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The effects of hydrogen pressure and temperature on the methylcyclopentane conversion on Rh catalysts

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Abstract

The effect of hydrogen pressure (pH_2) and temperature (T) was investigated on the hydrogenolytic ring opening of methylcyclopentane (MCP) over silica and alumina supported rhodium catalysts. Strong dependence could be seen in the activity and in distribution of ring opening products as a function of reaction conditions. Temperature and hydrogen pressure did not affect the position of the first C–C bond rupture. However, the final ring opening product distribution was largely influenced by the reaction conditions due to the different ability of intermediates to undergo further hydrogenolysis.

Keywords: Rh catalysts; Methylcyclopentane ring opening; Hydrogen pressure and temperature effect

1. Introduction

The discovery of the C_5-cyclic isomerization route [1] made it important to understand the ring opening (RO) mechanism, as one of its reaction steps. Several studies were carried out with different active metal catalysts [2] and with different reactants (various alkylcyclopentanes) [3]. Among others, the effect of support [4,5], particle size (dispersion) [5–8], temperature [9], hydrogen pressure [10,11], catalyst pretreatment [12–14], poisoning [15–17] were investigated. An early recognition [18] of the influence of mean particle size on the selectivity of methylcyclopentane (MCP) RO over Pt made a strong impression on later studies. The rate of dehydrogenation (α,α,β,β-tetraadsorbed species for selective RO) and the geometry of the intermediate (edgewise) were frequently adopted. However, the validity of this is strongly questionable on other metals, like Ir and Rh, as no real particle size effect was detected comparable to Pt. Further, the rate of dehydrogenation displays considerable differences shown by the olefin production on Pt at low pH_2 and high temperature [3,13]. Olefins were not produced by Ir [15,16] and Rh [4,7–9], both exhibiting higher fragmentation activity. Consequently, we cannot be satisfied with the application of the selective mechanism proposed for Pt, here, for rhodium. We can select such conditions (hydrogen pressure and temperature) for the MCP conversion on Rh (which is an active catalyst for fragmentation), where the selectivity of *both* single and multiple hydrogenolysis can change in wide ranges. Thus, comparing the two main types of reaction, we can get closer to the understanding of their mechanism(s).

2. Experimental

Five per cent Rh/Al_2O_3 and 5% Rh/SiO_2 were prepared by wet impregnation of the supports with

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aqueous solution of $RhCl_3 \cdot 3H_2O$. After impregnation and drying at 393 K, the silica supported catalyst was calcined in air at 723 K for 4 h and reduced in H_2 at 773 K. The alumina supported catalyst was reduced at 573 K. The dispersion (D) of the catalysts was determined by H_2–O_2 titration, assuming a stoichiometry of $H, O/Rh = 1$.

The catalytic experiments were carried out in a closed circulation loop glass reactor [19] connected to a CP 9001 gas chromatograph with a 50 m squalane coated steel capillary column and an FID detector. A standard MCP pressure of 10 Torr was used and the hydrogen pressure was varied between 120 and 480 Torr. The reaction temperatures ranged from 468 to 513 K. The sampling took place after 5 min. Thus, TOF values were calculated assuming a contact time of 5 min. Selectivities (S) were expressed on the basis of moles of MCP reacted rather than considering the product moles formed, i.e. disregarding mole number increase due to fragmentation. This can be helpful identifying the percentage of reactant participating in RO or in fragmentation. The term "ring opening products" (ROPs) refers to saturated C_6-products, while "fragments" mean products contain less than six carbon atoms. Activities and selectivities were determined at conversion values between 0.5 and 10%.

3. Results

RO (C_6-alkanes) and hydrogenolysis products ($<C_6$-fragments) were formed from MCP on 5% Rh/SiO_2 ($D = 36\%$) and 5% Rh/Al_2O_3 ($D = 21\%$). No unsaturated hydrocarbons were detected. The selectivities did not change during longer runs up to ∼20% conversion values, indicating that secondary reactions were not important. Thus, the product selectivities on different catalysts could be compared even at different conversion levels.

Table 1
Activity and selectivity pattern in the conversion of MCP over Rh catalysts[a]

	$T = 468$ K		$T = 513$ K	
	10:120[b]	10:480[c]	10:120[b]	10:480[c]
Rh/Al_2O_3				
TOF (h^{-1})	23	60	39	145
$S(<C_6)$ (%)	13.3	1.4	36	13.7
C_1[d]	54.6	51.4	61.8	51.3
i-C_5[d]	21.9	25.5	14.1	20.9
b/a	5.2	6.1	3.3	4.2
b/c	1.6	2.2	1.3	1.8
Rh/SiO_2				
TOF (h^{-1})	6.3	31	15	162
$S(<C_6)$ (%)	14.8	4.4	62.2	26
C_1[d]	56.4	53.2	68.8	54.9
i-C_5[d]	21.5	27.9	7.9	19.1
b/a	11.2	20.5	4.6	8.8
b/c	1.6	2.5	1.4	2

[a] a: n-hexane; b: 2MP; c: 3MP; C_1: methane; i-C_5: i-pentane.
[b] $MCP:H_2 = 10:120$.
[c] $MCP:H_2 = 10:480$.
[d] Normalized to 100% fragments.

