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Hydrogenative ring opening of propylcyclopropane over silica-supported Pt and Pd catalysts

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The effects of temperature and hydrogen pressure on the hydrogenative ring opening of propylcyclopropane over Pt/SiO_2 and Pd/SiO_2 catalysts were studied. Temperature dependence in the 323–373 K temperature range in a pulse system was investigated, while a static recirculation reactor was used for hydrogen pressure dependence measurements. The ring-opening reactions took place exclusively at all temperatures and hydrogen pressures studied. Monotonous increase was observed for the reactivity of propylcyclopropane as a function of temperature. At constant temperature, the reaction rate vs. hydrogen pressure dependence curves passed through a maximum indicating dissociative adsorption over both Pt and Pd catalysts. The scission of the sterically less hindered direction (producing 2-methylpentane) was the major reaction pathway on both catalysts with practically identical regioselectivity values. On the basis of these results a *selective* mechanism was proposed for the ring-opening reaction.

Keywords: propylcyclopropane; Pt and Pd/SiO_2 catalysts; effects of temperature and hydrogen pressure; mechanism of ring opening

1. Introduction

The transition metal-catalyzed transformations of alkyl-substituted cycloalkanes and especially those of cyclopentanes and cyclopropanes are well-known and popular areas of catalytic research [1–4]. We previously [5,6] surveyed most results on the transformations of cyclopropane derivatives over transition metal catalysts, here only basic conclusions are summarized, as follows:

The earlier literature stated that the adsorption of cyclopropane derivatives is weak, or they react from the gas phase with the strongly adsorbed hydrogen [7]. However, in more recent investigations comparative studies of the adsorption strength of cyclopropane and hydrogen resulted in the conclusion that cyclopropane adsorbs more strongly than hydrogen [8].

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The regioselectivity of the hydrogenative ring-opening reactions was also studied. All authors agree that the ring opens selectively and, in some cases, exclusively in the sterically less hindered direction over conventionally used transition metal catalysts. Recently published papers confirmed this conclusion in the reactions of methylcyclopropane and hydrogen over supported Mo [9], Ru [10], Rh, Pt and Pd [11] catalysts. Propylcyclopropane as a reactant was not popular in catalytic investigation, probably because it is not an easily accessible compound.

Recently we described results concerning hydrogenative ring opening of propylcyclobutane over transition metal catalysts [12,13], where unusual regioselectivity was observed [12]. The high excess of the sterically more hindered ring-opening product was interpreted through a side-chain anchored intermediate. Our major aim is now a more detailed investigation on the role of the propyl side-chain in these metal-catalyzed hydrogenative ring-opening reactions.

In this study, we report on the effects of temperature and hydrogen pressure on the transformation of propylcyclopropane over Pt/SiO_2 and Pd/SiO_2 catalysts. The emphasis is placed on hydrogen dependence measurements, which are expected to reveal important mechanistic information concerning the ring-opening reactions.

2. Experimental

Propylcyclopropane was kindly donated by the Bragin Laboratory of the Zelinkskii Institute (Moscow). It was gas chromatographically pure and was used without further purification, except for a couple of freeze–evacuate–thaw cycles before preparation of the reaction mixture in the hydrogen pressure dependence measurements.

Pt and Pd catalysts supported on silica (Cab-O-Sil, BDH product) were made by impregnation and were characterized [5] as reported earlier. The dispersions of the catalysts were determined by hydrogen or CO chemisorption and were checked by transmission electron microscopy. Characteristic data on the catalysts are listed in table 1.

Table 1
Characteristic data on the catalysts

Catalyst	Loading (%)	Chemisorption		TEM[a]	
		D^b (%)	d^c (nm)	D^b (%)	d^c (nm)
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

[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.

The reactions were carried out in a conventional pulse microreactor system (1 μl pulses), and a static recirculation system (1.33 kPa propylcyclopropane and different amounts of hydrogen) (for more details, see ref. [14]). Measurements were reproducible within 10%. Oxygen-free hydrogen for surface characterization and catalytic measurements was prepared with a Matheson 8326 hydrogen generator. A Carlo Erba Fractovap Mod GV gas chromatograph (thermal conductivity detector) with a 1.2 m long 17% bis-methoxyethyladipate/Chromosorb PAW column (263 K, hydrogen flow rate: 30 cm^3 min^{-1}, pulse system) and a Chrom 4 gas chromatograph (flame ionization detector) with 4 m long 15% squalane/Chromosorb PAW column (323 K, recirculation system) were used for analysis.

