

Reactivity of the hydrocarbon C–C bonds as a function of the reaction conditions in the conversion of C₆ alkanes and methylcyclopentane over Rh catalysts

D. Teschner^{a,*}, D. Duprez^b, Z. Paál^a

^a Institute of Isotope and Surface Chemistry, Chemical Research Center, Hungarian Academy of Sciences,
P.O. Box 77, H-1525 Budapest, Hungary

^b Laboratoire de Catalyse en Chimie Organique, UMR 6503, 40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France

Received 19 April 2001; accepted 16 August 2001

Abstract

The conversion of 3-methylpentane (3MP), 2-methylpentane (2MP), *n*-hexane (*n*H), and methylcyclopentane (MCP) was investigated on 0.3 and 10% Rh/Al₂O₃ and 5% Rh/SiO₂ as a function of hydrogen pressure and temperature. The catalysts were prepared by the incipient wetness method. Metal accessibility was 57, 18 and 36%, which corresponded to mean particle size of 1.5, 5 and 2.5 nm, respectively. The hydrogenolytic cleavage of hydrocarbon C–C bonds was the main reaction. Skeletal isomers (up to 20%) were formed from methylpentanes on 10% Rh/Al₂O₃. C₅-cyclization was a minor reaction (less than 10%) and was promoted by low *p*(H₂). Particle size effect was clearly observed in the non-degradative reaction path; this route was favored by larger Rh particles. Single splitting of C–C bonds was catalyzed at high hydrogen coverage. Decreasing *p*(H₂) caused “deepening” of the hydrogenolysis and the catalysts lost much of their activity. The hindrance in the re-hydrogenation of the surface intermediate of fragmentation was proposed to explain the positive hydrogen order. The role of further hydrogenolysis of particular fragments or ring opening intermediates was significant at low *p*(H₂). Reaction conditions governed the desorption or the further reactions of the surface intermediates. For instance, fragments were produced in the conversion of MCP mainly from branched ring opening intermediates. The fragmentation patterns of hexane isomers were successfully applied for modeling the fragment distribution of MCP. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rh catalysts; Hydrogenolysis; Desorption hindrance

1. Introduction

A study of several metal blacks [1] revealed that four metals: Pt, Pd—and to a lesser extent—Ir and Rh were able to catalyze the closure of C₆ alkanes to a C₅-cycle as well as the non-degradative opening of that ring. Others such as Co, Ni, Ru or Os showed

almost exclusively extensive hydrogenolysis yielding mainly methane. However, small particles of Ni [2] and Ru [3] advanced single splitting rather than multiple hydrogenolysis. An opposite behavior was found in the conversion of methylcyclopentane (MCP) on Rh, inasmuch as a higher ratio of fragments was produced on smaller particles [4]. Accordingly, the influence of particle size in different systems should not be the same, or another more dominant effect conceals it.

Changes in the dispersion of the catalyst cause selectivity alteration in structure sensitive reactions.

* Corresponding author. Tel.: +36-1-3922222;

fax: +36-1-3959075.

E-mail address: teschner@iserv.iki.kfki.hu (D. Teschner).

Well-known examples are the ring opening of MCP on Pt catalysts [5–8] or the hydrogenolysis of 2,2,3,3-tetramethylbutane (2233TMB) on Rh/alumina [9,10]. Variation in the particle size or in the exposed crystal facet changed the main reaction route due to modification of the prevailing surface intermediate. Modification of the rhodium particle size affected markedly the turnover frequency (TOF) of the hydroconversion of several alkanes [9,10]. This was generally accompanied by rather marginal alteration in the reaction selectivities. The only exception was already mentioned hydrogenolysis of 2233TMB, where the positions of the C–C bond cleavage changed dramatically.

“Archetypal” molecules containing special structural parts, “units”, are great significant in testing catalysts. Such an archetypal molecule is neohexane (2,2-dimethylbutane), which was very sensitive to the nature of metals applied in its reaction [11]. The main reaction modes [12] were regarded to be governed by an electronic effect [13]. In the approach of *C₂-unit mode* and *iso-unit mode* introduced by Foger and Anderson [12], rhodium can be termed as a metal catalyzing reactions in the *C₂-unit mode*. This would mean the reaction of bonds containing only primary or secondary carbon atoms. The predominance of the neopentane fragment from 2,2-dimethylbutane supports this statement [9,11].

Rhodium has a great importance in present-day heterogeneous catalysis; its association with Pt having an utmost importance in car exhaust afterburners [14,15]. Rhodium is a high-activity catalyst for the hydrogenolytic cleavage of hydrocarbon C–C bonds, and promotes skeletal rearrangement to a lower extent. 100% fragmentation selectivity was reported in the conversion of *n*-hexane (*n*H) on Rh films at 523 K [16]. Supported Rh catalysts produced some methylpentanes from *n*H with different selectivities. Coq et al. [10] found about 1% isomers on several Rh/SiO₂ or Rh/TiO₂ at 493 K. Schepers et al. [17] found 9% methylpentanes on 2% Rh/SiO₂ at 523 K increasing to 13% at 623 K. Anderson and Burch [18], in turn, reported *higher* isomer selectivities at *lower* temperature. The ring opening of MCP was always selective on Rh, the rupture of the C–C bond near to the methyl group was hindered [4,9,17,19]. Similar reluctance to cleave bonds in the vicinity of a *tertiary* carbon atom was also found in the conversion

of methylpentanes [19,20]. The selectivity of isomers was about 10% here.

Several mechanisms were proposed to explain the variety of hydrocarbon reactions on metals. Single or multiple site mechanisms with 1,2-, 1,3-, 1,4-, 1,5-adsorbed geometries were suggested. Coq and Figueras [9] offered two large classes of surface intermediates in the conversion of alkanes over supported rhodium catalysts, metallocarbenes prevailing on large Rh particles, and π -adsorbed allyl species independently of the particle size.

The surface hydrogen availability—affected by the pressure of hydrogen, the temperature and carbonaceous deposits—can drastically influence the activity as well as the reaction selectivity [21]. The lack of surface hydrogen on Rh can induce more severe dehydrogenation of the adsorbed reactant contributing to complete degradation of the hydrocarbon molecule rather than desorption of the unsaturated surface species. The multiple degradation process during one sojourn of the reactant can occur either as multiple terminal splitting or as a complete degradation of one of the specific possible product without its desorption [3].

The aim of this work was to clarify the reactivity of individual C–C bonds as a function of the surface hydrogen availability in the conversion of different alkanes and MCP on rhodium. This knowledge may lead us to a better identification of possible surface intermediates of hydrocarbon conversion on Rh. The hydrogenolysis of the primary ring opening products of MCP was regarded to explain the multiple degradation of MCP.

