ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Journal of Catalysis 254 (2008) 49–63

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Study of $Ir/WO_3/ZrO_2$–SiO_2 ring-opening catalysts: Part II. Reaction network, kinetic studies and structure–activity correlation

Sébastien Lecarpentier, Jacob van Gestel, Karine Thomas, Jean-Pierre Gilson, Marwan Houalla [*]

Laboratoire Catalyse et Spectrochimie, ENSICAEN-Université de Caen-CNRS, 6 Bd. Maréchal Juin, 14050 Caen cedex, France

Received 19 July 2007; revised 23 November 2007; accepted 25 November 2007

Abstract

The present paper is the second part of a systematic study of the influence of W and Ir loading on the activity of $Ir/WO_3/ZrO_2$–SiO_2 catalysts for the ring-opening reaction of naphthenic molecules using methylcyclohexane (MCH) as a model compound. A series of Si-stabilized tungstated zirconias, WO_x/ZrO_2–SiO_2, containing up to 3.5 atom W/nm^2, was prepared. Ir-based catalysts containing up to 1.2 wt% were obtained by impregnation of these solids. Characterization of the metal dispersion and catalyst acidity was described in a previous article. The objective of the present study was to determine the best metal/acid balance for optimal performance of $Ir/WO_x/ZrO_2$–SiO_2 catalysts in the ring-opening reaction of MCH. Monofunctional (acid WO_x/ZrO_2–SiO_2 or metal Ir/ZrO_2–SiO_2) and bifunctional ($Ir/WO_3/ZrO_2$–SiO_2) catalysts were examined. Based on the analysis of the yields and products distributions, a reaction network was proposed, and kinetic data (e.g., activation energies, initial rates) were calculated. Correlations between characterization results obtained earlier (e.g., acidity, dispersion) and catalytic performance are also reported. The monofunctional acid catalysts WO_x/ZrO_2–SiO_2 showed a low selectivity for ring opening. The ring-contraction activity developed for W surface density above a threshold value of 1 atom W/nm^2. This was attributed to the appearance and the development of a relatively strong Brönsted acidity monitored by infrared measurements. MCH ring contraction and C5 naphthene ring opening occur according to a classic acid mechanism. For low conversions, the monofunctional metal catalysts Ir/ZrO_2–SiO_2 exhibited significant selectivity for ring opening that decreased with increasing conversion. Because of the lack of ring-contraction products, the observed activity was attributed to the direct ring opening of the MCH. Ring opening and cracking occur according to a dicarbene mechanism. The study of MCH conversion on $Ir/WO_x/ZrO_2$–SiO_2 catalysts indicated that MCH ring contraction to alkylcyclopentanes occurs before ring opening. The best yields for ring opening were obtained with the 1.2% $Ir/WO_x/ZrO_2$ (1.5 atom of W/nm^2). Further increases in W surface density led to a decrease in the indirect ring-opening yield, attributed to a decrease in Ir dispersion. For bifunctional metal/acid catalysts, analysis of the mechanism is less straightforward. The activation energy for C6 ring contraction and indirect C6 ring opening is a function of the metal/acid ratio. For high ratios, indirect ring opening occurs essentially over metallic sites. A decrease in the metal/acid ratio enhances the contribution of acid mechanism.

Keywords: Tungstated zirconia; Iridium; Methylcyclohexane conversion; Selective ring opening

1. Introduction

To meet an increased demand for transportation fuels, the petroleum industry has to maximize the valorization of various feedstocks originating from distillation or treatment units. Specifically, the fluid catalytic cracking (FCC) process produces, in addition to gasoline, light gases, heavy products (e.g., high cycle oils [HCOs]) and coke, a significant fraction of light cycle oil (LCO), the boiling range of which is similar to that of diesel. To date, LCO is added to heating and heavy fuels to adjust their viscosity [1]. Because of the increasing demand for diesel, a more interesting application would be to blend the LCO fraction in the diesel pool. However, the LCO characteristics are very different from diesel specifications, especially in Europe. LCO contains from 0.2 to 0.7% of sulfur and from 48 to 69% of polyaromatics yielding a cetane index of 22–25 [1], compared with the European norms of an upper limit of 50 ppm of sulfur (10 ppm in January 2009), 11% of poly-

---

[*] Corresponding author. Fax: +33 2 31 56 73 50.
E-mail address: marwan.houalla@ensicaen.fr (M. Houalla).
URL: http://www-lcs.ensicaen.fr.

doi:10.1016/j.jcat.2007.11.016

aromatics, and a minimum cetane index of 51. Thus, the LCO fraction must be subjected to important transformations. Sulfur and nitrogen content can be reduced by conventional hydrotreatments and, if necessary, by other desulfurization techniques [2]. The polycyclic aromatic fraction can be lowered by hydrogenation, which also improves the cetane index. But this increase is not sufficient, and a ring opening of naphthenic compounds appears to be required [3–5]. Such ring opening must preferably be highly selective toward the formation of linear or mono-branched paraffins instead of multibranched ones, which exhibit a lower cetane index.

In principle, naphthene ring opening can be achieved by metal or acid catalysis. Previous studies of catalysis by metals focused on Ir-, Pt-, Ru-, and Rh-based solids. The hydrogenolysis ability of these solids increases in the order $\text{Pt} < \text{Rh} < \text{Ir} < \text{Ru}$ [6,7], whereas the ring-opening ability depends on a number of factors, such as particle size [8,9], the nature of the support [10], and the naphthenic compound [3,11]. Thus, for MCH conversion, large metal particles of alumina-supported Ir/Al_2O_3, Ru/Al_2O_3 [7] and Rh/Al_2O_3 [10] catalysts exhibited higher intrinsic activity, whereas the opposite results were reported for Rh/SiO_2 [10]. McVicker et al [3] examined the influence of the degree of substitution of the ring and the position of the substituting group. They noted that for Ir/Al_2O_3, the yield for methylcyclohexane ring opening is significantly higher than that for 1,2,4-trimethylcyclohexane. They also showed that the ring-opening yield for various C7-alkylcyclopentanes (ECP, 1,1-DMCP, 1,2-DMCP, 1,3-DMCP) is directly proportional to the number of unsubstituted C–C bonds present in a given isomer. Except for Ru-based catalysts, which exhibited essentially extensive cracking activity, Ni-, Pt-, Rh-, and Ir-based systems showed greater ring-opening activity for C5 rings than for C6 rings. Consistent with this finding, the results [3] demonstrated that the ease of converting two-ring naphthenes containing combinations of five- and six-membered rings over 0.9% Ir/Al_2O_3 is directly related to the relative number of saturated five-membered rings in the molecule.

The studies of acid-catalyzed ring opening have been performed primarily on zeolites. Kubicka et al. [12] showed that decalin ring opening is preceded by ring contraction. The activity is reportedly dependent on the number and strength of Brönsted acid sites and on the porosity of the support. Thus, the best ring-opening results were obtained with zeolites exhibiting medium acidity (Hβ-25, Hβ-75, and HY-12). The low activity measured with more acidic zeolites, such as mordenite, was attributed to coke formation. Similarly, Santikunaporn et al. [13] showed that intermediate acidity is a key factor in the ring-opening selectivity of decalin and tetralin molecules. With respect to the influence of porosity of the solids, previous studies have indicated that large-pore zeolites inhibit the dealkylation of alkylnaphthenes by limiting the steric hindrance [14,15]. In general, the use of large-pores zeolites favors the ring-opening reaction by limiting deactivation due to coke deposits [12,16,17].

A survey of the literature also shows that acid- or metal-catalyzed ring-opening reactions are enhanced by the use of bifunctional catalysts [13,18,19]. Doping zeolites with metals reportedly decreases the Brönsted acidity of the solids, leading to a decrease in cracking products. Similarly, the addition of an acid function to metals active for hydrogenolysis of C5 rings enhances C6 ring opening by promoting C6 to C5 ring contraction [3,20,21].

In general, a detailed examination of the results for metal, acid-catalyzed, and bifunctional ring-opening highlights the importance of judicious control of the metal to acid ratio in a given catalyst. Brönsted acid sites must be sufficiently strong and abundant to obtain good performance for ring-opening activity while limiting cracking.

The present work is a systematic study of the influence of the acidic and metallic functions on ring-opening activity. The selected catalytic system was Ir supported on tungstated zirconia. Zirconia appeared to be an attractive choice because of the possibility of modulating its acidity by controlled tungsten deposition [22,23]. Furthermore, the mesoporous nature of the support reduces the risk of diffusion limitations and enhanced cracking previously encountered in the case of some zeolites. Ir was selected because of its reportedly high C5 ring-opening activity [24]. Characterization of the metal dispersion and the catalyst acidity was described in a previous article [25]. Acidity and Ir dispersion were monitored by low-temperature (77 K) and ambient-temperature CO adsorption, respectively, followed by infrared spectroscopy.

The present paper describes the catalytic activity for the conversion of methylcyclohexane (MCH). The selection of MCH as a model molecule for the evaluation of C6 ring-opening activity was motivated by its relative simplicity, which limits the number of possible reaction products and facilitates the establishment of a reaction network, and subsequent kinetic modeling enabling structure-catalytic performance relationships [26]. Based on the proposed reaction network, kinetic parameters are calculated, and earlier characterization results (acidity; Ir dispersion) are correlated with the catalytic performance.

2. Experimental

2.1. Materials

Zirconia doped with 1.2 wt% silica was prepared by dropwise addition of a 10 M ammonium hydroxide solution to a 0.2 M solution of zirconyl chloride octahydrate ($ZrOCl_2$, FLUKA) up to a pH of 9.9. Preliminary experiments indicated that substantial stabilization of the surface of the tetragonal zirconia support can be achieved through the incorporation of 1.2 wt% Si [25]. Thus, subsequent studies of the influence of W deposition were conducted with this solid. The silicon was introduced before precipitation using the prerequisite amount of $SiCl_4$. The precipitated material was heated at 363 K for 48 h and then left to stand at room temperature for 96 h in the solution. The final product was recovered by vacuum filtration. It was then redispersed in deionized water to remove residual chlorine and filtered. This operation was repeated until no traces of Cl^- could be detected with an $AgNO_3$ solution. The washed product was dried at 393 K for 16 h and calcined in air at 1023 K for 3 h.

The W phase (0–12 wt% W) was deposited by impregnation of the support using an ammonium metatungstate solution, followed by calcination at 1023 K for 3 h. The Ir (0–1.2 wt%) was added by impregnation with an iridium chloride solution, followed by calcination at 723 K with a 20% O_2 + 80% N_2 flow of 25 ml/min. The catalyst was reduced in situ in flowing H_2 at 623 K at atmospheric pressure before use. The tungstated zirconias were designated ZSiWx, where x is the W surface density expressed as at. W/nm^2. The series of Ir deposited on tungstated zirconia was designated yIr/ZSiWx, where y is the nominal weight percentage of Ir in the catalysts.