Catalysts were pretreated either in flowing hydrogen (flow rate: 30 cm^3 min^{-1}) or in 26.6 kPa hydrogen at 473 K (Pt/SiO_2) and 523 K (Pd/SiO_2) for 1 h. A fresh sample of catalyst (10 mg) was used in each experiment. In the hydrogen pressure dependence studies initial rates were always determined on the basis of product yield vs. time functions. These rates were converted to turnover frequency [15] (TOF: molecule exp. $atom^{-1}$ s^{-1}) data based on the exposed metal atoms determined by hydrogen or CO chemisorption.

3. Results

3.1. TEMPERATURE DEPENDENCE OF RING-OPENING REACTIONS

As it is known, various transformations can be observed in the transition metal-catalyzed reactions of cyclic hydrocarbons. These transformations in general are hydrogenative ring opening (the products are saturated aliphatic hydrocarbons with unchanged number of carbon atoms), cracking (the products are hydrocarbons with shorter chain than ring-opened products) skeletal isomerization, ring enlargement (which produces a saturated hydrocarbon ring with more carbon atoms than in the original). However, cyclopropane derivatives are highly reactive compounds, thus ring-opening reactions can occur even at low temperatures where the above mentioned reactions cannot be observed. For the sake of simplicity the temperature dependence was investigated in such a range (323–373 K). The results are summarized in table 2. They show that the conversion increases with increasing temperature, in contrast with alkyl-substituted cyclobutanes studied earlier, where a temperature optimum was observed [13].

In agreement with earlier results on the metal-catalyzed ring opening of cyclopropanes [1–6,9–11], cleavage of the sterically less hindered C–C bond (formation of 2-methylpentane) is the major ring-opening route. However, this is in contrast with the regioselectivity observed in the ring opening of propylcyclobutane (fig. 1).

Temperature dependence measurements over Pd/SiO_2 catalyst were not carried out, because the ring opening probably occurred at low temperatures similarly to

Table 2
Temperature dependence of conversion and product distribution in the hydrogenative ring opening of propylcyclopropane over Pt/SiO_2 catalyst in a pulse system [a]

T (K)	Conversion (%)	2-methylpentane (%)	*n*-hexane (%)
323	76	75	25
333	79	67	33
348	96	78	22
373	100	77	23

[a] 10 ± 0.1 mg of catalyst, hydrogen (flow rate: 30 cm^3 min^{-1}).

Pt and the formation of Pd β-hydride phase is a well-known fact at these low temperatures (below 353 K) [16]. The formation of β-hydride is negligible for highly dispersed catalysts ($D > 45\%$); however, large Pd particles are transformed to a large extent to $PdH_{0.7}$ at low temperatures [17] (e.g., Pd/SiO_2 catalyst with 13.8% dispersion consists of 90% $PdH_{0.7}$ and 10% metallic Pd [18]). A study of the ring opening of methylcyclopropane showed that the rate of the ring opening decreased significantly over Pd/SiO_2 with low dispersion and no changes were observed over 45% dispersion [17].

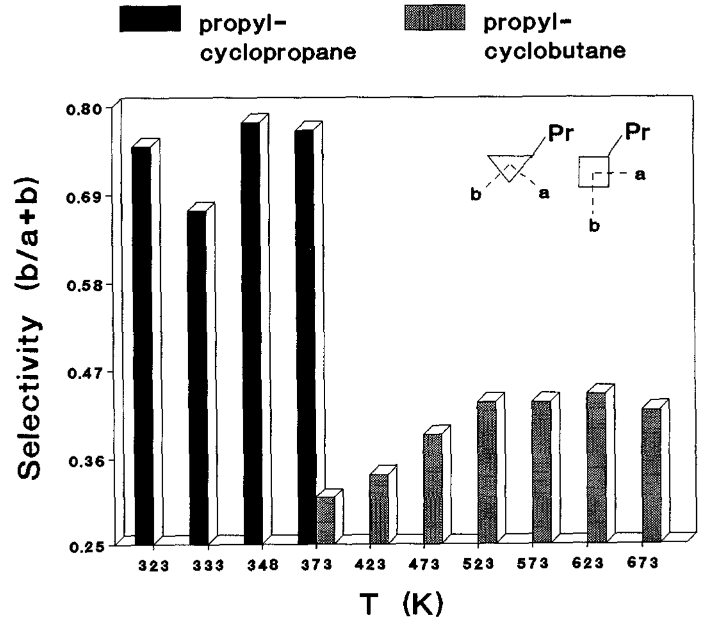

Fig. 1. Temperature dependence of the regioselectivity in the hydrogenative ring-opening reactions of propylcyclopropane and propylcyclobutane (from ref. [12]) over Pt/SiO_2 catalyst in a pulse system.

