.

[b] No 3-Me-pentane.

tribution shows approximately statistical ring scission. In some cases, however, the formation of *n*-hexane (the sterically most hindered ring-opening path) took place with the highest rate. Similar ring-opening selectivities are observed over the working catalysts for both compounds.

3.3. H–D exchange reactions of surface hydroxyl groups

The OH content of the surface of silica is, in general, low. However, an appreciable amount of surface OH groups can be detected on our support (a fumed silica, Cab-O-Sil type) and naturally, on Pt/SiO$_2$ and Pd/SiO$_2$

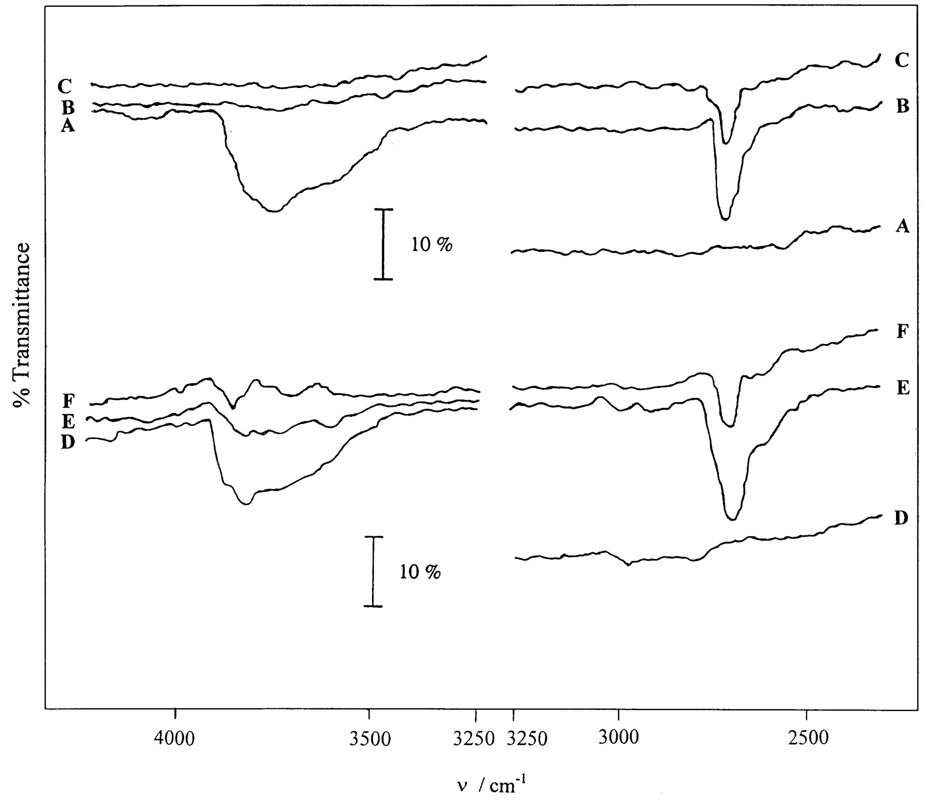


Figure 3. Absorption patterns of Pt/SiO$_2$ and Pd/SiO$_2$ catalysts after various treatments. (A) Pd/SiO$_2$, pretreatment in hydrogen at 523 K for 2 h followed by evacuation for 2 h; (B) Pd/SiO$_2$, pretreatment in deuterium at 523 K for 2 h, followed by evacuation for 2 h; (C) D$_2$ pretreated Pd/SiO$_2$, in argon at 673 K, for 0.5 h; (D) Pt/SiO$_2$, pretreatment in hydrogen at 523 K for 2 h followed by evacuation for 2 h; (E) Pt/SiO$_2$, pretreatment in deuterium at 523 K for 2 h, followed by evacuation for 2 h; (F) D$_2$ pretreated Pd/SiO$_2$, in argon at 673 K, for 0.5 h.