2. Experimental

0.3 and 10% Rh/Al₂O₃ and 5% Rh/SiO₂ were prepared by wet impregnation of the supports with aqueous solution of RhCl₃·3H₂O. After impregnation and drying at 393 K the silica-supported catalyst was calcined in air at 723 K and reduced in H₂ at 773 K. The alumina-supported catalysts were reduced at 573 K. The dispersion of the catalysts were measured by H₂–O₂ titration assuming a stoichiometry of H/Rh = 1. The values were found to be 57, 18 and 36% corresponding to mean particle size of 1.5, 5, and 2.5 nm respectively, in the above order.

The catalytic experiments were carried out in a closed-loop apparatus connected to a CP 9001 gas chromatograph equipped with a 50 m CP-Sil 5CB capillary column. The conversion of 3-methylpentane (3MP), 2-methylpentane (2MP), *n*H, and MCP was investigated. The reactants were of Merck, GC grade. The traces of impurities (<0.4%) in the reactants were corrected for when calculating the product composition. A standard hydrocarbon pressure of 10 Torr was used and the hydrogen pressure was varied between 60 and 480 Torr. The reaction temperatures ranged from 453 to 513 K. The sampling took place after 5 min. Regeneration between runs was carried out with 30 Torr air for 2 min followed by evacuation and 3 min hydrogen treatment with 100 Torr at reaction temperature.

The turnover frequencies were calculated as the number of hydrocarbon reacted per one surface Rh atom per hour. Selectivities (*S*) were expressed as moles of hydrocarbon reacted rather than product moles. These two values are different due to mole

number increase during hydrogenolysis. The selectivities did not change during longer runs up to ~20% conversion and we kept the conversion lower than 15%. This means that secondary reactions following readsorption of products were not important, thus the product selectivities on different catalysts could be compared, even at different conversion levels. This behavior of Rh showing constant selectivities up to high conversion level was also recognized earlier [22]. To describe the pattern of hydrogenolysis for different bonds, we used the reactivity factor, ω defined by Leclercq et al. [23] as the actual rate of rupture divided by the expected (statistical) rate of rupture. The fragmentation factor, ζ [1] represents the average number of fragments per hydrocarbon molecule decomposed. "Multiple" and "terminal" fission (i.e. the simultaneous or stepwise breakdown to methane) can be distinguished by the use of the M_f parameter [24] which relates the amount of larger fragments to that of methane.

Table 1
Activity and selectivity pattern in the conversion of 3MP over Rh catalysts^a

| CH: <i>p</i> (H ₂) (Torr), <i>T</i> = 483 K | TOF (h ⁻¹) | Hydrogenolysis | | | | | Isomerization | | C ₅ -cyclization to MCP, <i>S</i> _{MCP} |
|--|------------------------|-----------------------|------------|---------------|----------------|---------|-----------------------|-----------------|--|
| | | <i>S</i> _C | ω_I | ω_{II} | ω_{III} | ζ | <i>S</i> _i | 2MP/ <i>n</i> H | |
| <i>10% Rh/Al₂O₃</i> | | | | | | | | | |
| 10:60 ^b | 22 | 82.5 | 0.8 | 1.64 | 0.46 | 2.86 | 7.9 | 1.52 | 9.6 |
| 10:60 | 20 | 90.5 | 0.81 | 1.65 | 0.45 | 2.65 | 12.5 | 1.76 | 7.0 |
| 10:120 | 39 | 77.0 | 0.69 | 1.75 | 0.4 | 2.44 | 17.7 | 1.99 | 5.3 |
| 10:240 | 84 | 77.1 | 0.57 | 1.82 | 0.4 | 2.31 | 20.6 | 2.14 | 2.3 |
| 10:360 | 134 | 79.1 | 0.47 | 1.81 | 0.45 | 2.23 | 20.1 | 2.34 | 0.8 |
| 10:480 | 171 | 82.3 | 0.42 | 1.79 | 0.5 | 2.22 | 17.4 | 2.57 | 0.3 |
| <i>0.3% Rh/Al₂O₃</i> | | | | | | | | | |
| 10:60 ^b | 19 | 91.3 | 0.65 | 1.82 | 0.36 | 2.49 | 3.6 | 1.91 | 5.1 |
| 10:60 | 14 | 93.1 | 0.63 | 1.87 | 0.32 | 2.43 | 4.8 | 2.14 | 2.1 |
| 10:120 | 45 | 92.3 | 0.56 | 1.9 | 0.32 | 2.47 | 5.8 | 2.26 | 1.9 |
| 10:240 | 98 | 92.6 | 0.53 | 1.97 | 0.27 | 2.34 | 6.3 | 2.14 | 1.1 |
| 10:360 | 149 | 94.8 | 0.48 | 1.98 | 0.28 | 2.35 | 4.7 | 2.24 | 0.5 |
| 10:480 | 191 | 95.9 | 0.43 | 2.01 | 0.28 | 2.32 | 3.9 | 2.25 | 0.2 |
| <i>5% Rh/SiO₂</i> | | | | | | | | | |
| 10:60 ^b | 10 | 94.8 | 0.46 | 1.76 | 0.5 | 3.49 | 3.8 | 6.55 | 1.4 |
| 10:60 | 13 | 90.3 | 0.42 | 1.87 | 0.42 | 3.05 | 7.0 | 5.18 | 2.7 |
| 10:120 | 31 | 87.9 | 0.35 | 1.97 | 0.36 | 2.66 | 10.1 | 4.16 | 2.0 |
| 10:240 | 54 | 85.9 | 0.33 | 1.98 | 0.38 | 2.35 | 12.7 | 4.68 | 1.4 |
| 10:360 | 79 | 86.0 | 0.32 | 1.98 | 0.4 | 2.24 | 13.1 | 4.49 | 0.9 |
| 10:480 | 83 | 86.9 | 0.3 | 1.99 | 0.42 | 2.19 | 12.6 | 4.22 | 0.5 |

^a ω_I : calculated from *n*C₅ fragment; ω_{II} : calculated from *i*C₅ fragment; ω_{III} : calculated from *n*C₄ fragment.

^b 498 K reaction temperature.

3. Results

Tables 1–4 present the activity and selectivity patterns for the conversion of 3MP, 2MP, *n*H and MCP, respectively, as well as the reactivity and fragmentation factors. The major reaction on Rh was the splitting of C–C bond(s) along with minor isomerization and C₅-cyclization.