2.2. *Methylcyclohexane ring opening*

Methylcyclohexane (MCH) ring opening was carried out at a total pressure of 5 MPa and a temperature range of 523–598 K in a continuous-flow fixed-bed microreactor containing 0.25–1 g of catalyst diluted in silicon carbide. The partial pressures of hydrogen and MCH were set at 4.8 and 0.2 MPa, respectively.

MCH was delivered through a liquid chromatography pump (Gilson 302). The product gas mixture was collected at atmospheric pressure and analyzed online with a Varian 3400 gas chromatograph equipped with a flame ionization detector and a Chrompack CP-SIL 5 CB WCOT fused silica capillary column.

Before testing, each catalyst was activated in situ under atmospheric pressure at 673 K with flowing dry air for 2 h, cooled to 623 K under flowing dry He and reduced at 623 K in a dry hydrogen flow for 1 h. The MCH reactant was dried over activated 3A zeolite. Hydrogen (Air Liquide, Grade I) and helium (Air Liquide, Grade U) gases were further purified from water and oxygen contaminants with 3A zeolite and BTS (FLUKA) traps.

The MCH conversion was calculated from the equation

$$f = 100\{(\text{Area}_{(\text{total})} - \text{Area}_{\text{MCH}})/\text{Area}_{(\text{total})}\},$$

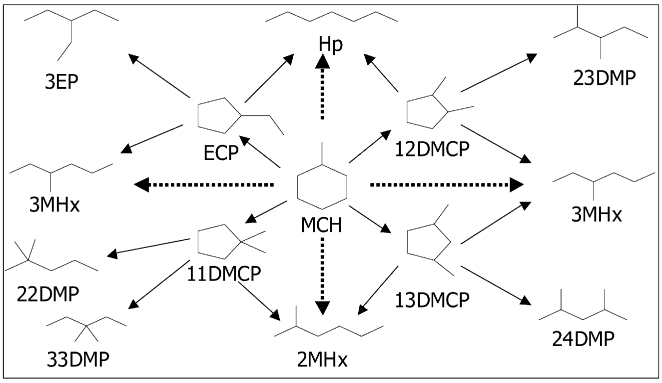
where $\text{Area}_{(\text{total})}$ designates the total peak areas of the chromatogram and Area_{MCH}, the peak area for MCH. The weight yield was expressed by $R_i = 100\{\text{Area}_{\text{product } i}/\text{Area}_{(\text{total})}\}$. The weight selectivity of a group of products was evaluated by $S_i = 100\{R_i/f\}$. The weight selectivity S' of a product i within a group of products j was calculated from the relation $S'_i = 100\{R_i/R_j\}$. For the molar selectivity of a product within the cracking group, the peak area for a given compound was corrected for the differences of molecular weight.

3. Results

3.1. *Reaction network*

3.1.1. *Methodology*

The following section describes the methodology adopted in the present study with respect to the experimental protocol, product classification, and combined use of contact time and reaction temperature to achieve an extended variation of conversion. A bifunctional catalyst 1.2Ir/ZSiW2.5 was used for the purpose of illustration.



Scheme 1. Possible products formed on conversion of MCH.

3.1.1.1. Reaction products Scheme 1 shows the products that could be obtained by ring opening of methylcyclohexane. To simplify the figure, the cracking products, containing <7 atoms of carbon, were not included. Two types of ring opening are noted:

- *Direct ring opening* (broken arrows) by hydrogenolysis of the C–C endocyclic bond of MCH by the metallic function
- *Indirect ring opening* (continuous arrows) by ring contraction of the MCH to alkylcyclopentane on the acidic function of the catalysts followed by hydrogenolysis of an endocyclic C–C bond of the alkylcyclopentane.

As can be seen from Scheme 1, more linear C_7H_{16} hydrocarbons are obtained by direct ring opening. Note that for the same number of carbon atoms, linear chain hydrocarbons exhibit higher cetane index than their branched counterparts. In the present article, the products are grouped as follows:

- *Cracking* (products with fewer than 7 carbon atoms).
- *Ring contraction* (C_7H_{14} isomers): ethylcyclopentane (ECP); dimethylcyclopentane (1,1-DMCP, 1,2-DMCP, 1,3-DMCP).
- *Ring opening* (C_7H_{16} isomers): *n*-heptane (Hp); methylhexanes (2-MHx, 3-MHx); dimethylpentanes (2,3-DMP, 3,3-DMP, 2,4-DMP, 2,2-DMP), 3-ethylpentane (3EP); 2,2,3-trimethylbutane (2,2,3-TMB).

3.1.1.2. Time-on-stream experiments In a given test, MCH conversion was measured at four different temperatures (523, 528, 573, and 598 K) and three contact times (10, 13, and 20 g h/mol) for each temperature. To monitor the eventual deactivation of the catalyst, conversion in standard conditions (572 K, $W/F = 20$ h g/mol) was measured periodically. No significant deactivation was detected for the duration of the experiment (96 h). In standard conditions, the yields for ring opening, ring contraction, and cracking were 40, 18, and 23%, respectively.

3.1.1.3. Variation of MCH conversion by combined changes in contact time and reaction temperature In a typical reaction test, the variation of MCH conversion is obtained by changing the contact time at a given temperature or by varying the reaction temperature at a given contact time. These two approaches were combined in the present study to obtain a wider range of variation of conversion. Although this is not a very rigorous treatment of the results, it has the advantage of giving a clearer picture of the evolution of various products with MCH conversion. An example of this approach is shown in Fig. 1 for the 1.2Ir/ZSiW2.5 catalyst. The ring-contraction products are primary in nature, whereas those of ring opening and cracking are secondary in nature. Alkylcyclopentanes obtained by ring contraction are subsequently hydrogenolyzed to form ring-opening products. The decrease in the ring-opening selectivity for high MCH conversions is associated with the cracking of ring-opening products.

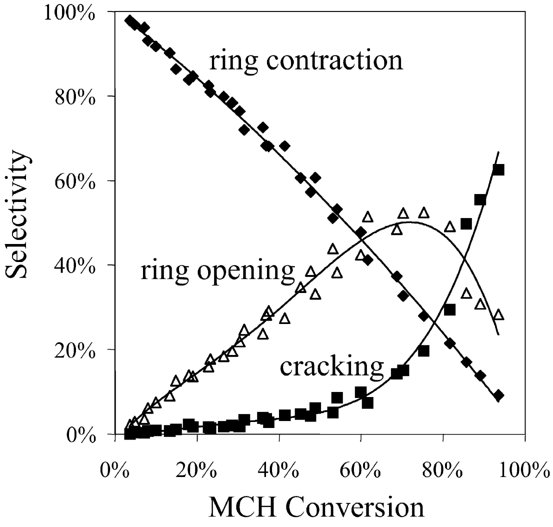


Fig. 1. Selectivity of ring contraction, ring opening, and cracking obtained with the catalyst 1.2Ir/ZSiW2.5 as a function of MCH conversion for temperatures between 548 and 598 K and for contact times of 1–20 g h/mol.

3.1.2. *Monofunctional acid catalysts (ZSiWx): influence of W surface density*

3.1.2.1. Activity Fig. 2a shows, for a series of ZSiWx catalysts (with $x = 0$; 0.6; 0.9; 1.5; 2.5; 3.4), the variation of MCH conversion as a function of W surface density for a contact time of 20 g h/mol at a reaction temperature of 573 K. The results indicate no significant MCH conversion for W surface densities $\leqslant 0.9$ at/nm^2. Further increases in W surface density lead to a significant increase in conversion. Fig. 2b reports for active catalysts, the yields of various types of products as a function of contact time. For all contact times, the yields for ring-contraction largely exceed those measured for ring opening.

3.1.2.2. Selectivity Fig. 3a depicts, for the ZSiWx series, the selectivity for the three types of products: ring contraction, ring opening, and cracking as a function of MCH conversion at 548 K. The results clearly show that for a given conversion, essentially the same selectivities are obtained for the three active catalysts. This suggests that similar types of active sites are present in these solids (e.g., Brönsted acid sites of similar strengths). Note that the selectivity for ring contraction tends toward 100% with decreasing conversion, whereas that for ring opening and cracking tends toward 0%. This indicates that the ring contraction reaction precedes the ring-opening and cracking reactions. In the absence of a metallic function, the mechanism for ring opening is purely acidic, by β-scission. The cracking products consisted primarily of C3 and C4, characteristic of acid-catalyzed cracking. Furthermore, minor amounts of olefins and aromatics were detected, which agrees with this mechanism. Clearly, active monofunctional acid catalysts (ZSiWx) were not selective for ring opening.

Fig. 3b shows the selectivities for C_7H_{14} isomers within the ring contraction products obtained with the ZSiWx series as a function of MCH conversion. The extrapolation to zero of the ring-contraction yield indicates that 1,3-DMCP is the main isomer, followed by 1,2-DMCP and ECP in comparable amounts

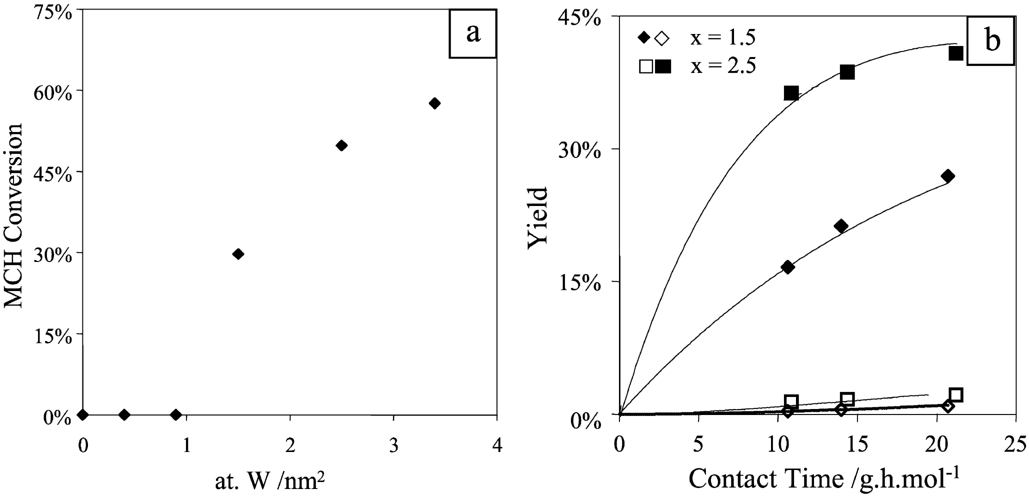


Fig. 2. (a) MCH conversion at 573 K for a contact time of 20 g h/mol as a function of tungsten surface density. (b) Yields for ring contraction (full symbols) and ring opening (open symbols) obtained with ZSiW1.5 and ZSiW2.5 at 573 K as a function of contact time.