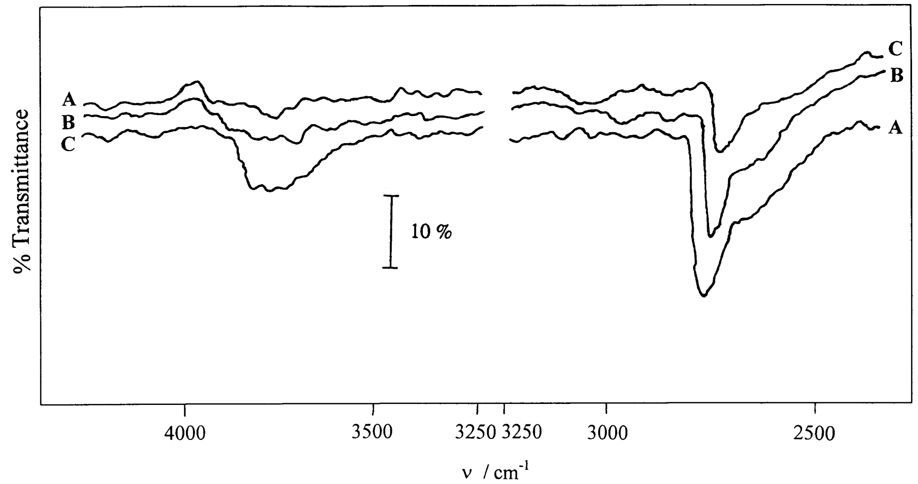


Figure 4. Absorption patterns of Pt/SiO$_2$ catalyst after various treatments. (A) Pretreatment in D$_2$ at 523 K for 2 h, followed by evacuation for 2 h; (B) after contact for 0.5 h with methylcyclobutane at 473 K, followed by evacuation for 2 h; (C) after contact for 0.5 h with methylcyclobutane at 623 K, followed by evacuation for 2 h.

catalysts in the 3300–3700 cm^{-1} wavenumber range (figure 3, curves A and D). This broad OH band can be transformed by a D$_2$ pretreatment at 523 K to a sharper OD band in the 2500–2750 cm^{-1} region (figure 3, curves B and E). After this pretreatment, practically only OD groups are found on the surface. The amount of OD groups strongly decreases after a high temperature heat treatment (673 K, 0.5 h) as a result of surface dehydration (figure 3, curves C and F).

A 0.5 h contact time of the deuterated catalyst samples with 1.33 kPa methylcyclobutane at 473 K over platinum catalyst results in a decrease in the intensity of the OD band, accompanied by the appearance of the broad OH band (figure 4 , curves A and B). A similar treatment with a new portion of methylcyclobutane at 623 K brings about a further decrease in the OD band and the concomitant increase in the intensity of the OH band (figure 4, curve C).

A similar procedure with methylcyclobutane over palladium catalyst resulted in the same trend except for the differences between spectra C and D (figure 5). When the hydrocarbon adsorption was studied at 673 K a further decrease in the OD band intensity was observed without the significant increase in the intensity of the OH band.

Using methylcyclopentane in the surface H–D exchange study the picture is almost the same over Pt/SiO$_2$ and Pd/SiO$_2$. In both cases the hydrocarbon adsorption resulted in the decrease of the OD band intensity with concomitant increase in the OH band intensity. Moreover, the OD band is practically absent after the adsorption of methylcyclopentane over Pt/SiO$_2$ at 623 K (figure 6). Palladium is not as effective in this H–D exchange reaction as platinum, however, the changes in the intensity of the OD and OH bands are significant, especially in the lower temperature region (figure 7).