3.1. Activity

As a general tendency, positive hydrogen order was observed. Maximum rates characteristic of hydrocarbon conversion on metals [21,25] were reached in our hydrogen pressure range almost exclusively at the lowest temperature. Fig. 1 shows a typical example, obtained in the 3MP conversion on 0.3% Rh/alumina. The figure is in agreement with the earlier observation that the maximum rates are shifted to higher hydrogen pressures with increasing reaction

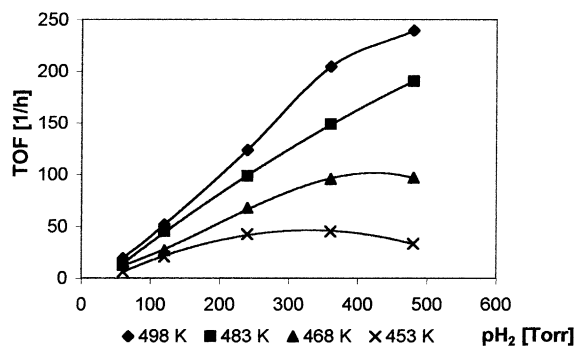


Fig. 1. Turnover frequencies for the conversion of 3MP on 0.3% Rh/Al₂O₃ as a function of hydrogen pressure at four different temperatures.

temperature [21,25,26]. In the conversion of hexane isomers, the silica-supported catalyst was always less active than Rh/alumina. No real particle size effect was observed with the latter catalysts. Contrary to

Table 2
Activity and selectivity pattern in the conversion of 2MP over Rh catalysts^a

| CH:p(H ₂) (Torr), T = 483 K | TOF (h ⁻¹) | Hydrogenolysis | | | | | | Isomerization | | C ₅ -cyclization to MCP, S _{MCP} |
|--|------------------------|----------------|----------------|-----------------|------------------|-----------------|------|----------------|-----------------|---|
| | | S _C | ω _I | ω _{II} | ω _{III} | ω _{IV} | ζ | S _i | 3MP/ <i>n</i> H | |
| <i>10% Rh/Al₂O₃</i> | | | | | | | | | | |
| 10:60 ^b | 15 | 80.9 | 0.63 | 2.21 | 1.22 | 0.65 | 2.72 | 10.5 | 1.17 | 8.6 |
| 10:60 | 18 | 79.5 | 0.6 | 2.18 | 1.25 | 0.7 | 2.52 | 14.3 | 1.31 | 6.2 |
| 10:120 | 37 | 77.7 | 0.58 | 2.13 | 1.34 | 0.69 | 2.41 | 16.8 | 1.18 | 5.5 |
| 10:240 | 67 | 78.8 | 0.52 | 1.95 | 1.62 | 0.69 | 2.21 | 18.7 | 0.94 | 2.5 |
| 10:360 | 100 | 81.1 | 0.46 | 1.83 | 1.87 | 0.69 | 2.21 | 17.6 | 0.98 | 1.3 |
| 10:480 | 113 | 84.1 | 0.41 | 1.67 | 2.13 | 0.69 | 2.19 | 15.1 | 0.98 | 0.8 |
| <i>0.3% Rh/Al₂O₃</i> | | | | | | | | | | |
| 10:60 ^b | 9 | 91.0 | 0.73 | 2.51 | 1.25 | 0.39 | 2.75 | 6.7 | 1.67 | 2.3 |
| 10:60 | 13 | 91.2 | 0.7 | 2.49 | 1.4 | 0.36 | 2.45 | 6.0 | 1.52 | 2.8 |
| 10:120 | 36 | 92.0 | 0.65 | 2.42 | 1.63 | 0.32 | 2.42 | 5.9 | 1.31 | 2.1 |
| 10:240 | 80 | 95.7 | 0.51 | 2.2 | 1.97 | 0.4 | 2.41 | 3.8 | 1.42 | 0.5 |
| 10:360 | 119 | 96.8 | 0.44 | 1.98 | 2.33 | 0.4 | 2.4 | 2.9 | 1.32 | 0.3 |
| 10:480 | 150 | 97.2 | 0.42 | 1.96 | 2.42 | 0.39 | 2.37 | 2.5 | 1.22 | 0.3 |
| <i>5% Rh/SiO₂</i> | | | | | | | | | | |
| 10:60 ^b | 8 | 94.3 | 0.2 | 1.62 | 2.52 | 0.67 | 3.21 | 4.3 | 2.05 | 2.4 |
| 10:60 | 7 | 90.5 | 0.22 | 2.17 | 2.2 | 0.6 | 3.13 | 6.7 | 2.1 | 2.8 |
| 10:120 | 16 | 90.7 | 0.25 | 2.42 | 1.98 | 0.55 | 2.79 | 7.2 | 2.08 | 2.1 |
| 10:240 | 38 | 89.8 | 0.34 | 2.57 | 1.72 | 0.52 | 2.56 | 8.7 | 2.18 | 1.5 |
| 10:360 | 41 | 88.4 | 0.44 | 2.68 | 1.53 | 0.46 | 2.41 | 10.2 | 2.37 | 1.5 |
| 10:480 | 46 | 88.7 | 0.51 | 2.63 | 1.46 | 0.45 | 2.31 | 10.1 | 2.1 | 1.1 |

^a ω_I: calculated from *n*C₅ fragment; ω_{II}: calculated from *i*C₅ fragment; ω_{III}: calculated from *i*C₄ fragment; ω_{IV}: calculated from C₃ fragment.

^b 498 K reaction temperature.

Table 3
Activity and selectivity pattern in the conversion of *n*H over Rh catalysts^a