3.2. EFFECTS OF HYDROGEN PRESSURE ON THE HYDROGENATIVE RING-OPENING REACTIONS

On the basis of the present temperature dependence studies and earlier results concerning the transformations of alkyl-substituted cyclopropanes, the hydrogen pressure dependence was determined at 318 K over Pt/SiO_2 and at 373 K over Pd/SiO_2 catalyst. The latter temperature was selected to avoid the formation of Pd β-hydride as mentioned above. Even though we found the reaction rate to be relatively high at 373 K, this temperature was chosen because the amount of β-hydride was shown to be negligible [5].

Hydrogen pressure dependence of propylcyclopropane over Pt/SiO_2 and Pd/SiO_2 catalysts was investigated in the 0–70 kPa pressure range. Results are depicted in figs. 2 and 3. It can be seen that the initial rate of product formation vs. hydrogen pressure functions passed through a maximum over both catalysts. The reaction rate was higher over platinum than palladium. The rate maximum, however, can be found in an identical region (around 30 kPa hydrogen pressure).

Regioselectivity data were similar to those observed in the temperature dependence studies and opposite to the regioselectivity of hydrogenative ring opening of propylcyclobutane. The major direction of ring opening was the scission of the sterically less hindered C–C bond. Regioselectivity data of propylcyclopropane ring opening and earlier results of propylcyclobutane for comparison are given in table 3.

4. Discussion

The experimental data show that ring-opening reactions take place exclusively

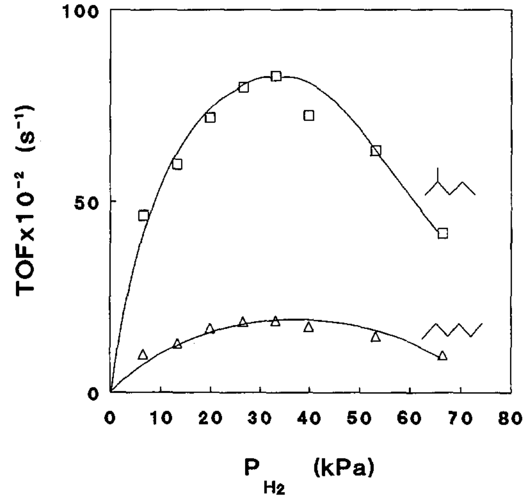

Fig. 2. Hydrogen pressure dependence curves in the hydrogenative ring-opening reactions of propylcyclopropane over Pt/SiO_2 catalyst at 318 K.

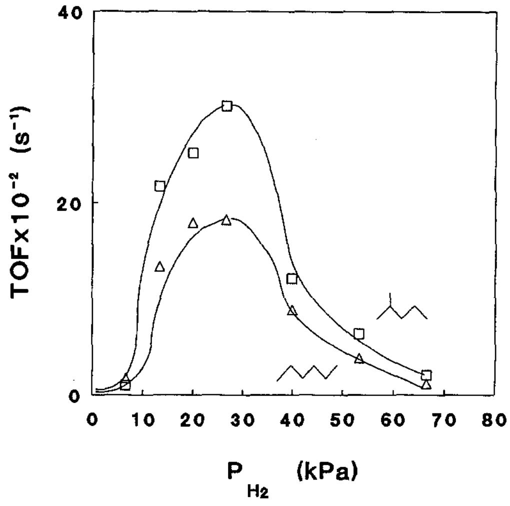

Fig. 3. Hydrogen pressure dependence curves in the hydrogenative ring-opening reactions of propylcyclopropane over Pd/SiO_2 catalyst at 373 K.

at the temperature and hydrogen pressure range studied. This is not surprising, since at these relatively low temperatures side-reactions as mentioned above cannot be expected. Similarly, the formation of surface carbonaceous deposits is very slow at these temperatures, thus a considerable effect on the reaction rate or selectivity cannot be observed. The hydrogen rich surface without hydrogen poor carbonaceous overlayer ensures that the reaction rate (or conversion) increases monot-