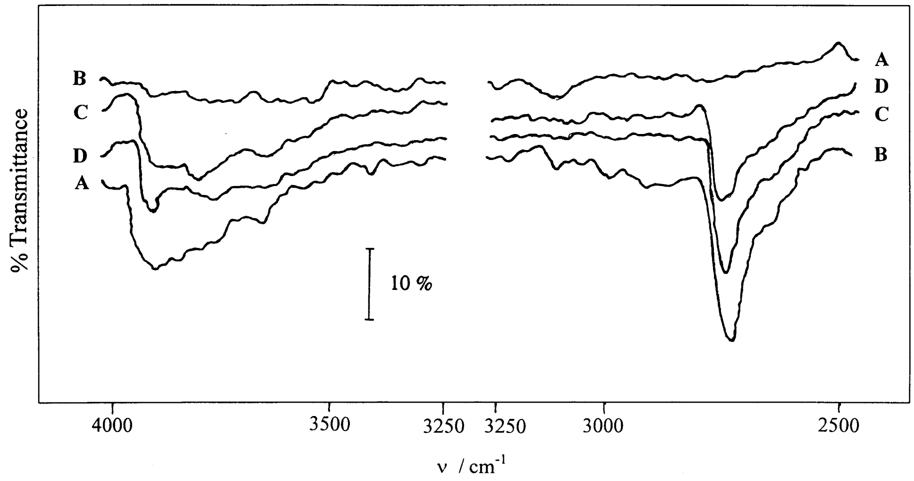


Figure 5. Absorption patterns of Pd/SiO$_2$ catalyst after various treatments. (A) Pd/SiO$_2$, pretreatment in hydrogen at 523 K for 2 h followed by evacuation; (B) pretreatment in D$_2$ at 523 K for 2 h, followed by evacuation for 2 h; (C) after contact for 0.5 h with methylcyclobutane at 523 K, followed by evacuation for 2 h; (D) after contact for 0.5 h with methylcyclobutane at 673 K, followed by evacuation for 2 h.

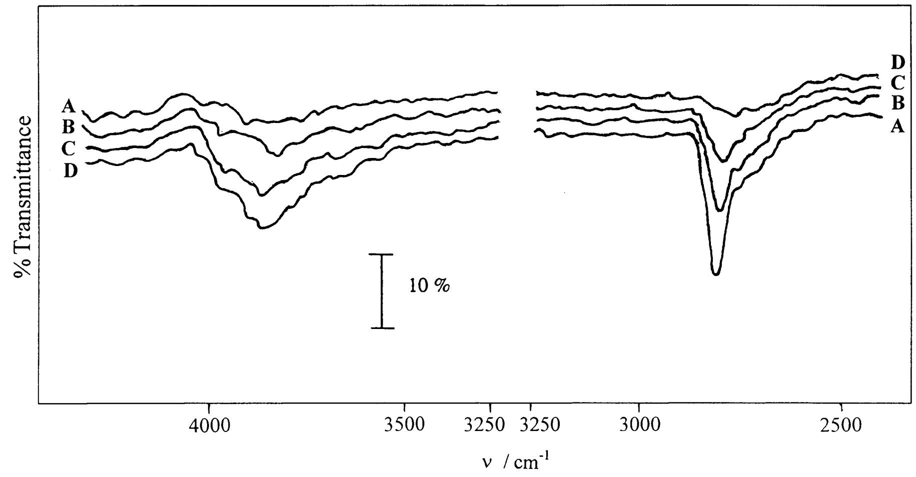


Figure 6. Absorption patterns of Pt/SiO$_2$ catalyst after various treatments. (A) Pretreatment in D$_2$ at 523 K for 2 h, followed by evacuation for 2 h; (B) after contact for 0.5 h with methylcyclopentane at 473 K, followed by evacuation for 2 h; (C) after contact for 0.5 h with methylcyclopentane at 573 K, followed by evacuation for 2 h; (D) after contact for 0.5 h with methylcyclopentane at 623 K, followed by evacuation for 2 h.