| CH: <i>p</i> (H ₂) (Torr), <i>T</i> = 483 K | TOF (h ⁻¹) | Hydrogenolysis | | | | | Isomerization | | C ₅ -cyclization to MCP, <i>S</i> _{MCP} |
|--|------------------------|-----------------------|------------|---------------|----------------|---------|-----------------------|---------|--|
| | | <i>S</i> _C | ω_I | ω_{II} | ω_{III} | ζ | <i>S</i> _i | 2MP/3MP | |
| <i>10% Rh/Al₂O₃</i> | | | | | | | | | |
| 10:60 ^b | 32 | 86.7 | 1.29 | 0.89 | 0.82 | 2.83 | 7.6 | 1.53 | 5.7 |
| 10:60 | 28 | 83.5 | 1.34 | 0.91 | 0.75 | 2.62 | 9.4 | 1.56 | 7.1 |
| 10:120 | 54 | 85.2 | 1.23 | 0.97 | 0.8 | 2.47 | 10.9 | 1.72 | 3.9 |
| 10:240 | 88 | 88.7 | 0.97 | 1.08 | 0.95 | 2.34 | 10.1 | 1.89 | 1.2 |
| 10:360 | 92 | 90.7 | 0.89 | 1.13 | 0.98 | 2.28 | 8.4 | 1.94 | 0.9 |
| 10:480 | 100 | 92.3 | 0.78 | 1.18 | 1.04 | 2.23 | 7.2 | 2.02 | 0.5 |
| <i>0.3% Rh/Al₂O₃</i> | | | | | | | | | |
| 10:60 ^b | 11 | 92.5 | 1.45 | 0.85 | 0.7 | 2.81 | 4.2 | 1.06 | 3.3 |
| 10:60 | 16 | 93.4 | 1.25 | 0.92 | 0.83 | 2.69 | 4.0 | 1.27 | 2.6 |
| 10:120 | 42 | 94.5 | 1.24 | 0.95 | 0.81 | 2.5 | 4.0 | 1.45 | 1.5 |
| 10:240 | 65 | 95.7 | 1.1 | 1.0 | 0.9 | 2.42 | 3.5 | 1.45 | 0.8 |
| 10:360 | 94 | 97.6 | 0.8 | 1.07 | 1.14 | 2.52 | 2.1 | 1.53 | 0.3 |
| 10:480 | 101 | 97.5 | 0.89 | 1.07 | 1.04 | 2.37 | 2.2 | 1.5 | 0.3 |
| <i>5% Rh/SiO₂</i> | | | | | | | | | |
| 10:60 | 15 | 97.8 | 0.89 | 0.89 | 1.21 | 3.98 | 1.8 | 1.17 | 0.4 |
| 10:120 | 25 | 97.0 | 0.94 | 0.88 | 1.19 | 3.47 | 2.2 | 1.42 | 0.8 |
| 10:240 | 34 | 97.0 | 1.06 | 0.89 | 1.06 | 2.76 | 2.7 | 1.59 | 0.3 |
| 10:360 | 34 | 97.0 | 1.2 | 0.86 | 0.94 | 2.59 | 2.8 | 1.76 | 0.2 |
| 10:480 | 33 | 96.9 | 1.28 | 0.84 | 0.88 | 2.53 | 3.1 | 1.89 | 0 |

^a ω_I : calculated from *n*C₅ fragment; ω_{II} : calculated from *n*C₄ fragment; ω_{III} : calculated from C₃ fragment.

^b 498 K reaction temperature.

Table 4
Activity and selectivity pattern in the conversion of MCP over Rh catalysts

| CH: <i>p</i> (H ₂) (Torr), <i>T</i> = 498 K | TOF (h ⁻¹) | Ring opening | | | | Fragmentation, <i>S</i> _C |
|--|------------------------|------------------------|------|------|------------|---|
| | | <i>S</i> _{RO} | 2MP | 3MP | <i>n</i> H | |
| <i>10% Rh/Al₂O₃</i> | | | | | | |
| 10:60 | 15.3 | 55.7 | 28.6 | 19.1 | 8.0 | 44.3 |
| 10:120 | 29.3 | 63.6 | 32.5 | 21.0 | 10.1 | 36.4 |
| 10:240 | 66.7 | 79.2 | 41.1 | 25.3 | 12.8 | 20.8 |
| 10:360 | 91.8 | 84.3 | 45.4 | 25.4 | 13.5 | 15.7 |
| 10:480 | 148.0 | 89.5 | 49.4 | 27.1 | 13.0 | 10.5 |
| <i>0.3% Rh/Al₂O₃</i> | | | | | | |
| 10:60 | 11.7 | 42.1 | 21.2 | 16.1 | 4.8 | 57.9 |
| 10:120 | 20.1 | 49.1 | 25.3 | 18.3 | 5.5 | 50.9 |
| 10:240 | 49.4 | 60.8 | 31.4 | 21.0 | 8.4 | 39.2 |
| 10:360 | 64.6 | 67.7 | 35.2 | 23.4 | 9.1 | 32.3 |
| 10:480 | 104.1 | 71.2 | 37.5 | 23.4 | 10.3 | 28.8 |
| <i>5% Rh/SiO₂</i> | | | | | | |
| 10:60 | 9.9 | 44.2 | 24.2 | 16.1 | 3.9 | 55.8 |
| 10:120 | 20.8 | 54.6 | 30.4 | 19.5 | 4.7 | 45.4 |
| 10:240 | 52.9 | 69.8 | 40.8 | 23.2 | 5.8 | 30.2 |
| 10:360 | 90.2 | 81.2 | 49.4 | 26.2 | 5.6 | 18.8 |
| 10:480 | 129.5 | 84.3 | 52.0 | 26.3 | 6.0 | 15.7 |

this, in the conversion of MCP a clear influence of dispersion appeared; larger Rh particles were more active, in good agreement with [9].

3.2. Selectivity

The conversion of MCP yielded two main classes of products: ring opening products and fragments. The relative importance of multiple splitting increased with increasing temperature and decreasing hydrogen pressure. The influence of hydrogen pressure was thus opposite to what one would expect on the basis of reaction stoichiometry. This indicates that the dehydrogenation of the surface intermediate is, likely, higher in the case of fragmentation [15,27,28]. The selectivity of fragments was larger with lower metal loading, thus with a more dispersed catalyst. The ring opening occurred “selectively” (typical for Rh), the rupture in the proximity of the methyl group was hindered. As the multiplicity of C–C bond breaking increased, $S(2MP)$ displayed the highest decrease in the ring opening products.

In the conversion of hexane isomers, the main reaction was hydrogenolysis together with minor isomerization and MCP formation. The highest selectivity of C_5 -cyclization was reached at the lowest hydrogen pressure. This influence of hydrogen differs from earlier observations on platinum [26] where the optimum in C_5 -cyclization was obtained at higher $p(H_2)$ compared to fragmentation. This effect of $p(H_2)$ suggests that higher dehydrogenation is needed to reach the required geometry for C_5 -cyclization. The effect of temperature was less important, but clear influence of particle size was observed. Rhodium, like Ir [29], is a rather poor catalyst of the interconversion of hexane isomers as compared to Pt or Pd. However, a remarkable amount of isomerization occurred on 10% Rh/alumina in contrast to literature data [9,10,17–20]. The effect of particle size on the isomerization selectivity was also obvious. Generally, larger particles produced more isomers. Branched C_6 reactants yielded higher amount of isomers. High temperature was found to be disadvantageous for isomerization in good agreement with [18]. Maximum selectivities of isomerization of branched C_6 can be seen as a function of hydrogen pressure on silica-supported Rh. These maximum selectivities were shifted towards higher hydrogen