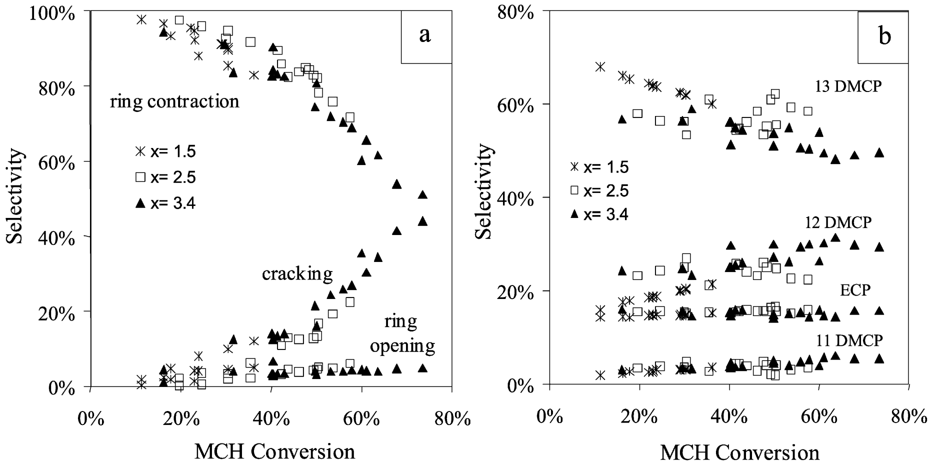


Fig. 3. Selectivities obtained with ZSiWx catalysts ($x = 1.5, 2.5, 3.4$) as a function of MCH conversion at 548 K and for contact times between 10 and 20 g h/mol. (a) Selectivities for ring contraction, ring opening, and cracking. (b) Selectivities of C_7H_{14} isomers within the ring-contraction group of products.

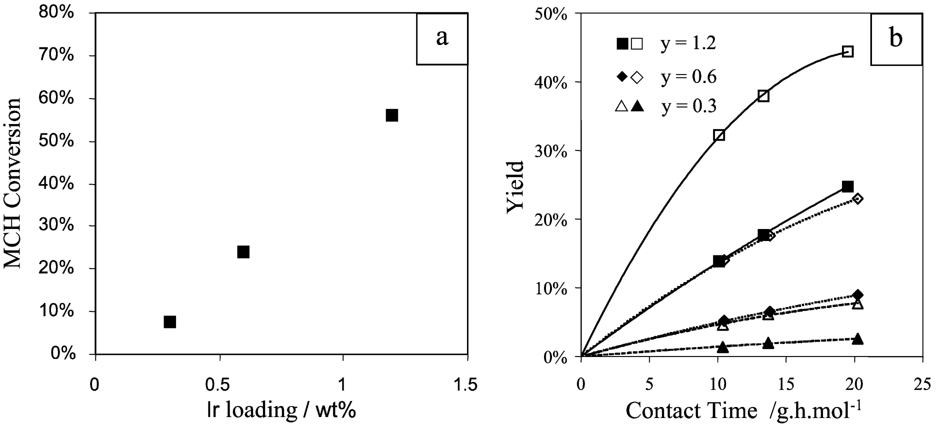


Fig. 4. (a) MCH conversion obtained with yIr/ZSiW0 catalysts as a function of Ir content at 573 K and for a contact time of 14 g h/mol. (b) Yields for ring opening (open symbols) and cracking (full symbols) obtained with the yIr/ZSiW0 catalysts ($y = 0.3$; 0.6; 1.2 wt% Ir) as a function of contact time and at a reaction temperature of 573 K.

and 1,1-DMCP as a minor product. The low ECP selectivity at low conversion is indicative of the presence of strong Brönsted acid sites [3].

3.1.3. Monofunctional metallic catalysts yIr/ZW0: influence of Ir content

3.1.3.1. Activity Fig. 4a shows the variation of MCH conversion as a function of Ir content for the yIr/ZSiW0 catalysts at a given contact time of 14 g h/mol and a reaction temperature of 573 K. A steady increase in conversion with increasing Ir content can be seen. Fig. 4b shows the yield in ring-opening and cracking products for the catalyst yIr/ZSiW0 as a function of contact time and at a reaction temperature of 573 K. No ring-contraction products were detected. This is consistent with the absence of an acid function. Direct ring opening is the predominant reaction observed.

3.1.3.2. Selectivity Fig. 5a reports the selectivities for ring opening and cracking for yIr/ZSiW0 catalysts ($y = 0.3$; 0.6; 1.2 wt% Ir) as a function of MCH conversion. In these solids, the zirconia support is not sufficiently acidic to isomerize MCH; thus, only direct ring opening of the C6 ring and cracking products were detected. Note that catalysts containing different Ir loadings exhibited similar selectivity for a given conversion. This reflects the fact that only metal-catalyzed reactions are involved. For low conversions, the selectivities for ring opening and cracking were around 80% and 20%, respectively. The ring-opening products were primarily 2 and 3 methylhexanes, characteristic of a selective breaking of a nonsubstituted carbon–carbon bond of MCH on Ir (Scheme 1). The ability of Ir to open C6 rings has been reported by McVicker et al. [3]. The selectivity for cracking (20%) observed at low MCH conversions suggests that some of the cracking products are primary in nature.

The cracking products consisted primarily of C_1 and C_6 compounds in comparable amounts (Fig. 5b). In principle, this can be attributed to dealkylation of MCH. However, the amount of cyclohexane detected was much lower than that would be expected from such a process. A more likely explanation is to attribute C_1 and C_6 formation to a “deep” hydrogenolysis. Consistent with this interpretation is the fact that the main C6 products observed were 2 and 3 methylpentanes, which could be formed by hydrogenolysis of ring-opening products

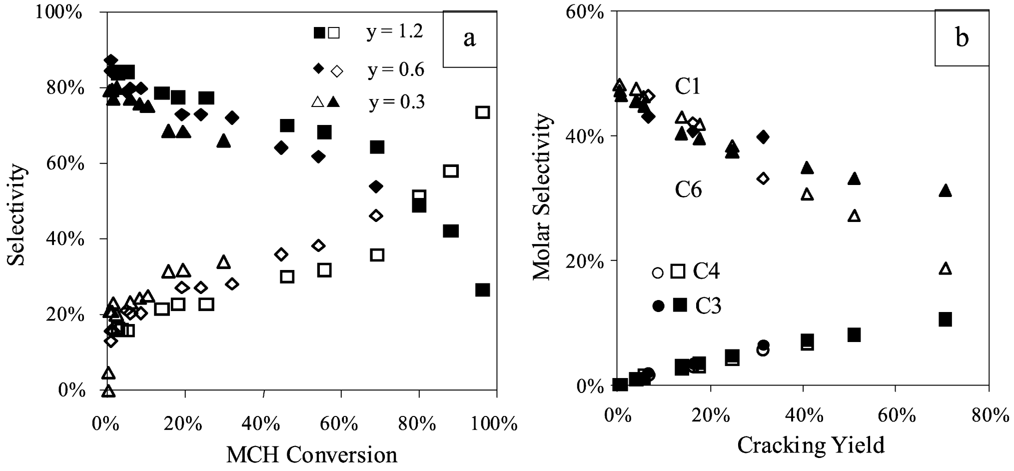


Fig. 5. (a) Selectivity for ring opening (full symbols) and cracking (open symbols) obtained with the yIr/ZSiW0 catalysts ($y = 0.3$; 0.6; 1.2 wt% Ir) as a function of MCH conversion. (b) Selectivity within the cracking products obtained with the catalysts 1.2Ir/ZSiW0 and 0.6Ir/ZSiW0 as a function of cracking yield.

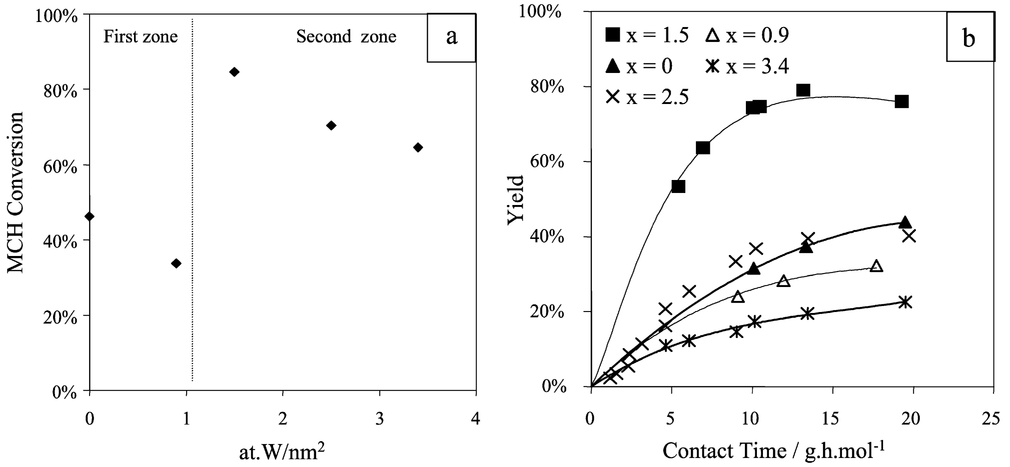


Fig. 6. (a) MCH conversion as function of tungsten surface density for 1.2Ir/ZSiWx catalysts for a contact time of 20 g h/mol. (b) Ring-opening yield obtained with the series 1.2Ir/ZSiWx as a function of contact time at a reaction temperature of 573 K.

2 and 3 methylhexanes. This second breaking of the C–C bond may occur without desorption of methylhexane intermediates (MHx), which may explain why cracking appears partially as a primary reaction. The ring-opening selectivity decreased with increasing MCH conversion, which can be attributed to deep hydrogenolysis.

3.1.4. Bifunctional catalysts (1.2Ir/ZWx): influence of W surface density

3.1.4.1. Activity Fig. 6a shows the variation of MCH conversion for 1.2Ir/ZSiWx catalysts as a function of W surface density for a reaction temperature of 573 K and a contact time of 20 g h/mol. Two different zones can be distinguished. For low W surface densities (i.e., catalysts with an acidity not sufficient for MCH ring contraction), MCH conversion was relatively low. For W surface densities $\geqslant 1.5$ at. W/nm^2 (i.e., catalysts sufficiently acidic to promote MCH ring contraction), MCH conversion decreased with increasing W surface density. It should be noted that the 1.2Ir/ZSiW0.9 catalyst exhibited a lower activity than that measured for the 1.2Ir/ZSiW0 solid. This can be tentatively explained by a decreased dispersion of the Ir phase on W addition [25].