4. Discussion

The formation of a surface carbonaceous overlayer in transition metal catalyzed hydrocarbon reactions is a well-known fact [22]. It is also known that the temperature has an important effect on the rate and selectivity of ring-opening reactions, by regulating both the hydrogen coverage of the metal surface and the extent of coking. By raising the temperature, the originally clean metal surface is very quickly contaminated with carbonaceous material to such an extent that the relative contribution of competitive surface reactions (i.e. ring opening, cracking, ring enlargement, aromatization and dehydrogenation) changes. In the present case the carbonaceous overlayer simply covers the active surface and decreases the number of exposed metal atoms. As a result, a conversion maximum tendency is observed for the temperature dependences.

It is worth mentioning that the formation of Pd β-hydride phase is generally observed in hydrogenative reactions at lower temperatures ($<$ 353 K). However, no products were formed below 423 K, thus the selectivity influencing effect of the β-hydride phase could not be detected [23].

The results obtained from the hydrogen pressure dependence studies lead us to several conclusions as follows. The first problem is whether any information concerning the structure of the adsorbed species can be deduced from the shapes of the hydrogen pressure curves and the regioselectivity data. In earlier papers [3,18,24–26] and also in a recent book [27], this topic has been discussed extensively. In the present case the results shown in figure 2b allow us to consider the shape of these curves as an indicator of dissociative or molecular adsorption. As it can be seen the formation rate of the two possible products formed vs. the hydrogen pressure curves show

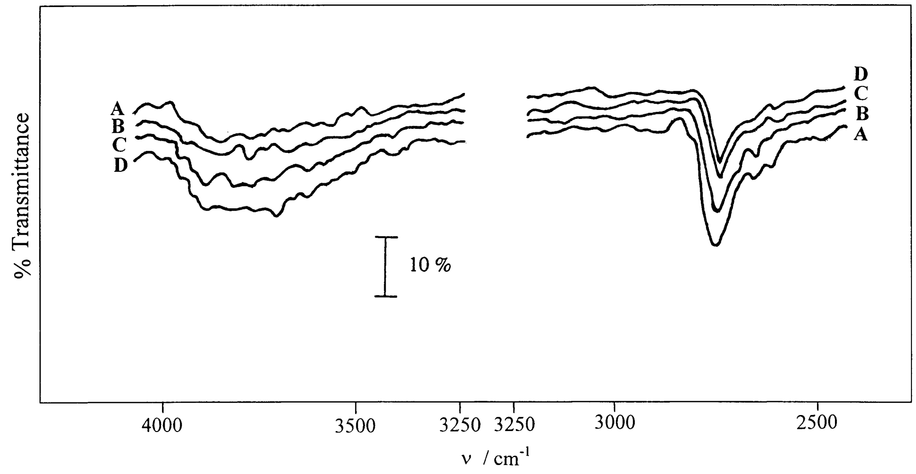


Figure 7. Absorption patterns of Pd/SiO$_2$ catalyst after various treatments. (A) Pretreatment in D$_2$ at 523 K for 2 h, followed by evacuation for 2 h; (B) after contact for 0.5 h with methylcyclopentane at 523 K, followed by evacuation for 2 h; (C) after contact for 0.5 h with methylcyclopentane at 623 K, followed by evacuation for 2 h; (D) after contact for 0.5 h with methylcyclopentane at 673 K, followed by evacuation for 2 h.

different characteristics, proving that simple physical adsorption can be excluded.

As a result, we can consider that (i) if dissociative adsorption occurs then a maximum curve is expected since the high hydrogen excess inhibits the C–H bond rupture,

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

or (ii) if the large hydrogen excess does not hinder the reaction (monotonic increase or saturation), it indicates that molecular adsorption takes place (only C–C bond rupture occurs),

$$C_nH_{2n}(g) \rightleftharpoons C_nH_{2n}(a).$$

Regioselectivity data may lend further support to this conclusion; moreover, they provide information concerning the geometry of the surface intermediates. When the regioselectivity is close to statistical, a flat-lying adsorbed species is suggested for the ring-opening reaction according to the approximately equal accessibility of both ring C–C bonds to the surface active centers. In contrast, in highly regioselective ring opening an edge-on surface intermediate is proposed because the edge type adsorption provides more probability for the rupture of the C–C bond directly adsorbed, while the C–C bond sterically farther has less opportunity to take part in a surface reaction. According to our basic conclusions mentioned before and the literature data the most probable adsorbed intermediates are illustrated in figure 8.