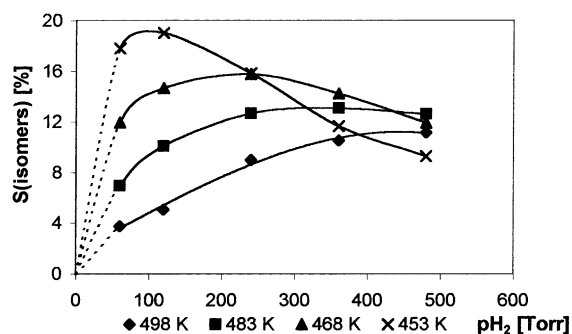


Fig. 2. Isomerization selectivities in the conversion of 3MP on 5% Rh/SiO₂ as a function of hydrogen pressure at four different temperatures. It was assumed that the isomer selectivity was zero at $p(H_2) = 0$.

pressures as the temperature increased (Fig. 2). On alumina-supported Rh rather low or medium $p(H_2)$ values favored the isomerization and no shift with T was observed. More remarkable contrast between the two different supported Rh was obtained from the distribution of isomers (2MP/3MP, 2MP/ nH and 3MP/ nH). While the Rh/silica showed high 2MP/ nH and 3MP/ nH ratios, these ratios were lower for the alumina-supported catalysts. This may point to different isomerization mechanisms prevailing in these two cases.

3.3. Hydrogenolysis patterns

As was emphasized above, the main reaction on Rh was the hydrogenolytic breaking of C–C bonds. Although, Rh was termed to be a metal preferring single hydrogenolysis [1], the selectivity of the smaller, complementary fragments (C_1 – C_5 , C_2 – C_4) was always higher than its larger counterparts. Accordingly, the fragmentation factor was always higher than 2. On Rh/silica multiple hydrogenolysis was also observed (see Table 3).

The effect of hydrogen pressure on the multiplicity of C–C bond cleavages was concordant independently of the reactant molecule. The highest number of fragments was found always at the lowest hydrogen pressure and at the highest temperature. A similar shift towards multiple hydrogenolysis (up to $\zeta = 5$) with increasing temperature (up to 573 K) was obtained earlier in the conversion of 3MP on Rh black

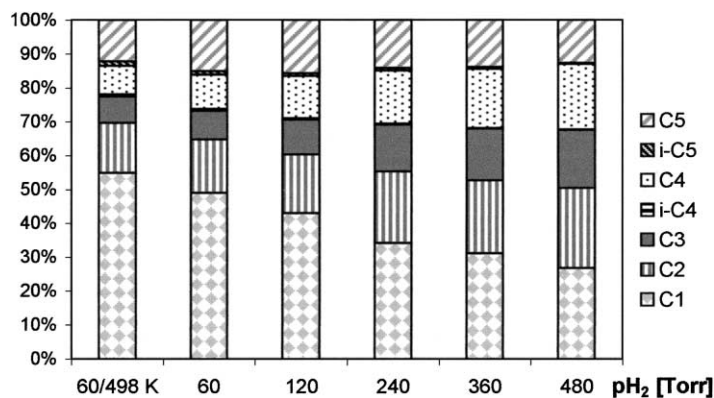


Fig. 3. Fragment distribution from $n\text{H}$ obtained over 10% $\text{Rh}/\text{Al}_2\text{O}_3$ as a function of hydrogen pressure at 483 K ($\Sigma < \text{C}_6 \equiv 100\%$). Additional distribution (at 60 Torr $p(\text{H}_2)$ and 498 K) is included.

[22]. A variation in the multiplicity of fragmentation as a function of $p(\text{H}_2)$ is represented in Fig. 3 on the example of the fragmentation pattern of $n\text{H}$ on 10% Rh/alumina. While the selectivity of n -pentane was almost constant, methane increased continuously at the expense of C_2 – C_4 products as the hydrogen pressure decreased. This means that the decrease of the surface hydrogen availability caused several consecutive C–C bond ruptures preferably in fraction of products that would otherwise desorb as C_2 and C_4 . A similar pattern was found in the hydrogenolysis of 2MP on the same catalyst (Fig. 4). The values of M_f were always higher than unity (1.2–13). $M_f > 1$ corresponds to

“random or internal” hydrogenolysis [24]. The complex picture seen in Figs. 3 and 4 can be best described as a further degradation of species produced by internal hydrogenolysis superimposed on single C–C bond ruptures.

The behavior of rhodium yielding mainly branched ring opening products from MCP, i.e. its reluctance to break C(III)–C(II) bonds was observed with the 2MP and 3MP reactants, too. Thus, the reactivity factors (ω) for a bond containing *tertiary* carbon atom was always lower than unity. On the other hand, the cleavage of bissecondary or primary–secondary C–C bonds was always favored.

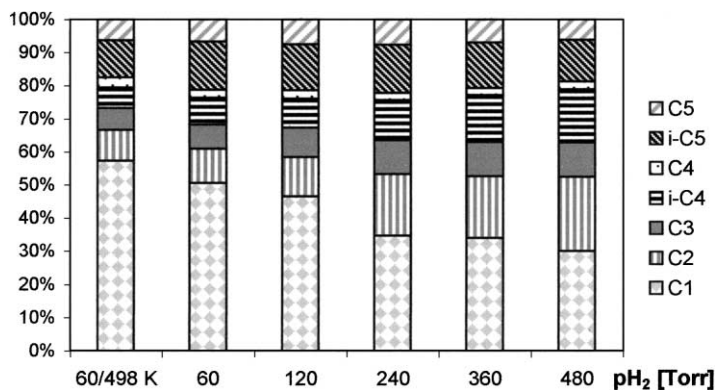


Fig. 4. Fragment distribution from 2MP obtained over 10% $\text{Rh}/\text{Al}_2\text{O}_3$ as a function of hydrogen pressure at 483 K ($\Sigma < \text{C}_6 \equiv 100\%$). Additional distribution (at 60 Torr $p(\text{H}_2)$ and 498 K) is included.

4. Discussion

4.1. Non-degradative reactions

Alkanes underwent on Rh catalysts mainly hydrogenolysis, and skeletal rearrangement was marginal, due, likely, to the ability for multiple H–D exchange [30] and for metallocarbene formation [31]. However, 10% Rh/Al₂O₃ produced a remarkable amount of non-degradative products and a clear influence of reaction conditions and metal loading, i.e. dispersion appeared important in the non-degradative reaction path. Isomerization selectivity higher by a factor of 2–3 was observed on Rh/alumina with larger metal particles. A similar, but slightly less pronounced, effect on C₅-cyclization was also observed.