Fig. 6b shows the variation of ring-opening yield for 1.2Ir/ZSiWx catalysts as a function of contact time for a reaction temperature of 573 K. For the sake of clarity, ring contraction and cracking yields were not included. Note that for the same contact time (20 g h/mol), the evolution of ring-opening yield was similar to that observed for the MCH conversion.

3.1.4.2. Selectivity Fig. 7 shows the ring-opening selectivity for 1.2Ir/ZSiWx catalysts. Two different patterns for the evolution of the selectivity with MCH conversion can be distinguished. For low W surface densities ($x \leqslant 0.9$ at. W/nm^2), the ring-opening selectivity, which was very high for low conversions, decreased with increasing MCH conversion. For higher W surface densities, the selectively increased with increasing conversion up to a maximum reached for MCH conversion between 65 and 75%, followed by a decrease for higher conversions.

As noted earlier, catalysts with low W surface densities (1.2Ir/ZSiW0 and 1.2Ir/ZSiW0.9) exhibited weak acidity and

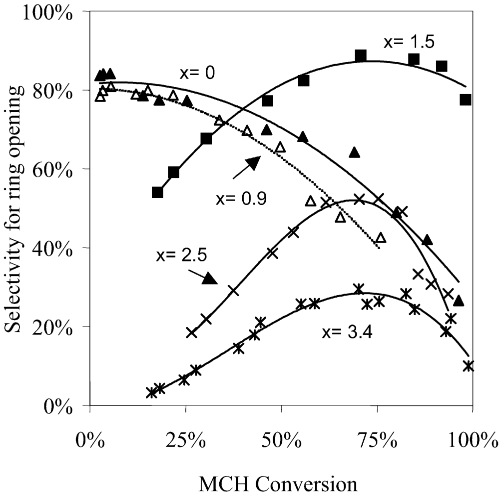


Fig. 7. Ring-opening selectivity obtained with the 1.2Ir/ZSiWx catalysts as a function of MCH conversion.

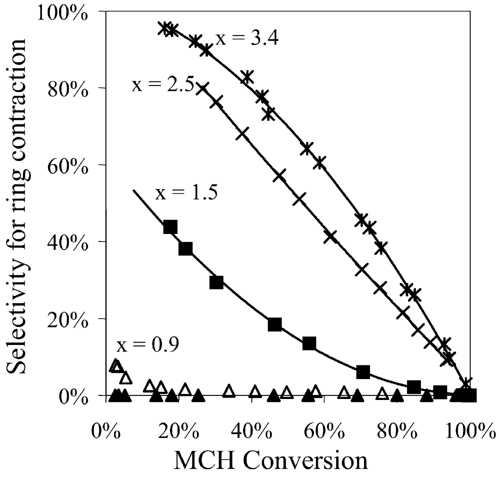


Fig. 8. Selectivity for ring contraction obtained with the 1.2Ir/ZSiWx catalysts as a function of MCH conversion.

thus negligible ring contraction activity. Hence, ring-opening products are typical of those observed for direct opening of the C6 ring. The behavior of the remaining catalysts (presence of a maximum) appears to characterize indirect ring opening. The best ring-opening selectivity was observed for 1.2Ir/ZSiW1.5 (ca. 90% selectivity for 75% conversion) [26]. Further increases in W surface density led to a significant decrease in the maximum selectivity for ring opening.

Fig. 8 shows the ring contraction selectivity for 1.2Ir/ZSiWx as a function of MCH conversion. The results show that for low conversions, catalysts active for ring contraction exhibited a selectivity of ca. 100%. This indicates that ring contraction of MCH to alkylcyclopentane was the first step in ring opening. Similar results have been reported by Schultz et al. [20] for the conversion of cyclohexane. For a given conversion, the ring contraction selectivity increased with increasing W surface density. Thus, the observed decrease in ring-opening selectivity (Fig. 7) around 75% conversion with increasing W surface density can be associated with an increase in ring contraction selectivity, because no major changes in cracking selectivity were noted (Fig. 8). The increase in ring contraction selectivity can be qualitatively explained by a decrease in ring-opening activity due to the observed decrease in Ir dispersion with increasing W surface density [25].

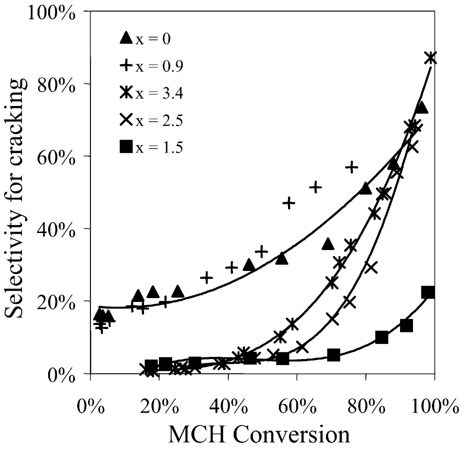


Fig. 9. Selectivity for cracking obtained with the 1.2Ir/ZSiWx catalysts as a function of MCH conversion.

Fig. 9 shows the cracking selectivity for the same catalysts. At low conversions, the 1.2Ir/ZSiW0 and 1.2Ir/ZSiW0.9 catalysts exhibited around 20% cracking, indicating a behavior typical of monofunctional metallic catalysts. (Cracking products are in part primary in nature.) For higher W surface densities, the selectivity for cracking at low conversions was negligible reflecting the secondary nature of cracking compounds. The observed increase in selectivity with increasing conversion can be attributed to the cracking of ring-opening products.

Fig. 10 shows the distribution within the group of cracking products for 1.2Ir/ZSiWx catalysts ($x = 0$ and 3.4) as a function of cracking weight yield. Analysis of the results shows that C1 and C6 cracking products characteristic of deep hydrogenolysis were essentially obtained with the monofunctional metallic catalyst 1.2Ir/ZSiW0. In contrast, cracking products for the 1.2Ir/ZSiW3.4 catalyst consisted primarily of C3 and C4 compounds typically found in acid-cracking. The catalyst 1.2Ir/ZSiW1.5 exhibited an intermediate behavior. These results suggest that the addition of W decreases the hydrogenolysis ability of Ir (by decreasing the number of exposed metal centers) and increases the cracking of ring-opening products over Brönsted acid sites of the support.

3.1.5. Bifunctional catalysts (yIr/ZW1.5): influence of Ir content

In the previous section, analysis of the influence of W surface density in the case of bifunctional catalysts 1.2Ir/ZSiWx showed superior performance in ring-opening activity for $x = 1.5$. Catalysts with such a W surface density and different Ir contents were examined. As shown in Fig. 11a, no significant improvement in activity of the ZSiW1.5 solid occurred on addition of 0.3% Ir. This is consistent with the catalytic performance for toluene hydrogenation reported earlier [25]. Further increases in Ir content bring about a sharp increase in MCH conversion. Fig. 11b shows the weight yields for ring opening and ring contraction obtained with yIr/ZSiW1.5

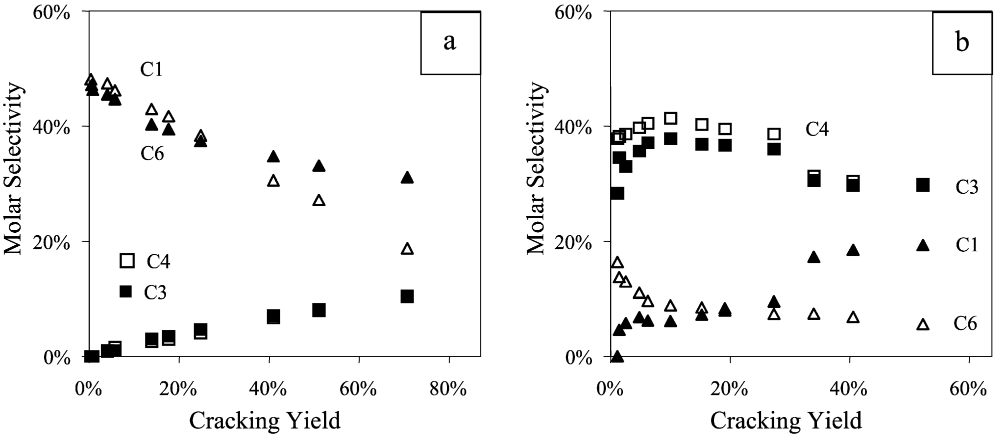


Fig. 10. Molar selectivity for C1, C6, C3 and C4 products as a function of cracking yield for 1.2Ir/ZSiW0 (a) and 1.2Ir/ZSiW3.4 (b) catalysts.

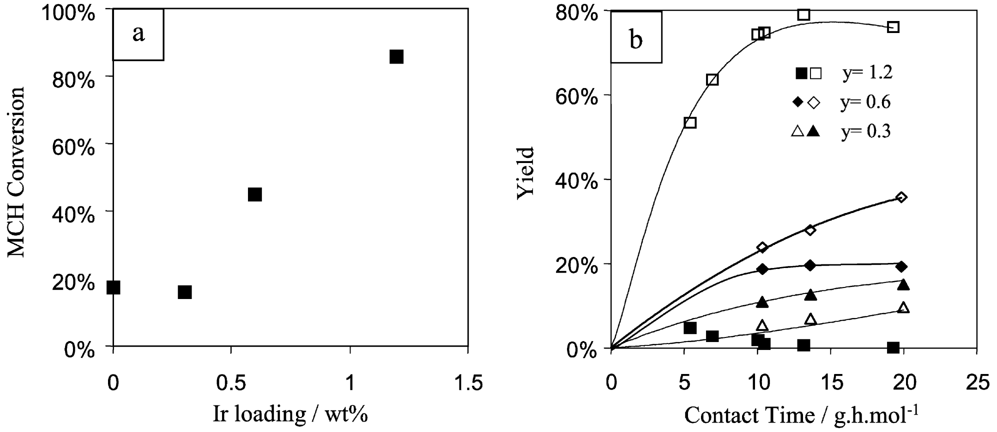
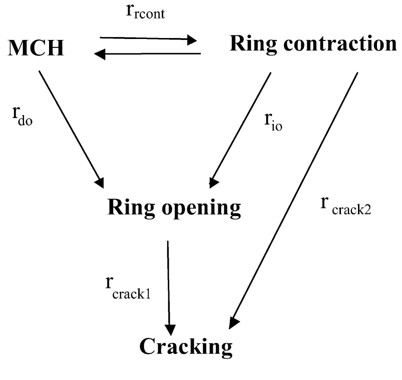


Fig. 11. (a) MCH conversion obtained with the yIr/ZSiW1.5 catalysts as a function of Ir content at 573 K for a contact time of 14 g h/mol. (b) Yields for ring opening (open symbols) and ring contraction (full symbols) obtained with the catalyst yIr/ZSiW1.5 as a function of contact time at a reaction temperature of 573 K.

catalysts. The results show that the ring-opening yield sharply increased with increasing Ir content from 0.3 to 1.2 wt%, reaching ca. 80% for a contact time 14 g h/mol and at a reaction temperature of 573 K.