On the basis of the previous studies and present results, hydrogenative ring opening by an associative mechanism can take place with highly strained three- and four-membered ring systems exclusively, however, in the case of cyclobutanes only at higher temperature (above 573 K). This is exactly what we observed for the isopentane formation, which occurs via an associative mechanism over platinum at 623 K (figures 1b and 2b, intermediate **1**), while the pentane formation takes place through dissociative adsorption according to the adlineation mechanism (intermediate **10**) proposed by Kramer et al. [28,29]. Another example was observed over palladium at 673 K (figure 2e), where surface species **3** and **4** are suggested as probable intermediates since the regioselectivity is close to statistical. In all other cases the mechanism of ring opening is most likely dissociative over both catalysts and the presence of intermediates **3**–**6**, **9**–**12**, and **14** is proposed at lower temperatures while surface species of more unsaturated character (**7**, **8**, **13**, **15**) are suggested at higher temperatures.

The bimodal TOF vs. hydrogen pressure curves observed in the ring opening of methylcyclobutane over Pt/SiO$_2$ (figures 1a and 2a) suggest that several intermediates with different hydrogen content exist as a function of the hydrogen pressure. In the lower hydrogen pressure range probably highly unsaturated (**9**–**15**) while at higher pressures more saturated (**3**–**8**) surface species predominate in the ring-opening reaction.

It is interesting to note that the maxima of the TOF vs. hydrogen pressure curves are observed at higher

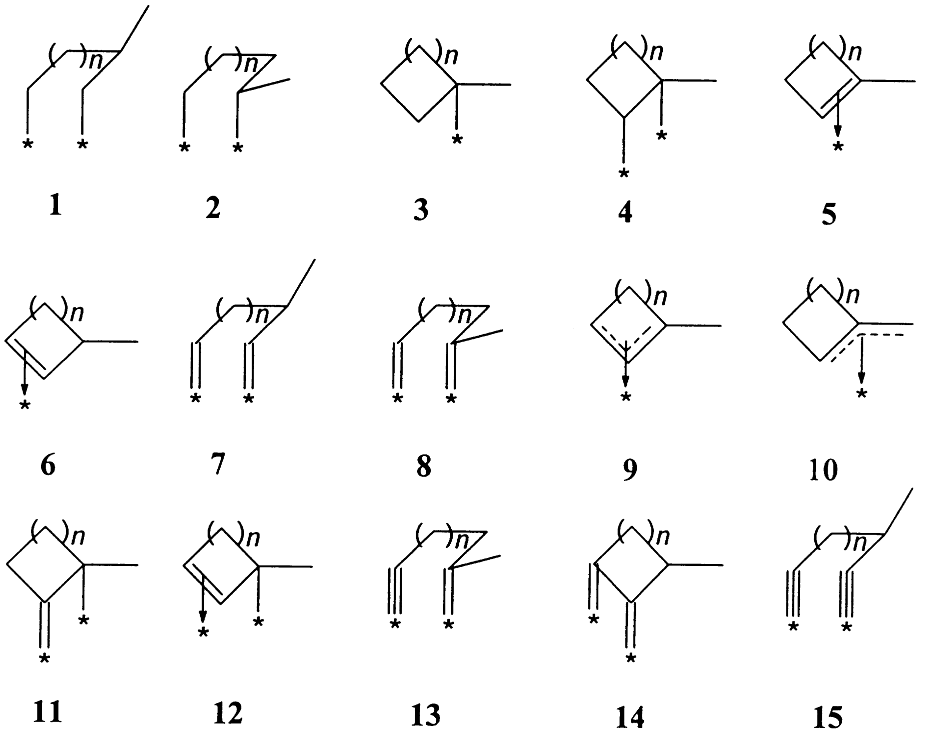


Figure 8. Structural representation of the most probable intermediates assumed in the hydrogenative ring opening of methylcyclobutane and methylcyclopentane ($n = 1, 2$).