The same active center was proposed to be involved in both hydrogenolysis and skeletal rearrangement [32] and only the local environment (carbonaceous deposit, blocking layers, hydrogen availability) may determine the prevailing route, thus the reaction selectivity. The investigations [33–35] on “coke sensitivity” of different hydrocarbon reactions attributed the enhanced selectivity of non-degradative transformations to formation of carbonaceous adsorbates preventing excessive dehydrogenation of the surface intermediates. The favored accumulation of such a carbonaceous overlayer on larger Rh surfaces might be the reason for the increased isomerization and cyclization selectivity on the 10% Rh/Al₂O₃ catalyst. In the absence of surface carbon, the multiply dehydrogenated species would then suffer C–C bond cleavages. However, too much coke on the surface means rather small hydrogen coverage, which may also dramatically increase the dehydrogenation and the multiplicity of hydrogenolysis. The maximum selectivity of isomerization as a function of p_{H_2} points to the importance of the surface hydrogen availability (Fig. 2).

Alkane isomerization can proceed through two main routes: by bond-shift and by C₅-cyclic mechanism [31]. The prevailing reaction route was found to depend on the nature and the dispersion of the metal [36]. Since the C₅-cyclic mechanism requires a chemisorbed MCP-like intermediate, the similar ratio of the C₆ alkanes from the isohexanes and from MCP was regarded as an indicator of this mechanism. Another argument can be the appearance of MCP in the products. Generally, rhodium shows “selective” ring

opening, i.e. hindrance in *n*H production. Despite the formation of MCP, rather low 2MP/*n*H ratios were observed on Rh/alumina, which suggests only a small contribution of C₅-cyclic mechanism. On Rh/SiO₂ much higher branched/normal C₆ ratios (2MP/*n*H up to 6.5) were found. Although, the 2MP/*n*H ratio from the MCP feed (10–12) was not reached, the contribution of C₅-cyclic type of isomerization on Rh/SiO₂ might be higher. Thus the prevailing mechanism (bond-shift vs. C₅-cyclic) seems to be support dependent.

4.2. Degradative reactions

Rhodium, being a highly active catalyst for hydrogenolysis, produced mainly fragments. Single splitting of C–C bonds was catalyzed rather than multiple degradation to methane [1,22]. The values of fragmentation factor presented in Tables 1–4 supports this finding. However, increasing temperature and decreasing $p(\text{H}_2)$ caused “deepening” of the hydrogenolysis. Further hydrogenolysis of primary fragments (see Figs. 3 and 4) can be attributed to the hindrance in the desorption [37] which facilitates the successive breakdown of the molecules during one sojourn on the surface. The positive hydrogen order seen in activity can be satisfactorily explained by the hindrance in the re-hydrogenation of the surface intermediates. This may be a typical example of the “kinetic selectivity” [38].

The position of the cleavage is another characteristic feature of the process. This was visualized by the use of ω reactivity factors (Tables 1–4). Breaking a C–C bond containing a *tertiary* atom was always unfavorable in good agreement with [39]. The dissociative adsorption can occur most easily on *tertiary* carbon atom. An interaction of the neighboring metal atom with the bonds in β - or in γ -position to the *tertiary* carbon atom would hinder the reaction in α -position. The increasing amount of methane as the hydrogen pressure decreased was mainly caused by the further degradation of C₂–C₄ surface intermediates.

Our previous papers [4,40] discussed the mechanism of MCP ring opening on Rh catalysts. Fig. 5 which contains the selectivities of ring opening products and that of 2MP + fragments as the function of reaction conditions will help in explaining the proposed mechanism. The possibility of the first C–C

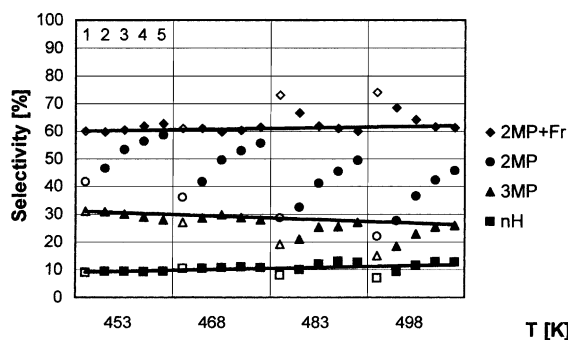


Fig. 5. Selectivity comparison for nH , 3MP, 2MP and 2MP + fragments from the conversion of MCP on 10% Rh/Al₂O₃. Each temperature includes five increasing hydrogen pressures abbreviated as follows: (1) 60 Torr, (2) 120 Torr, (3) 240 Torr, (4) 360 Torr and (5) 480 Torr. They are shown at the lowest temperature for clarity. Results denoted by filled symbol have been taken from Ref. [4] and the empty symbols represent additional new and important points at low $p(H_2)$.

bond breaking in a given position is independent of the reaction conditions, contrary to the observed ring opening product distribution (ROPD). However, the final ROPD is determined by the competition between further hydrogenolysis of ring opening intermediates and their desorption (“kinetic selectivity”). The prevailing route strongly depends on T and $p(H_2)$. The reactivity of the surface ring opening intermediates (denoted by the subscript s) to undergo further hydrogenolysis was in the following order:

$$[2MP]_s > [3MP]_s > [nH]_s.$$

Consequently, the fragments were produced “formally” from the branched hexane isomers.

To prove this picture, we can use the fragment distributions obtained from the hydrogenolysis of 2MP and 3MP and compare them with that of MCP. The following calculation was performed on 10% Rh/Al₂O₃. Fig. 6 shows a typical distribution of fragments from MCP. More than 50% of the fragments was methane and its selectivity increased slightly as hydrogen pressure decreased. Such high C₁ selectivity from open-chain alkanes was only observed at the lowest $p(H_2)$. The difference seen between the fragment distribution of MCP and of open-chain hydrocarbons is due to the dominating single hydrogenolysis in the conversion of alkanes at high $p(H_2)$. This is obviously not included in the fragment distribution of MCP, as ring opening plays this role in the conversion of MCP. The highest C₅-cyclization selectivity was obtained also at 60 Torr $p(H_2)$ which was advantageous to reach the required geometry. Consequently, we compared the distributions at 60 Torr hydrogen pressure (temperature = 498 K), where the importance of single hydrogenolysis was the lowest.