We focused mainly on the selectivity changes as the function of reaction conditions (T, pH_2). Table 1 depicts the TOF values, the relative importance of the fragmentation compared to RO and the typical values from the product distributions for the two catalysts as a function of the reaction conditions. Results measured at the two extremes in *both* temperature and hydrogen pressure are presented. As reported previously [8], the activity for the overall reaction shows a positive hydrogen order. This can be attributed to the strong positive hydrogen order of the RO reaction, since fragmentation had almost zero hydrogen order. Slightly increasing fragmentation activity for Rh/SiO_2 and maxima on Rh/Al_2O_3 with increasing pH_2 was found. Less fragments (compared to RO) were formed at higher pH_2. This apparently contradicts the reaction stoichiometry and indicates, instead, the different dehydrogenation of the respective surface intermediates. The positive hydrogen order for RO points to an *associative* surface species, contrary to [6,18]. Multiple C–C bond breaking was more pronounced on Rh/SiO_2, the differences were more marked at higher temperatures. Increasing dispersion contributed to higher fragmentation selectivity [8], however, even 0.3% Rh/Al_2O_3 ($D = 57\%$) (as reported in Ref. [8]) produced only 58% fragments under conditions when $S(<C_6)$ was 62% on Rh/SiO_2 ($D = 36\%$). Thus, dispersion changes cannot be the only reason for the higher fragmentation on Rh/SiO_2 and a support effect should also be suggested. The hydrogen pressure largely determined the multiplicity of hydrogenolysis (Table 1), thus one possible explanation can be the difference in the surface hydrogen concentration caused by the different hydrogen spillover ability of the two

supports [20,21]. This effect is also visible in the fragment distribution, the main fragments being CH_4 and *i*-pentane (Table 1). More than 50% of the fragments was methane, its amount increasing with temperature. Another main component was *i*-pentane. Other fragments appeared in similar, low amounts. Higher temperatures increased the methane selectivity at the expense of *i*-C_5. Higher pH_2 had an opposite effect: more *i*-pentane and less methane were formed. The most pronounced differences between the two catalysts can be seen at $T = 240\,K$ and $pH_2 = 120\,Torr$. Most of the MCP that produced fragments underwent total decomposition to methane on Rh/silica.

The RO of MCP occurred “selectively” [19], i.e. the rupture in the vicinity of methyl group (position “a”) was strongly hindered. Thus, mainly 2-methylpentane (2MP, rupture in position “b”) and 3-methylpentane (3MP, rupture in position “c”) were formed. Table 1 shows the distribution of ROPs (2MP/*n*H) as a function of temperature and pH_2. Changes in the reaction conditions caused drastic alteration in the ROP distribution. High hydrogen pressure and low temperature increased the relative importance of 2MP. Here, once again a clear support effect seems to operate, since the silica supported catalyst exhibits much higher “b/a” selectivity. The most marked differences in “b/a” can be seen when the fragment selectivity is the lowest.

The ratio breaking the two different bisecondary bonds (2MP/3MP) was between 1.3 and 2.5, i.e. rather close to the statistical value of 2. A slight variation of the ratio 2MP/3MP was seen as a function of T and pH_2. More 3MP was found at higher temperature and lower pH_2.

4. Discussion

The differences in RO of several alkylcyclopentanes could be sufficiently explained [3] based on assuming a flat-lying reaction intermediate [22]. The first step of the selective RO would be a dissociative adsorption via the tertiary carbon atom. The metal atom interacting with the tertiary C atom would then hold the ring in a way that the next metal atom could interact with the C–C bonds in position “b” or “c” [2,22]. This model could adequately explain RO far from the substituent. Low hydrogen pressure, i.e. strong dehydrogenation inhibited RO; olefin production prevailed on Pt while fragmentation increased on Rh. On Pt-black and EUROPT-1 with 1,2-dimethylcyclopentane (DMCP) reactant, high amount of olefins (mainly, with double bond between the two tertiary carbon atoms) were observed and only slight amount of olefins were formed from 1,1-DMCP even at low pH_2 [3].