hydrogen pressures over working catalysts, most likely because the surface carbonaceous overlayer built up during reaction decreases the available active metal surface. As a result, the calculated reaction rates decrease by an order of magnitude.

However, since the surface concentration of reactive species decreases with raising temperature, in higher temperature regions the extremes of TOF vs. hydrogen pressure curves (generally maxima) may shift towards the higher hydrogen pressures [7,30]. As a result, the extremes can become undetectable in the hydrogen pressure range applied. For instance in the case of methylcyclopentane the reaction rate increases in contrast with the literature data where almost always dissociative adsorption is proposed.

As an additional tool, surface H–D exchange reactions, however, may help exclude or confirm this possibility [31]. In most cases, after the contact with methylcyclobutane or methylcyclopentane, a significant reduction of OD band intensity and the concomitant development of the OH band were observed, indicating that hydrogen appears on the surface. This hydrogen originates exclusively from hydrocarbons. Naturally, the appearance of hydrogen in surface hydroxyl groups assumes and/or indicates the free hydrogen migration from surface metal particles to OD-groups. The further decrease in the OD-band intensity at 673 K without any decrease in OH-band intensity can be interpreted by the dehydration of the surface OD- and OH-groups. This explanation is proven by the results shown in figure 3, using catalyst samples without hydrocarbon treatment. Thus, the results of H–D exchange reactions of surface hydroxyl groups strongly support the conclusions based on the hydrogen pressure studies, which suggested dissociative adsorption. In some cases, however, when molecular adsorption was proposed, the IR spectroscopic measurements do not strengthen the conclusions based on the kinetic studies. In all cases, except for the reaction of methylcyclobutane over Pd/SiO_2 catalyst at 673 K, significant H–D exchange was found. This means, that these hydrogen pressure dependence curves should have a maximum, however, this maximum is most likely out of the hydrogen pressure range studied. As a consequence, dissociative adsorption is proposed according to the IR measurements also in these cases.

In the methylcyclopentane ring opening IR result leads to a proposal of the dissociative adsorption over both catalysts in contrast with kinetic measurements which suggested molecular adsorption in the hydrogen pressure range studied. Most likely, the rate maximum typical to dissociative adsorption should appear in the case of the initial catalysts, as well, as it is found over the working catalysts shown in figures 2c and 2f. According to the regioselectivity data, a flat-lying geometry is suggested for the intermediates of methylcyclopentane ring opening over both catalysts.

5. Conclusions

Hydrogen pressure dependence and surface IR measurements were applied to study the adsorbed surface intermediates in the metal-catalyzed ring-opening reactions of methylcyclobutane and methylcyclopentane. The reactivity of methylcyclobutane and methylcyclopentane strongly differs, methylcyclopentane reacts sluggishly even at high temperatures. Dissociatively adsorbed flat-lying species predominate in the ring-opening reactions of these methylcycloalkanes over Pt/SiO_2 and Pd/SiO_2 catalysts. A molecularly adsorbed, flat-lying intermediate is, however, suggested in the ring opening of methylcyclobutane over Pd/SiO_2 at 673 K and for the *i*-pentane formation over Pt/SiO_2 at 623 K. The results derived from surface H–D exchange measurements studied by IR spectroscopy provide additional information to give a more accurate description of surface intermediates involved in the ring-opening transformation.

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