To calculate the contribution of hexane isomers in further hydrogenolysis of ring opening intermediates we used Fig. 5 and Table 4. It is obvious that the ideal case—only ring opening products with no fragmentation—would result in about 60% 2MP, 30% 3MP and 10% nH . The decreases from these values at 498 K and 60 Torr $p(H_2)$ were 31.4% (60–28.6) for 2MP, 10.9% (30–19.1) for 3MP and 2% (10–8) for nH . Thus, using

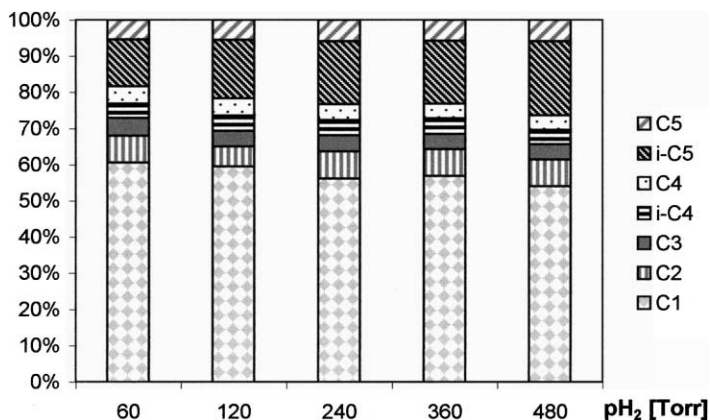


Fig. 6. Fragment distribution from MCP obtained over 10% Rh/Al₂O₃ as a function of hydrogen pressure at 498 K ($\Sigma < C_6 \equiv 100\%$).

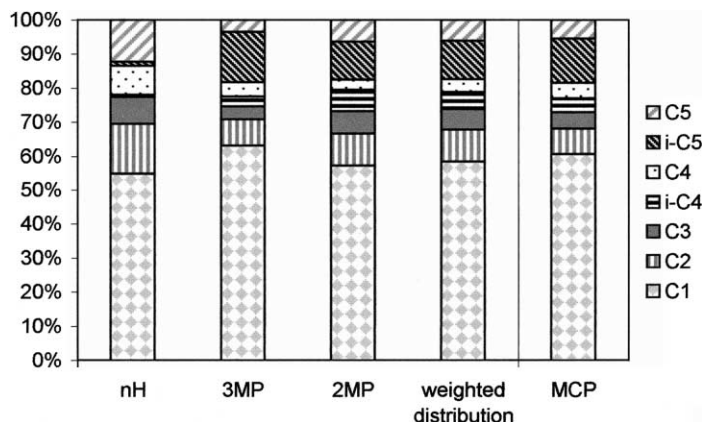


Fig. 7. Fragment distributions from *n*H, 2MP, 3MP, MCP and the weighted distribution at 498 K and 60 Torr hydrogen pressure ($\Sigma < C_6 \equiv 100\%$).

these values as factors we can calculate a weighted distribution modeling for the fragmentation of MCP by the hydrogenolysis pattern of hexane isomers. Fig. 7 reveals the comparison of the distributions. Due to the predominant weight factor for 2MP, the calculated distribution is similar to that of this alkane and fits well to the actual pattern observed. Similar analogies were obtained for the other two catalysts, too.

The flat-lying reaction intermediate for the selective ring opening of alkyl-cyclopentanes [25,41,42] explained adequately the MCP reactions on Rh [4,40]. The first step of the selective ring opening would be a dissociative adsorption via the *tertiary* carbon atom. The metal atom interacting with the *tertiary* carbon 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” (the three bisecundary bonds). This model could adequately explain ring opening far from the substituent.

Since fragmentation is the result of further hydrogenolysis of the ring opening intermediates, we can extend this model. Contrary to ring opening, which had a strong positive hydrogen order, “deep” fragmentation (Fig. 6) showed almost zero order [4]. Consequently, strong dehydrogenation occurred after the primary ring opening. Remembering that the fragment distributions from 2MP and MCP were similar (Fig. 7) and the further hydrogenolysis of

C₂ and *i*C₄ products caused the high selectivity of methane from 2MP (Fig. 4), the breaking up of the *i*C₄-like group—still attached by its *tertiary* carbon atom to the surface—caused the high (more than 50%) selectivity of methane in the fragments. The probability of breaking bonds in the C₅ ring in “b” and “c” position being equal (~60% 2MP, ~30% 3MP), this would indicate equal selectivities for *i*C₅ and *i*C₄ also in the fragments, as well. The absence of such a correlation verifies the preferred breaking up of *i*C₄ + C₂ surface species. This model can be easily visualized in terms of the two primary C atoms of the “isobutane” surface species situated above two interatomic hollows next to the chemisorption site and attached to the surface (Fig. 8). Sachtler [43] called these sites “Freundlich” sites. They are suitable for dissociative chemisorption leading to bond cleavages. In our temperature range C₂H and CH species can be stable on the surface of rhodium single crystal and can occupy the 3-fold hollow sites of a Rh(1 1 1) surface [44]. (Obviously, this multiple degradation process cannot be restricted to (1 1 1) surfaces.) These attachments could lead to the cleavage of the primary C atoms. Thus, the proposed geometry, the occupation of hollow sites and the partial desorption of surface C₁ species would explain the rather deep hydrogenolysis of MCP and the insensitivity of the fragment distribution to the hydrogen availability (Fig. 6).

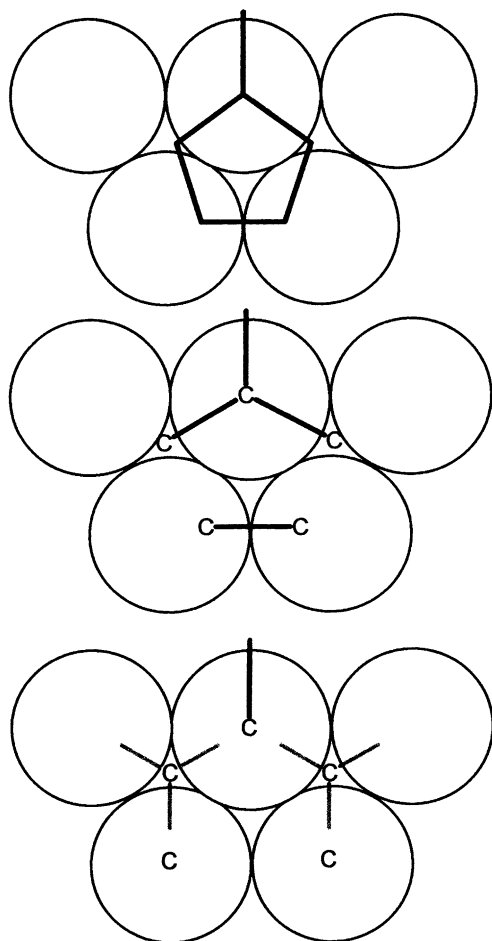


Fig. 8. Scheme of the breaking up of an MCP molecule on (111) Rh surface.