3.1.6. Reaction network and kinetic modeling

In agreement with the literature [3], the results obtained for the solid 1.2Ir/ZSiW0 illustrate the ability of Ir to open a 6-carbon atom cycle. Thus, a direct path for ring opening (r_{do}) must be considered in the proposed reaction network (Scheme 2). The evolution of the ring-opening selectivity indicates different behavior for catalysts containing sufficient W content to induce C6 to C5 ring contraction. It has been shown that for these solids, the ring contraction reaction precedes that of ring opening. Thus, the observed ring opening is that of alkylcyclopentanes formed on acid-catalyzed ring contraction of MCH. Such indirect path for ring opening is illustrated in Scheme 2 by two consecutive reactions: ring contraction (r_{rcont}) followed by ring opening (r_{io}). In the proposed reaction network, two possibilities for cracking are considered: cracking of the ring-opening products and direct cracking of C5 rings. Direct cracking from MCH by dealkylation has not been considered, because cyclohexane yield has been, consistently, very low. Note that the proposed reaction network differs from that reported in [12] by the cracking step of ring contraction products.



Scheme 2. Reaction network for the conversion of MCH over monofunctional (WO_3/ZrO_2–SiO_2; Ir/ZrO_2–SiO_2) and bifunctional (Ir/WO_3/ZrO_2–SiO_2) catalysts.

For kinetic modeling (see supplementary material), all of the reactions shown in Scheme 2 are considered to be first order. Initial rates are calculated for a reaction temperature of 523 K. For the optimization of initial rates ($r°$) and activation energies (E_a), the experimental data are treated as a function of the contact time and the reaction temperature. The reaction network

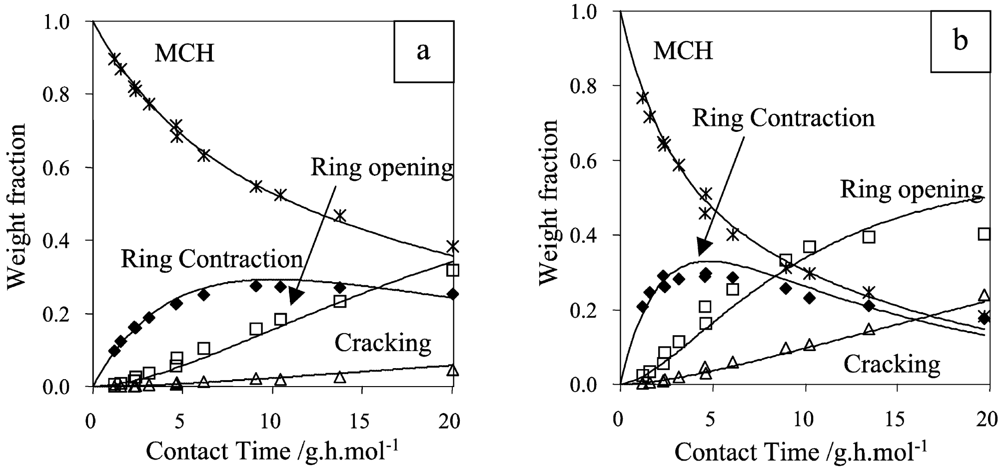


Fig. 12. Comparison between experimental weight fractions obtained for the 1.2Ir/ZSiW2.5 catalyst and those calculated using the proposed model. (a) Reaction temperature of 548 K. (b) Reaction temperature of 573 K.

Table 1
Initial rates at 523 K and activation energies expressed respectively in mol/(h kg) and kJ/mol obtained for ZSiWx catalysts

Catalyst	r_{rcont}	E_{rcont}	r_{io}	E_{io}	r_{crack2}	E_{crack2}
ZSiW1.5	9.4	38	1.2	50	2.3	59
ZSiW2.5	25.5	38	1.5	50	4.1	59
ZSiW3.4	33.6	38	1.4	50	7.9	59

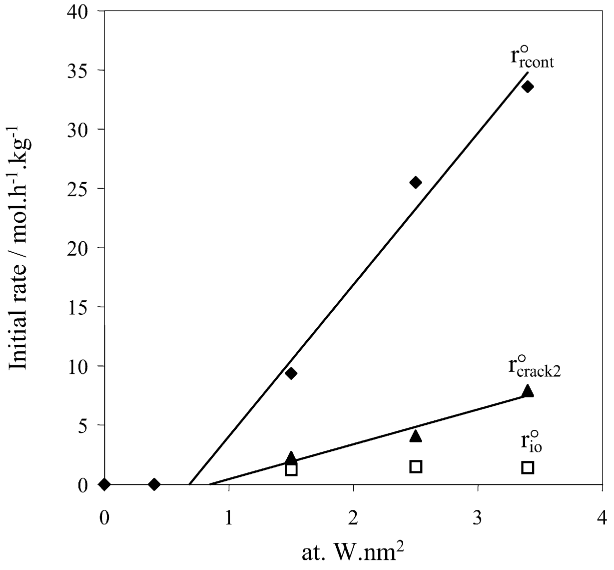


Fig. 13. Initial rates for ring contraction, indirect ring opening and cracking for the ZSiWx catalysts as a function of W surface density.

has been used to model the performances obtained with various catalysts. Fig. 12 shows, for the catalyst 1.2Ir/ZSiW2.5, the predicted (continuous lines) and experimental weight fractions of various groups of products and of unconverted MCH as a function of contact time for reaction temperatures of 548 and 573 K. A very good agreement was obtained between the calculated weight fractions and experimental results. Similar results were obtained for other solids. In the subsequent sections, we report on the use of this model to investigate the relationships between the kinetic parameters and characterization results.

3.2. *Kinetic studies*

3.2.1. *Monofunctional acid catalysts ZSiWx*

Table 1 reports the initial rates and activation energies calculated for the solids ZSiW1.5, ZSiW2.5, and ZSiW3.4. As noted earlier (Fig. 3a), for these solids, ring-opening compounds clearly appear as secondary products. The direct ring-opening path (r°_{do}) was thus deleted from the reaction network. Furthermore, fitting of the data gives a zero initial rate for the reaction of cracking of ring-opening products (r°_{crack1}). This can be attributed to low yields for ring-opening products. The activation energies for ring contraction (38 kJ/mol), indirect ring opening (50 kJ/mol), and cracking (59 kJ/mol) appear to be little affected by W surface density. This suggests a similar nature of the active sites (i.e., changes in the abundance of various active sites and not in their intrinsic activity with W surface density). W deposition on zirconia leads to the development of strong and relatively strong acid sites that were not present in the original support. For W surface densities >0.9 at./nm^2, the abundance of these acid sites increases with no apparent increase in their strengths [25].

Fig. 13 shows the evolution of the initial rates calculated for the ZSiWx as a function of W surface density. No significant ring contraction activity (r°_{rcont}) was detected for W surface densities $\leqslant 0.4$ at. W/nm^2. The activity appeared to develop for a W surface density around 0.7 at. W/nm^2 and increased steadily with a W surface density. Similar behavior was noted for the cracking reaction ($r^\circ_{\text{crack}2}$). The initial rate for indirect ring opening (r°_{io}) was consistently low and did not exhibit a clear evolution with W surface density.

3.2.2. *Monofunctional metal catalysts yIr/ZSiW0*

Table 2 reports the calculated initial rates and activation energies for the *y*Ir/ZSiW0 catalysts. No ring contraction products were detected for these catalysts. Thus, the indirect ring-opening (r°_{io}) pathway via ring contraction of MCH was not considered in the modeling of the results. The reaction network comprises two consecutive reactions: direct ring opening (r°_{od}) followed by cracking. Within the range of Ir loadings examined in the present study, the Ir content had no significant affect on the activation energy calculated for direct ring opening of MCH (about 138 kJ/mol). For the three catalysts, the activation energy for the cracking reaction ($r^\circ_{\mathrm{crack1}}$) was ca. 59 kJ/mol, and the activation energy was set at this value for optimization of other kinetic parameters.

Fig. 14 shows the initial rates as a function of Ir content. A minimum Ir content (0.25%) appears to be required for the development of direct ring-opening activity (r°_{do}). For higher loadings, a steady increase of the initial rate with Ir content can be seen. Similar behavior has been observed for CO adsorption [25]. The cracking rate ($r^\circ_{\mathrm{crack1}}$) increased sharply with addition of Ir, followed by a more progressive increase at higher Ir content.

Table 2
Initial rates at 523 K and activation energies expressed respectively in mol/(h kg) and kJ/mol obtained for *y*Ir/ZSiW0 catalysts

Catalyst	r_{do}	E_{do}	r_{crack1}	E_{crack1}
0.3Ir/ZSiW0	0.3	138	10.1	59
0.6Ir/ZSiW0	1.1	138	12.6	59
1.2Ir/ZSiW0	3.5	138	19.1	59

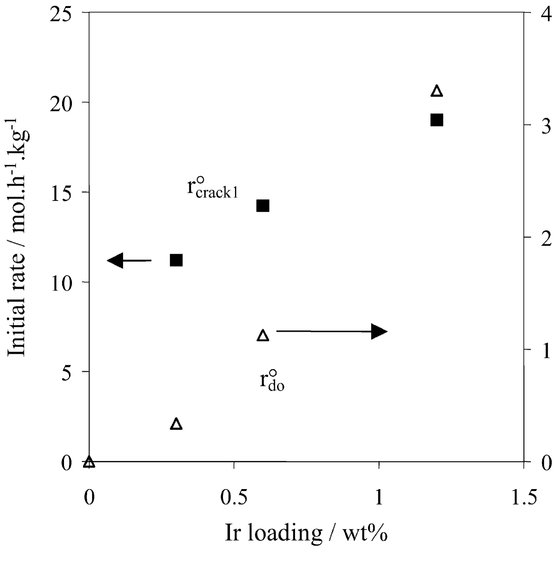


Fig. 14. Variation of the initial rates for direct ring opening and cracking as a function of Ir content for the *y*Ir/ZSiW0 catalysts ($y = 0.3$, 0.6, and 1.2 wt% Ir).