Alternatively, a single metal atom was proposed [23,24] as the possible active centre in hydrocarbon rearrangements. The same active centre would be involved in both hydrogenolysis and skeletal rearrangement of *n*-hexane [23] and only the local environment (carbonaceous deposit, blocking layer of TiO_x) may determine the prevailing route, and thus the reaction selectivity. We propose a similar model where the surface hydrogen availability would be the main factor in the “local environment” [10]. We suggest the same active site for RO and fragmentation, their intermediates differing only in the rate of dehydrogenation.

We found [8,26] correlation between the product distributions of the two main reactions (RO and fragmentation). Two different patterns of MCP RO were observed on Rh/Al_2O_3: (i) in the case of low metal loading and small particles ($d < 3\,nm$), the distribution of ROP did not change as a function of T and pH_2 and the ratio “b/a” was not too high, (ii) in the case of high metal loading and larger particles ($d > 3\,nm$), the ROP distribution was strongly dependent on the conditions. In the latter case, product distributions similar to Fig. 1 were obtained. This is a selectivity comparison for *n*-hexane, 3MP, 2MP and 2MP + fragments as a function of temperature and pH_2. Four increasing hydrogen pressures (120, 240, 360 and 480 Torr) are included at each temperature. Fig. 1 shows constant selectivities (with the exception of 2MP) for the three lower temperatures. This statement is almost valid for the whole temperature range if we leave out the point denoted by arrow. The latter point represents a measurement where the fragmentation selectivity was the highest. The constant *S*(3MP) and *S*(*n*H) values reveal that fragments were mainly produced after RO in position “b” and by subsequent C–C bond rupture(s) before desorption of the intermediate. The fragment distributions obtained from the hydrogenolysis of primary ROPs (hexane isomers) [25] support this model.

The different hydrogen pressure responses (“b/a”, “b/c” vs. pH_2 in Table 1) can be explained with the help of Fig. 1. The increase of the 2MP/*n*H and

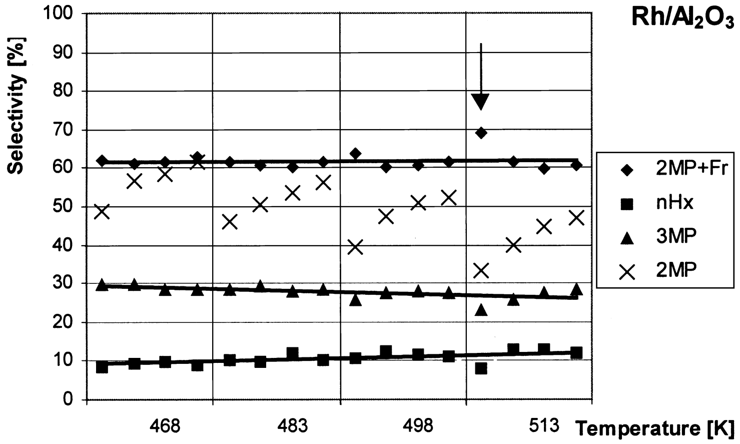

Fig. 1. Selectivity comparison for *n*-hexane, 2MP, 3MP and 2MP + fragments on Rh/Al_2O_3. Each temperature includes four increasing hydrogen pressures (120, 240, 360 and 480 Torr).

2MP/3MP ratios as a function of hydrogen pressure was the result of the decreasing fragmentation selectivity with pH_2. The amount of 2MP increased parallel to this. The *S*(*n*H) and *S*(3MP) values were, at the same time, constant, thus the ratios "b/a" and "b/c" increased. Similar explanation can be given for the temperature effect.

Fig. 2 contains the same selectivity comparison for Rh/SiO_2. Figs. 1 and 2 being similar, we conclude that there are no drastic changes in reaction mechanism. However, some differences are clearly visible. Rh/SiO_2 is between the two groups we proposed in [8]. *S*(*n*H) is still constant (decreased to ~5% compared with ~10% on Rh/Al_2O_3), and the variations of *S*(3MP) were similar to *S*(2MP). We observed [8] that *S*(*n*H) was ~10% on Rh/Al_2O_3 and did not depend on the dispersion (between 18 and 67%), thus a possible support effect may contribute to the bond breaking in "a" position. The effect of *T* and pH_2 in *S*(3MP) indicates that the further hydrogenolysis of the 3MP-intermediate starts at milder conditions for the silica supported Rh catalyst.