Table 3

Regioselectivity data in the hydrogenative ring-opening reactions of propylcyclopropane and propylcyclobutane at different hydrogen pressures over Pt/SiO_2 and Pd/SiO_2 catalysts

p_{H_2} (kPa)	Pt/SiO_2		Pd/SiO_2	
	PRCP[a]	PRCB[b]	PRCP[c]	PRCB[d]
6.7	0.82	0.35	0.46	0.21
13.3	0.82	0.15	0.63	0.24
19.9	0.81	0.27	0.55	0.28
26.6	0.81	0	0.62	0.33
33.2	0.83	–	–	0.28
39.9	0.79	0	0.56	0.27
53.2	0.81	–	0.62	0.33
66.5	0.80	0.38	0.59	0.34

[a] PRCP – propylcyclopropane, $T = 318$ K, $r_{2\text{-methylpentane}}/(r_{2\text{-methylpentane}} + r_{\text{hexane}})$.

[b] PRCB – propylcyclobutane, $T = 373$ K, $r_{3\text{-methylhexane}}/(r_{3\text{-methylhexane}} + r_{\text{heptane}})$. Data from ref. [12].

[c] PRCP – propylcyclopropane, $T = 373$ K, $r_{2\text{-methylpentane}}/(r_{2\text{-methylpentane}} + r_{\text{hexane}})$.

[d] PRCB – propylcyclobutane, $T = 523$ K, $r_{3\text{-methylhexane}}/(r_{3\text{-methylhexane}} + r_{\text{heptane}})$.

onously in the temperature range studied. Moreover, at 373 K the total amount of propylcyclopropane was transformed into its ring-opened products. It is in contrast with the ring opening of propylcyclobutane, where a temperature optimum was observed due to the rate lowering effect of hydrogen poor carbonaceous residues formed at high temperatures [12].

The shapes of the hydrogen pressure dependence curves suggest that propylcyclopropane adsorbs either dissociatively or the reaction can be interpreted by a simple Langmuir–Hinshelwood mechanism [19]. However, since alkylcyclopropanes adsorb more strongly than hydrogen [8], the competition is lost for hydrogen, which cannot remove the reactive intermediates from the surface. The adsorbed hydrogen probably only regulates the hydrogen content of the adsorbed species. The negative hydrogen order for the ring opening in the higher pressure range after the rate maximum indicates that the high excess of hydrogen inhibits the C–H bond rupture, namely dissociative adsorption occurs.

The regioselectivity data of the ring-opening reaction of propylcyclopropane show that the ring opens predominantly in the sterically less hindered direction. This is in striking contrast with the regioselectivities observed with propylcyclobutane [12]. A probable reason of this phenomenon is the difference in the relative rates of ring opening vs. side-chain anchoring for the two compounds. Cyclopropanes are highly strained compounds. Thus, it is reasonable to assume that the adsorption of propylcyclopropane through its side-chain is much slower than ring-opening reactions. The propyl group, consequently, affects selectivity only via steric hindrance ensuring a large excess of 2-methylpentane, especially over platinum. A comparison of the selectivity data of methyl- (Pt: ~0.9, Pd: ~0.6) [11], ethyl- (Pd: ~0.6) [20] and propylcyclopropane (Pt: ~0.8, Pd: ~0.6) supports this interpretation. These data obtained by independent research groups all show the decisive role of ring adsorption in determining ring-opening selectivities. Selectivity data on both catalysts suggest edge-on geometry for adsorbed surface species, however, flat-lying geometry probably also exists over Pd/SiO_2 catalyst.

In the case of propylcyclobutane, selectivity data prompted us to propose adsorption through both ring and side-chain carbon atoms [12]. In other words, due to the significantly less ring strain, ring opening should be slower than side-chain adsorption, consequently, propyl group anchoring leads to the prevailance of side-chain bonded edge-on adsorbed intermediates [12]. The importance of side-chain length in determining regioselectivity in the cyclobutane series becomes evident when these data are compared for methyl- (Pt: ~0.5, Pd: ~0.5) [21], ethyl- (Pt: ~0.4, Pd: ~0.4) [22] and propylcyclobutane (Pt: ~0.2, Pd: ~0.2) [12,23].

5. Conclusions

Hydrogen pressure dependence measurements revealed that propylcyclopropane adsorbs via dissociatively adsorbed edge-on intermediates. Since the ring-opening reaction is fast due to the highly strained ring, the regioselectivity-governing effect of the propyl side-chain observed for propylcyclobutane is lacking. Here steric hindrance overrides the adsorption effect.

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