3.2.3. *Bifunctional catalysts*

3.2.3.1. *1.2Ir/ZSiWx catalysts: influence of W surface density*

Table 3 reports the initial rates and activation energies calculated for the 1.2Ir/ZSiW*x* catalysts. As noted previously for the ZSiW*x* series, no ring contraction products were detected for W surface densities $\leqslant 0.4$ at. W/nm^2. The activation energy, E_{rcont}, obtained for the solid 1.2Ir/ZSiW0.9 (117 kJ/mol) was similar to that reported by McVicker et al. for MCH ring contraction over bifunctional catalysts (117–134 kJ/mol) [27]. For W surface densities $\geqslant 0.9$ at. W/nm^2, the activation energy for ring contraction decreased with increasing W surface density. This can be explained by an increased contribution of the acid mechanism (38 kJ/mol obtained for the ZSiW*x* series). This evolution appears to reflect the reported increased abundance of Brönsted acid sites and the decreased dispersion of the metallic phase with increasing W surface density [25]. The observed decrease in the activation energy for indirect ring opening is consistent with this hypothesis. In contrast, no significant changes in the activation energy for direct ring opening (E_{do}) with W surface density can be seen.

Fig. 15 shows the initial rates calculated from the experimental data for the 1.2Ir/ZSiW*x* catalysts as a function of W surface density. As noted for the ZSiW*x* solids, a minimum of W surface density appears to be required for the development of ring contraction activity (r°_{cont}). Above this threshold, the ring

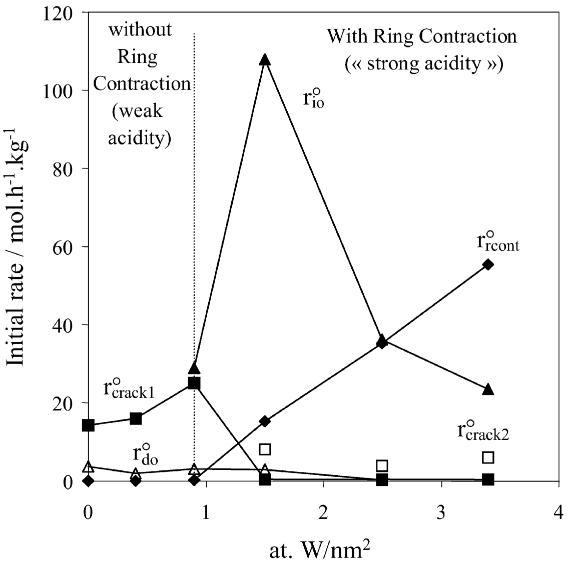


Fig. 15. Initial rates calculated from experimental data for 1.2Ir/ZSiW*x* catalysts as a function of W density.

Table 3
Initial rates at 523 K and activation energies expressed respectively in mol/(h kg) and kJ/mol obtained for the 1.2Ir/ZSiW*x* catalysts

Catalyst	r_{rcont}	E_{rcont}	r_{do}	E_{do}	r_{io}	E_{io}	r_{crack1}	E_{crack1}	r_{crack2}	E_{crack2}
1.2Ir/ZSiW0			3.5	138			19.1	59		
1.2Ir/ZSiW0.4			3.7	138			16	55		
1.2Ir/ZSiW0.9	0.2	121	3.0	121	28.8	126	26.2	59		
1.2Ir/ZSiW1.5	15.2	117	2.8	151	107.9	117	–	–	8.0	100
1.2Ir/ZSiW2.5	35.1	92	0.2	155	36.1	63	–	–	3.8	92
1.2Ir/ZSiW3.4	55.4	80			23.5	42	–	–	6.0	92

Table 4
Initial rates at 523 K and activation energies expressed respectively mol/(h kg) and kJ/mol obtained for the *y*Ir/ZSiW1.5 catalysts

% Ir	r_{rcont}	E_{rcont}	r_{do}	E_{do}	r_{io}	E_{io}	r_{crack1}	E_{crack1}	r_{crack2}	E_{crack2}
0	9.4	38			1.2	51			2.3	59
0.3	4.1	63	0.1	146	8.4	63			3.3	25
0.6	9.1	88	0.8	113	26.4	75	–	–	2.6	42
1.2	15.2	117	2.8	151	151	117	–	–	8.0	100

contraction rate increased linearly with increasing W surface density. The decrease in the initial rate for direct ring opening (r°_{do}) is consistent with the observed decrease in Ir dispersion. Note that for W surface densities $\geqslant 0.9$ at. W/nm^2, the indirect ring-opening rate was significantly higher than the direct ring opening. This confirms that C5 rings can be more readily opened than C6 rings. For W surface densities >1.5 at. W/nm^2, the rate for indirect ring opening decreased significantly with W. This agrees with the observed decrease in the dispersion of the Ir phase reported earlier [25]. For low W surface densities ($\leqslant 0.9$ at. W/nm^2), the high initial rate for cracking reflects the behavior observed for monofunctional metal catalysts *y*Ir/ZSiW0.

3.2.3.2. yIr/ZSiW1.5: Influence of Ir content Table 4 reports the initial rates and activation energies calculated for the *y*Ir/ZSiW1.5 catalysts. The activation energy for the ring-contraction reaction (E_{rcont}) increased with Ir content. This may be attributed to an evolution of the solids from monofunctional acid for ZSiW1.5 to bifunctional for Ir-rich catalysts. This interpretation is consistent with the activation energy (117–134 kJ/mol) reported by McVicker et al. [27] for MCH ring contraction in the case of a bifunctional catalyst. The activation energy for direct ring opening varied within a limited range (134 ± 21 kJ/mol) with Ir content. The calculated values were close to those observed with monofunctional metallic catalysts *y*Ir/ZSiW0 (138 kJ/mol). A parallel evolution of the activation energy for ring contraction (E_{rcont}) and that of indirect ring opening (E_{io}) can be seen. Note that there was no clear pattern for the variation in the activation energy for cracking of alkylnaphthenes (E_{crack2}) with varying Ir content.

Fig. 16 reports the initial rates for ring contraction (r°_{rcont}), direct ring opening (r°_{do}), indirect ring opening (r°_{io}), and cracking (r°_{do}) as a function of Ir content. The initial rate for ring contraction (r°_{rcont}) appeared to increase with Ir content. However, the rate calculated for the Ir-free solid ZSiW1.5 was higher than that determined for the solid with the lowest Ir content (0.3Ir/ZSiW1.5). The rate for indirect ring opening (r°_{io}) increased significantly with Ir content. The rate of direct ring opening (r°_{do}) also increased with Ir content; however, it remained ca. two orders of magnitude lower than that for indirect ring opening (r°_{io}). The initial rate for cracking (r°_{do}) was low for low Ir content, then increased steadily with increasing Ir loadings. A significant rate for cracking of ring-opening products (r°_{crack1}) was measured only for high Ir content.

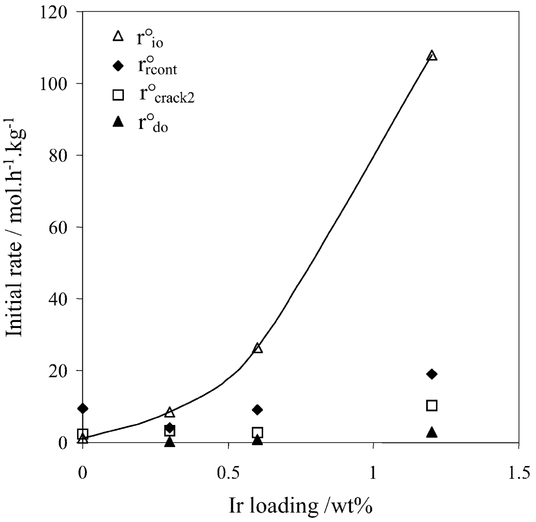


Fig. 16. Initial rates for ring contraction, direct and indirect ring opening, and cracking as a function of Ir content for *y*Ir/ZSiW1.5 catalysts.

4. Discussion

4.1. Monofunctional acid and metal catalysts: correlation structure–catalytic performance

4.1.1. Monofunctional acid catalysts ZSiWx: correlation with acidity measurements

As noted earlier, a minimum W surface density (ca. 0.9 at. W/nm^2) is required for the development of MCH ring-contraction activity. For higher values, the ring-contraction rate increased linearly with increasing W surface density. The lack of variation of the activation energy for ring contraction in the range of W surface densities investigated is indicative of the presence of Brönsted acid sites of similar strengths. Fig. 17 shows the initial ring contraction rate (r°_{rcont}) calculated for a reaction temperature of 523 K as a function of the areas of infrared bands at 2167 and 2175 cm^{-1} attributed to the interaction of CO with relatively strong and strong Brönsted acid sites, respectively [25,28]. There is a linear relationship between the abundance of these acid sites and the rate for MCH ring contraction to alkylcyclopentanes. No such correlation has been observed with Lewis acid sites. This is consistent with the hypothesis that active sites are associated with strong and relatively strong Brönsted acid sites of tungstated zirconia. Thus, the ring contraction mechanism is purely acidic [16,29,30], that is, protonation of methylcyclohexane forming carbenium ion and molecular hydrogen, followed by ring contraction via protonated cyclopropane intermediate (Scheme 3). Hydride trans-

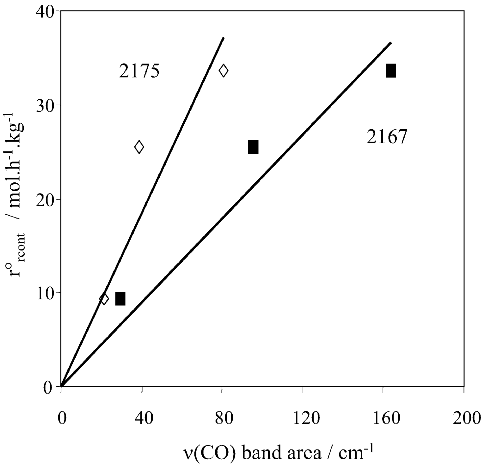


Fig. 17. Initial ring-contraction rate r_{rcont} at 523 K for ZSiWx catalysts as a function of the area of the infrared bands at 2167 and 2175 cm^{-1} characteristic of CO vibration.