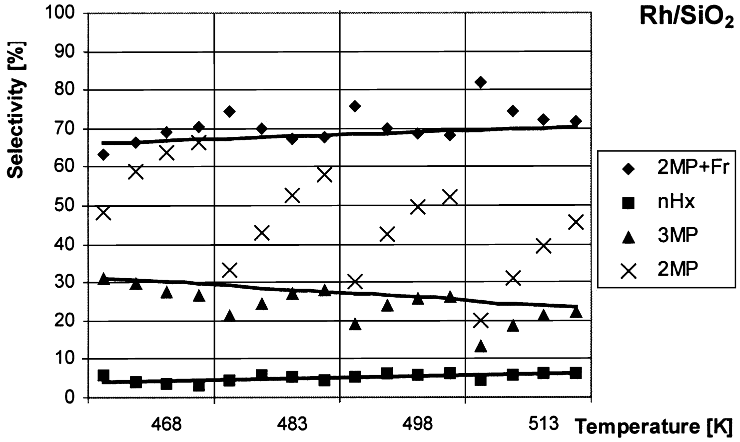

Fig. 2. Selectivity comparison for *n*-hexane, 2MP, 3MP and 2MP + fragments on Rh/SiO_2. Each temperature includes four increasing hydrogen pressures (120, 240, 360 and 480 Torr).

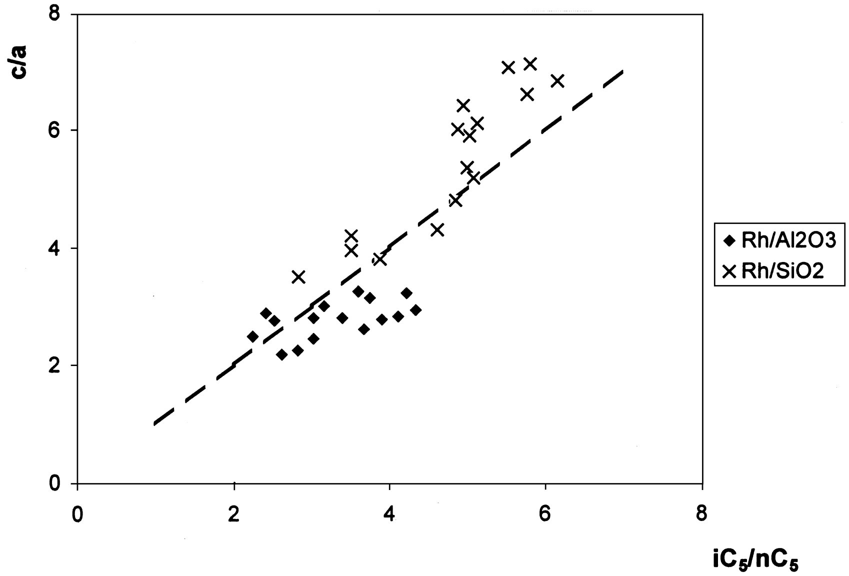

Fig. 3. Correlation between the ratio of 3MP to *n*-hexane (c/a) in the ROPs and the C_5-fragment ratio (i-C_5/n-C_5). Data obtained at each temperature and hydrogen pressures are included. The straight line represents the ideal case of $c/a = i\text{-}C_5/n\text{-}C_5$.

Figs. 1 and 2 indicate that the possibility of the first C–C bond breaking is independent of the reaction conditions and is only slightly affected by the support. However, the final ROP distribution is determined by the competition between further hydrogenolysis of RO-intermediates and their desorption. The prevailing route strongly depends on T and pH_2.

A correlation existed [26] between RO and fragment distribution. The governing effect of rhodium was still present in the fragment distribution as could be concluded from the pronounced production of *i*-pentane to *n*-pentane. The loose positive correlation between 3MP/*n*H and i-C_5/n-C_5 illustrated in Fig. 3 indicates that the effect of support on the bond breaking in position “a” is still present in the fragment distribution, thus the correlation is regardless of the support.

5. Conclusions

The following reaction mechanism is proposed for MCP conversion on rhodium: MCP is chemisorbed on a rhodium atom through its tertiary carbon atom (C–H bond breaking). Since the RO shows a positive hydrogen order, the intermediate leading to ROP is not strongly dehydrogenated. The inherent catalytic properties of Rh determines the probabilities of the position for the first C–C bond breaking (the support exerting a slight effect but no influence of the reaction conditions is visible) — “b”: 60–68%, “c”: ~30%, “a”: 2–10%.

The nearly “zero” hydrogen order for fragmentation indicates a higher dehydrogenation of the surface intermediates after the first C–C bond cleavage. The ability of the RO intermediates to undergo further hydrogenolysis was in the following order:

$$2MP > 3MP > nH$$

Thus fragments were produced mainly at the expense of branched isomers. Therefore, the final RO distribution is determined by the reaction conditions (T, pH_2) governing desorption, dehydrogenation and further C–C bond ruptures of the primary C_6-intermediates.

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