5. Conclusions

The main reaction of rhodium was hydrogenolysis; however, remarkable amount of isomers (up to 20%) and MCP (up to 10%) could also be found. Particle size effects appeared in the non-degradative reactions; this reaction being favored by larger particles. The hydrogen pressure effect on the MCP formation from hexane isomers suggests that a higher degree of dehydrogenation is needed to reach the required geometry for C₅-cyclization.

Although, Rh was termed to catalyzing single splitting of C–C bonds, the hydrogenolysis at low $p(\text{H}_2)$ can be rather “deep”. This pattern was accompanied

by decrease in the activity. Thus, we propose that re-hydrogenation of the surface intermediate is an important (“slow”) step in hydrogenolysis at low $p(\text{H}_2)$. The hindrance of desorption causes multiple C–C bond splitting on the surface of rhodium. The fragments from MCP are secondary products of ring opening intermediates. The fragmentation patterns of hexane isomers were successfully applied for modeling the fragment distribution of MCP.

References

- [1] Z. Paál, P. Tétényi, *Nature* 267 (1977) 234.
- [2] F.J. Schepers, E.H. van Broekhoven, V. Ponec, *J. Catal.* 96 (1985) 82.
- [3] B. Coq, A. Bittar, F. Figueras, *Appl. Catal.* 59 (1990) 103.
- [4] D. Teschner, K. Matusek, Z. Paál, *J. Catal.* 192 (2000) 335.
- [5] G. Maire, G. Plouidy, J.C. Prudhomme, F.G. Gault, *J. Catal.* 4 (1965) 556.
- [6] Y. Barron, G. Maire, J.M. Muller, F.G. Gault, *J. Catal.* 5 (1966) 428.
- [7] H. Glassl, K. Hayek, R. Kramer, *J. Catal.* 68 (1981) 397.
- [8] B. Török, J.T. Kiss, M. Bartók, *Catal. Lett.* 46 (1997) 169.
- [9] B. Coq, F. Figueras, *J. Mol. Catal.* 40 (1987) 93.
- [10] B. Coq, R. Dutartre, F. Figueras, T. Tazi, *J. Catal.* 122 (1990) 438.
- [11] R. Burch, Z. Paál, *Appl. Catal.* 114 (1994) 9.
- [12] K. Fogar, J.R. Anderson, *J. Catal.* 59 (1979) 325.
- [13] F. Garin, G. Maire, *Acc. Chem. Res.* 22 (1989) 100.
- [14] G.A. Somorjai, *Introduction to Surface Science and Catalysis*, Wiley, Chichester, UK, 1994.
- [15] V. Ponec, G.C. Bond, *Catalysis by Metals and Alloys, Studies in Surface Sciences and Catalysis*, Vol. 95, Elsevier, Amsterdam, 1995.
- [16] Z. Karpinski, J.K.A. Clarke, *J. Chem. Soc., Faraday Trans.* 71 (1975) 893.
- [17] F.J. Schepers, J.G. van Senden, E.H. van Broekhoven, V. Ponec, *J. Catal.* 94 (1985) 400.
- [18] J.B.F. Anderson, R. Burch, *Appl. Catal. A* 28 (1986) 255.
- [19] G. Del Angel, B. Coq, R. Dutartre, F. Figueras, *J. Catal.* 87 (1984) 27.
- [20] B. Coq, R. Dutartre, F. Figueras, A. Rouco, *J. Phys. Chem.* 93 (1989) 4904.
- [21] Z. Paál, in: Z. Paál, P.G. Menon (Eds.), *Hydrogen Effect in Catalysis*, Dekker, New York, 1988, p. 449.
- [22] Z. Paál, P. Tétényi, M. Dobrovolszky, *React. Kinet. Catal. Lett.* 37 (1988) 163.
- [23] G. Leclercq, L. Leclercq, R. Maurel, *J. Catal.* 50 (1977) 87.
- [24] J.R.H. Van Schaik, R.P. Dessing, V. Ponec, *J. Catal.* 38 (1975) 273.
- [25] Z. Paál, *Adv. Catal.* 29 (1980) 273.
- [26] Z. Paál, P.G. Menon, *Catal. Rev.-Sci. Eng.* 25 (1983) 223.
- [27] Z. Paál, P. Tétényi, in: G.C. Bond, G. Webb (Eds.), *Catalysis Specialists Periodical Reports*, Vol. 5, The Chemical Society, London, 1982, p. 80.

- [28] J.R. Anderson, *Adv. Catal.* 23 (1973) 1.
- [29] A. Majesté, S. Balcon, M. Guérin, C. Kappenstein, Z. Paál, *J. Catal.* 187 (1999) 486.
- [30] D.W. McKee, F.J. Norton, *J. Catal.* 3 (1964) 252.
- [31] F.G. Gault, *Adv. Catal.* 30 (1981) 1.
- [32] J.B.F. Anderson, R. Burch, J.A. Cairns, *J. Catal.* 107 (1987) 364.
- [33] A. Sárkány, *J. Chem. Soc., Faraday Trans. 1* 84 (1988) 2267.
- [34] Z. Paál, *J. Mol. Catal.* 94 (1994) 225.
- [35] P.G. Menon, *J. Mol. Catal.* 59 (1990) 207.
- [36] G. Maire, F. Garin, in: J.R. Anderson, M. Boudart (Eds.), *Catalysis, Science, and Technology*, Spinger, Berlin, 1984, p. 227.
- [37] A. Sárkány, P. Tétényi, *React. Kinet. Catal. Lett.* 9 (1978) 315.
- [38] L. Guzzi, K. Matusek, A. Sárkány, P. Tétényi, *Bull. Soc. Chim. Belg.* 88 (1979) 497.
- [39] Z. Paál, P. Tétényi, *React. Kinet. Catal. Lett.* 12 (1979) 131.
- [40] D. Teschner, Z. Paál, D. Duprez, *Catal. Today* 65 (2001) 185.
- [41] H. Zimmer, Z. Paál, *J. Mol. Catal.* 51 (1989) 261.
- [42] H. Zimmer, M. Dobrovolszky, P. Tétényi, Z. Paál, *J. Phys. Chem.* 90 (1986) 4758.
- [43] W.M.H. Sachtler, *J. Mol. Catal.* 25 (1984) 1.
- [44] B.E. Bent, Ph.D. Thesis, University of California, Berkeley, CA, 1986, cited by G.A. Somorjai, *Introduction to Surface Science and Catalysis*, Wiley, Chichester, UK, 1994.