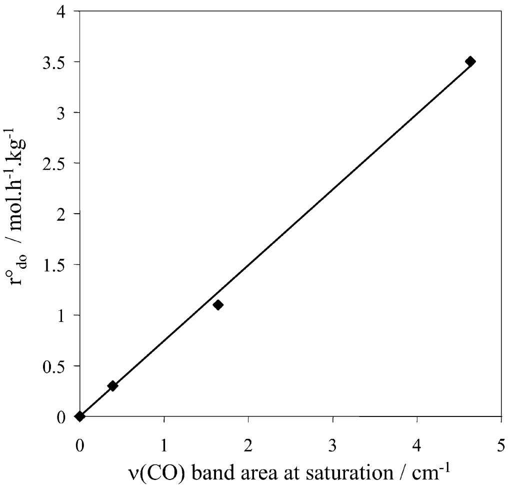
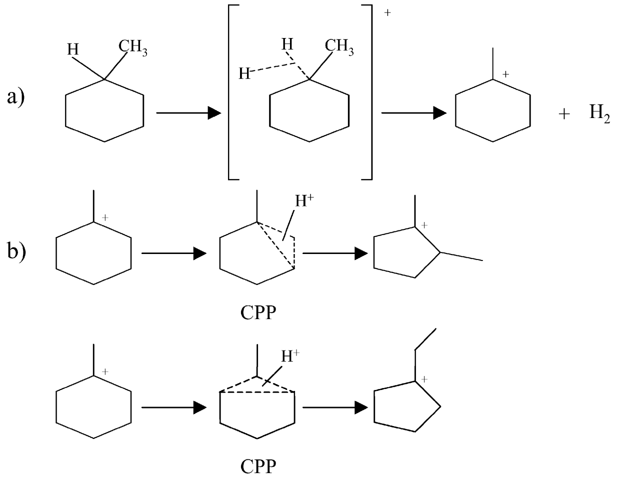


Fig. 18. Initial rate for MCH direct ring opening (r_{do}) over yIr/ZSiW0 catalysts as a function of the infrared band area for CO adsorbed at saturation on Ir.

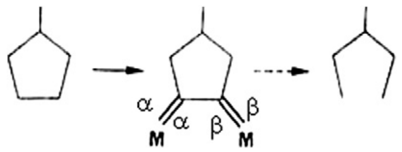
fer from another MCH molecule yields DMP or ECP. The rate for indirect ring opening remains low with an activation energy of ca. 50 kJ/mol. This activation energy can thus be considered characteristic of an acid-catalyzed mechanism. The cracking products were essentially C3 and C4 compounds, again consistent with this mechanism.

4.1.2. *Monofunctional metallic catalysts yIr/ZSiW0: correlation with Ir dispersion*

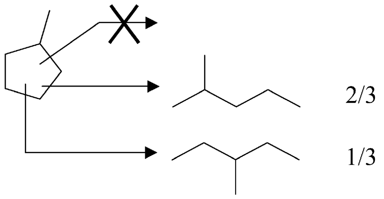
Fig. 18 shows, for the yIr/ZSiW0 catalysts, the initial rate for direct ring opening (r°_{od}) as a function of the area of the infrared band for CO adsorbed on Ir at saturation. A direct correlation between these two parameters can be seen, indicating that direct ring opening occurs on metallic Ir sites by hydrogenolysis. The threshold observed for the development of ring-opening activity and for the detection of the infrared bands of CO adsorbed on Ir suggest that part of the Ir is not accessible to the reactants and the IR probe molecule. This appears to be in contradiction with toluene hydrogenation results showing a direct relationship between hydrogenation rate and Ir content [25]. An activation energy of 138 kJ/mol was calculated for the hydrogenolysis of a 6-carbon atom ring on Ir. The low amount of n-heptane observed points to a selective ring opening by cleavage of unsubstituted C–C bonds, consistent with a dicarbene mechanism (Scheme 4). This has been previously reported for methylcyclopentane ring opening [31] (Scheme 5) and by McVicker for methylcyclohexane ring opening on 0.9% Ir/Al_2O_3 catalyst [3]. A fraction of MCH is converted by hydrogenolysis without desorption yielding cracking compounds as primary products.



Scheme 3. One possible acid mechanism for ring contraction: (a) carbenium ion formation; (b) ring contraction via protonated cyclopropane intermediate; adapted from [12,14].



Scheme 4. Dicarbene mechanism for ring opening [31].



Scheme 5. Selective ring opening of methylcyclopentane via a dicarbene mechanism.

4.2. *Bifunctional catalysts: correlation structure–catalytic performance*

4.2.1. *Ir/ZSiWx catalysts: influence of W surface density and correlation with Brönsted acidity and Ir dispersion*

Fig. 19 shows the initial ring-contraction rate (r°_{rcont}) calculated for a reaction temperature of 523 K as a function of the relatively strong and strong Brönsted acid sites (areas of the νCO vibration infrared bands at 2167 and 2175 cm^{-1}, at-

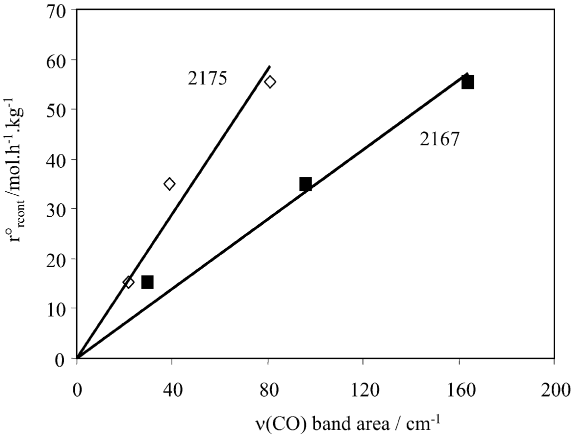


Fig. 19. Initial ring-contraction rate r_{rcont} at 523 K for the 1.2Ir/ZSiWx catalysts as a function of the areas of the infrared CO vibration bands at 2167 and 2175 cm^{-1}.

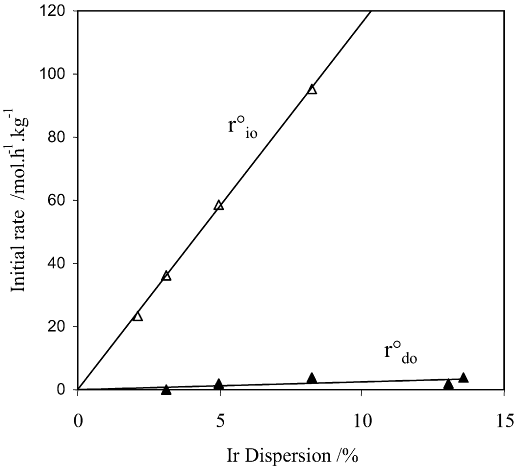


Fig. 20. Initial rates for direct and indirect ring opening as a function of the Ir dispersion obtained for 1.2Ir/ZSiWx catalysts.

tributed to the interaction of these sites with CO [25,28]). The results indicate a direct relationship between the abundance of these acid sites and the rate for MCH ring contraction to alkylcyclopentanes. Note that higher initial ring-contraction rates were observed for these solids compared with the corresponding ZSiWx catalysts. This indicates the participation of a bifunctional mechanism for ring contraction on Ir deposition. The increase in W surface density for a given Ir content led to an increase in the number of Brönsted acid sites and a decrease in the number of metallic centers due to the observed decrease in Ir dispersion. Consequently, the surface metal/acid ratio decreased with increasing W surface density. This results in a greater contribution of the acid mechanism for ring contraction, reflected in a decrease of activation energy E_{cont} from 121 to 80 kJ mol^{-1} (Table 3). The same behavior was observed for the activation energy of indirect ring opening (E_{io}). Fig. 20 reports the initial rates for direct r°_{do} and indirect r°_{io} ring-opening reactions for 1.2Ir/ZSiWx as a function of Ir dispersion. A direct correlation can be seen between the initial rate for indirect ring opening and Ir dispersion, indicating that metal sites are involved in the reaction of indirect ring opening. The evolution of the initial rate for direct ring opening r°_{do} exhibited similar behavior; however, the correlation was less straightforward because of the low rates measured and thus the high uncertainty associated with the results.

The rate for C5 ring opening, r°_{io}, at 523 K decreased for W surface density $\geqslant$1.5 at. W/nm^2 (Fig. 15) and appears to be directly related to Ir dispersion. The rate of direct ring opening, r°_{do}, also decreased with increasing W surface density; however, in this case, the activation energy (E_{do}) was not significantly affected by the W surface density (Table 3). This is a further indication that two different mechanisms are in play for ring-opening reactions.

4.2.2. *yIr/ZSiW1.5 catalysts: influence of Ir loading and correlation with Ir dispersion*

For monofunctional metal catalysts, the introduction of a small amount of Brönsted acid sites of sufficient strength on W deposition drastically changed the reaction network. The preferred pathway became ring contraction, followed by ring opening. The activation energy for ring contraction increased progressively with increasing Ir content from a value that could be considered typical for an acid mechanism (38 kJ/mol) to that representative of a bifunctional metal/acid system (117 kJ mol^{-1}) [27]. A similar behavior was observed for the activation energy of indirect opening of a 6-carbon atom ring (evolution from 50 to 117 kJ/mol). This indicates a similar change of mechanism from acid to bifunctional with increasing Ir content. Taking into consideration that little variation in Ir dispersion was observed for this series, such a change in mechanism can be explained by a decrease in the distance of the metal-acid center with increasing Ir content at constant dispersion, leading to the participation of more Brönsted acid sites in a bifunctional mechanism. We discuss this hypothesis later.

Analysis of the results for direct ring opening shows that within the range of Ir loadings considered, the activation energy for direct ring opening does not change with Ir content. This can be taken as an indication that direct ring opening of MCH occurs by the same mechanism operating for monofunctional metal and bifunctional metal/acid systems. Fig. 21 represents the initial rates for direct (r°_{do}) and indirect ring opening (r°_{io}) versus the rates for toluene hydrogenation measured for the yIr/ZSiW1.5 catalysts. Both initial rates appear to be directly correlated with the rate for toluene hydrogenation, suggesting that direct and indirect ring-opening reactions are correlated with the abundance of accessible metal sites. The correlation observed between the initial rate for direct or indirect ring opening and that for toluene hydrogenation illustrates the essential role of the metallic function for ring-opening reaction.

4.3. *MCH ring-opening mechanism*

Our results indicate that direct ring opening occurs on metal sites by a dicarbene mechanism as proposed in the literature [3,31]. The close similarity in the calculated values of the activation energy over solids of the yIr/ZSiW0, yIr/ZSiW1.5, and

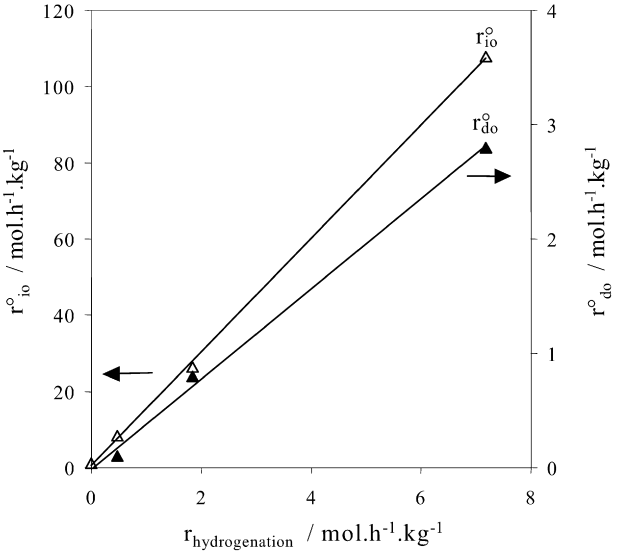


Fig. 21. Correlation between initial rates of direct and indirect ring opening versus toluene hydrogenation rate for *y*Ir/ZSiW1.5 catalysts.

1.2Ir/ZSiW*x* series suggests that the reaction is not very sensitive to the acidity of the support or to Ir particle size; only the number of accessible metallic sites appears to determine the reaction rate.

With respect to the mechanism for indirect ring opening, the situation is more complex. The parallel evolution of the activation energies for ring opening and ring contraction cannot be explained by one type of mechanism (metal or acid). Several hypotheses may be considered:

- An acid mechanism (Scheme 3). This hypothesis can be discarded, because it fails to account for the observed increase in the initial rate for ring opening with increasing Ir content for the *y*Ir/ZSiW1.5 solids.
- A dicarbene mechanism (Scheme 4) over the metal sites as proposed for the direct ring opening of MCH. This mechanism is consistent with the observed relation between the reaction rate and the number of accessible metal sites. For catalysts with sufficient acidity to ring-contract MCH, ring opening becomes a reaction consecutive to ring contraction (indirect ring opening). The isomer thus formed can readsorb over the metal, in line with the dicarbene mechanism; however, for indirect ring opening, a variation in the activation energy for the solids *y*Ir/ZSiW1.5 and 1.2Ir/ZSiW*x* was observed, whereas no such variations were noted for direct ring opening. Thus, the results cannot be fully explained by a dicarbene mechanism.
- A bifunctional mechanism for both indirect ring opening and ring contraction. One such mechanism proposed by Walter [32] consists of hydride abstraction by an acid site (proton) with hydrogen formation, ring contraction by the protonated cyclopropane intermediate, and ring opening by β-scission, without desorption of dimethylcyclopentane or ethylcyclopentane intermediates. The metal hydrogenates the olefin thus formed and regenerates Brönsted acidity. Without desorption of the intermediate, ring contraction and ring-opening products will be formed in parallel reactions (dimethylcyclopentene or ring opening). Thus, ring-opening products will be detected as primary compounds. This is in apparent contradiction with the observed selectivities. Only when the desorption rate of dimethylcyclopentene is much higher than that of ring opening may ring-opening products appear as secondary species. In that case, the proposed mechanism may account for the observed results and cannot be excluded.
- Ring opening by two parallel mechanisms, a dicarbene mechanism over the metallic sites and a β-scission mechanism over the acid sites. The activation energy measured in the case of an acid mechanism for ring opening of MCP over Ir-free acid catalysts was 50.2 kJ/mol, whereas that of MCH ring opening over metallic Ir sites was ca. 138 kJ/mol. Assuming the same activation energy for C5 and C6 ring opening, the two mechanisms (β-scission over acid sites and dicarbene mechanism over metal sites) lead to a weighted contribution of each activation energy. For low Ir dispersion and high W surface density (1.2Ir/ZSiW3.4), the calculated activation energies reflect a predominant acid mechanism. In contrast, for relatively high Ir dispersion and low W surface density (1.2Ir/ZSiW 1.5), metallic mechanism predominates. The proposed intervention of two parallel mechanisms is consistent with the observed evolution of selectivity.

5. Conclusion

The present work studied the catalytic performances of monofunctional acid (ZSiW*x*) or metal (*y*Ir/ZrW0) and bifunctional (1.2Ir/ZW*x* and *y*Ir/ZW1.5) catalysts for the ring-opening reaction of MCH. Kinetic analysis based on our proposed reaction network allowed the determination of initial rates and activation energies for various reactions. From the comparison of the results with previous characterization of the metallic and acid functions, we can draw the following conclusions:

- Monofunctional acid catalysts (ZSiW*x*) display low selectivity for ring opening. The isomerization activity develops for W surface density above a threshold value of 1 atom W/nm^2. This is attributed to the appearance and the development of a relatively strong Brönsted acidity monitored by infrared measurements. Over these acid solids, contraction and indirect opening of C5 rings occur according to a classic acid mechanism by β-scission described previously.
- Monofunctional metal catalysts (*y*Ir/ZrW0) display high selectivity for ring opening that decreases with increasing conversion. Because of the lack of isomerization products, the observed activity is attributed to the direct MCH ring opening. Over these catalysts, ring opening and cracking occur according to a dicarbene mechanism.
- The study of MCH conversion on bifunctional (1.2Ir/ZW*x* and *y*Ir/ZW1.5) catalysts indicates that MCH isomerization to alkylcyclopentanes occurs before ring opening. The best yields for ring opening are obtained with the 1.2Ir/ZW1.5

catalyst. Further increases in W surface density lead to a decrease in the indirect ring-opening rate, attributed to a decrease in Ir dispersion. For bifunctional metal/acid catalysts, analysis of the mechanism is less straightforward. The activation energy for ring contraction and indirect C5 ring opening is a function of the metal/acid ratio. For high ratios, indirect ring opening occurs essentially over metallic sites. A decrease in the metal/acid ratio enhances the contribution of acid mechanism.

This detailed study (Part I [25] and II) prepares the ground for a better understanding of bifunctional catalysts. This could lead to even more effective Ir-based catalysts for such molecules as decalin, tetralin, and alkyl-naphthalenes, which are more representative of a deeply hydrotreated LCO produced in the FCC unit of an oil refinery.

Acknowledgments

The work of S.L. was supported by a PhD thesis grant from the French Ministry of Education. The authors thank Drs. C. Collet, W. Vermeiren, and J.-P. Dath (Total S.A.) for fruitful discussions.

Supplementary material

The online version of this article contains the development of the kinetic equations.

Please visit DOI: 10.1016/j.jcat.2007.11.016.

References

[1] V.P. Thakkar, S.F. Abdo, V.A. Gembicki, J.F. McGehee, in: Proc. NPRA, Annual Meeting, San-Francisco, 13–15 March 2005, UOP LLC, Des Plaines, Illinois, USA, AM-05-53.
[2] W.C. Baird, J.G. Chen, G.B. McVicker, US Patent 6623626 (2001), assigned to ExxonMobil.
[3] G.B. McVicker, M. Daage, M.S. Touvelle, C.W. Hudson, D.P. Klein, W.C. Baird, B.R. Cook, J.G. Chen, S. Hantzer, D.E.W. Vaughan, E.S. Ellis, O.C. Feeley, J. Catal. 210 (2002) 137.
[4] R.C. Santana, P.T. Do, M. Santikunaporn, W.E. Alvarez, J.D. Taylor, E.L. Sughrue, D.E. Resasco, Fuel 85 (2006) 643.
[5] P.T. Do, W.E. Alvarez, D.E. Resasco, J. Catal. 238 (2006) 477.
[6] J.L. Carter, J.A. Cusumano, J.H. Sinfelt, J. Catal. 20 (1971) 223.
[7] C.G. Walter, B. Coq, F. Figueras, M. Boulet, Appl. Catal. A 133 (1995) 95.
[8] J.L. Carter, J.A. Cusumano, J.H. Sinfelt, J. Phys. Chem. 70 (1966) 2257.
[9] J.R. Anderson, Y. Shimoyama, in: J.W. Hightower (Ed.), Proc. 5th ICC, vol. 1, North-Holland, Amsterdam, 1972, p. 695.
[10] G. Del Angel, B. Coq, R. Dutartre, F. Figueras, J. Catal. 87 (1984) 27.
[11] H. Zimmer, Z. Paal, J. Mol. Catal. 51 (1989) 261.
[12] D. Kubicka, N. Kumar, P. Mäki-Arvela, M. Tiitta, V. Niemi, T. Salmi, D.Y. Murzin, J. Catal. 222 (2004) 65.
[13] M. Santikunaporn, J.E. Herrera, S. Jongpatiwut, D.E. Resasco, W.E. Alvarez, E.L. Sughrue, J. Catal. 228 (2004) 100.
[14] C.J. Egan, G.E. Langlois, R.J. White, J. Am. Chem. Soc. 84 (1962) 1204.
[15] J. Weitkamp, S. Ernst, Catal. Today 19 (1994) 107.
[16] H.S. Cerqueira, P.C. Mihindou-Koumba, P. Magnoux, M. Guisnet, Ind. Eng. Chem. Res. 40 (2001) 1032.
[17] A. Corma, V. Gonzalez-Alfaro, A.V. Orchillés, J. Catal. 200 (2001) 34.
[18] D. Kubicka, N. Kumar, P. Mäki-Arvela, M. Tiitta, V. Niemi, T. Salmi, D.Y. Murzin, J. Catal. 227 (2004) 313.
[19] T. Sugii, Y. Kamiya, T. Okuhara, Appl. Catal. A 312 (2006) 45.
[20] H. Schultz, J. Weitkamp, H. Eberth, in: J.W. Hightower (Ed.), Proc. 5th ICC, vol. 2, North-Holland, Amsterdam, 1972, p. 1229.
[21] G. Onyestyak, G. Pal-Borbély, H.K. Beyer, Appl. Catal. A 229 (2002) 65.
[22] T.N. Vu, J. van Gestel, J.-P. Gilson, C. Collet, J.P. Dath, J.C. Duchet, J. Catal. 231 (2005) 453.
[23] T.N. Vu, J. van Gestel, J.-P. Gilson, C. Collet, J.P. Dath, J.C. Duchet, J. Catal. 231 (2005) 468.
[24] G.B. McVicker, M.S. Touvelle, C.W. Hudson, D.E.W. Vaughan, M. Daage, S. Hantzer, D.P. Klein, E.S. Ellis, B.R. Cook, O.C. Feeley, J.E. Baumgartner, US Patent 5763731, 1998, ExxonMobil.
[25] S. Lecarpentier, J. van Gestel, K. Thomas, M. Houalla, J. Catal. 245 (2007) 45.
[26] S. Lecarpentier, J. van Gestel, J.P. Gilson, J.P. Dath, C. Collet, FR2006-01616, (2006), assigned to Total and CNRS.
[27] G.B. McVicker, O.C. Feeley, J.J. Ziemiak, D.E.W. Vaughan, K.C. Strohmaier, W.R. Kliewer, D.P. Leta, J. Phys. Chem. B 109 (2005) 2222.
[28] O. Cairon, K. Thomas, T. Chevreau, Microporous Mesoporous Mater. 46 (2001) 207.
[29] J. Weitkamp, Ind. Eng. Chem. Prod. Res. Dev. 21 (1982) 55.
[30] P.A. Jacobs, J.A. Martens, Stud. Surf. Sci. Catal. 58 (1991) 445.
[31] F.G. Gault, Adv. Catal. 30 (1981) 28.
[32] C.G. Walter, Ph.D. thesis, Montpellier (1995).