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Ring opening of decalin and methylcyclohexane over alumina-based monofunctional WO_3/Al_2O_3 and Ir/Al_2O_3 catalysts

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ABSTRACT

Ring-opening reactions of decalin and MCH were studied over monofunctional acid (WO_3/Al_2O_3) and metal (Ir/Al_2O_3) catalysts containing, respectively, up to 5.3 at. W/nm^2 and 1.8 wt% Ir. The catalysts were characterized by X-ray diffraction, Raman spectroscopy, low-temperature CO adsorption followed by infrared spectroscopy, and H_2 chemisorption. A reaction network was proposed for both molecules and used to determine the kinetic parameters. Kinetic modeling allowed relating characterization results and catalytic performance. For WO_3/Al_2O_3 catalysts, ring contraction precedes ring opening of both molecules. The evolution of ring contraction activity was consistent with the development of relatively strong Brønsted acid sites. Ring opening occurs according to a classic acid mechanism. For Ir/Al_2O_3 catalysts, only direct ring opening was observed. Ring opening proceeds mostly via dicarbene mechanism. Analysis of products indicated that monofunctional metal catalysts are better suited than acid solids for upgrading LCO.

1. Introduction

In order to meet an increasing demand for diesel, especially in Europe, oil refiners have the option to blend some of the Light Cycle Oil (LCO) fraction, produced in the Fluid Catalytic Cracking (FCC) process, with the diesel pool. However, with the exception of the carbon number, the LCO does not meet current diesel specifications, especially in Europe. It contains high amounts of polyaromatics (*ca.* 48–69%) and low cetane number (*ca.* 18–25) when compared to the European norms (polyaromatics: upper limit of 11% – cetane number: minimum of 51). Hence, the LCO must be deeply hydrotreated. The polycyclic aromatic fraction can be lowered by hydrogenation, which also improves the cetane index. However, this increase is not sufficient, and a ring opening of naphthenic compounds appears to be required for LCO to significantly contribute to the diesel pool. As illustrated in Table 1, the cetane number significantly increases when a molecule such as decalin with two naphthenic rings is converted into linear or mono-branched paraffins. Ring opening must, thus, be highly selective toward these products. Naphthene ring opening can be achieved over metal, acid and bifunctional catalysts. One of the simplest mono-naphthenic molecule, and as a consequence the most studied, is methylcyclohexane (MCH). This model molecule consists of a six-carbon atom ring with one alkyl ramification. This limits the number of possible reaction products and facilitates the establishment of a reaction network. As a result, hydroconversion of MCH and other similar single-ring naphthenes has been the subject of many studies [1–24]. However, MCH cannot be considered as representative of the LCO mixture, and thus, its use as a probe molecule to study the LCO upgrading reaction can be questioned. The LCO product distribution shows that it consists mainly of two-ring aromatic systems [25], making two-ring naphthenes such as decalin, in hydrotreated feeds, a logical choice as probe molecules for the study of LCO upgrading. In contrast to studies involving mono C_4, C_5, and C_6 naphthenic rings, literature concerning selective ring opening of model molecules containing two fused rings for LCO upgrading, such as decalin, tetralin, or naphthalene, is more limited [16,26–35]. The study of such molecules is very often hindered by the analytical difficulties, due to the complexity of ring opening and other concomitant reactions (e.g., isomerization and cracking). Detailed identification of the intermediates and products obtained in these reactions is required for a better understanding of the mechanism of ring opening reaction and an appropriate selection of the most suitable catalytic system [36].

Acid-catalyzed ring opening of naphthenes has been mainly studied on zeolites [3–5,19,28,29,33,37,38]. The majority of these studies involve single-ring molecules [3–5,19,37,38]. Recently, several studies have attempted to gain insight into the acid-catalyzed ring opening of decalin [28,29,33]. Kubicka et al. [28] and

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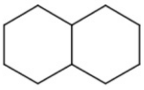
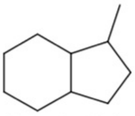
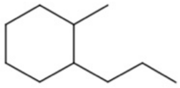
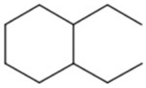
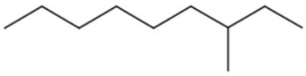
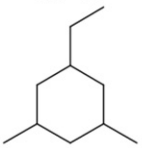
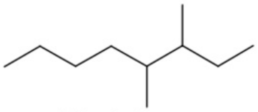
Table 1
Cetane number of some relevant decalin ring-opening products [35].

	Ring contraction products	One-ring opening products	Two-ring opening products
 Decalin CN = 36	 Methyl-bicyclo[4.3.0]nonane CN = 25	 1-methyl-2-propylcyclohexane CN = 39	 Decane CN = 77
		 Dimethylcyclohexane CN = 39	 Methylnonane CN = 48
		 Ethyldimethylcyclohexane CN = 30	 Dimethylnonane CN = 39

Santikunaporn et al. [29] showed that decalin ring opening over zeolites is preceded by ring contraction (e.g., isomerization from a cyclohexyl to a cyclopentyl ring). Kubicka et al. [28] also reported that Brønsted acidity influences the ring-opening yield. The best performance was obtained for catalysts with moderate Brønsted acidity (Hβ-25, Hβ-75 and HY-12 zeolites) with, virtually, no activity observed for catalysts with low Brønsted acidity (MCM-41) and fast deactivation due to coke deposits with solids exhibiting strong Brønsted acid sites (H-mordenite-20). It is believed that ring opening of naphthenes over acid catalysts proceeds on Brønsted acid sites and is initiated by protolytic dehydrogenation followed by chain reactions of the carbenium ions formed (e.g., ring contraction, β-scission, alkylations and hydride transfer) [4,28,33].

McVicker et al. [16] investigated selective ring opening of naphthenic molecules over several metals (Ru, Rh, Ni, Ir and Pt). It was observed that Ru, Rh and Ni exhibit similar preference for cleaving unsubstituted C–C bonds, but are generally less selective than Ir. Pt is much less active but can break substituted C–C bonds, leading to an approximately statistical product distribution [8]. Paál et al. [39] reported that metals such as Rh, Pd, Ir and Pt promote single hydrogenolysis of 3-methylpentane and methylcyclohexane, whereas multiple fragmentation (i.e., leading to the formation of compounds with less than 7 carbon atoms) was observed for Co, Ni, Cu, Ru, Ag, Re and Os. Overall, the literature shows that iridium-based catalysts exhibit high activity and selectivity for ring opening of C_5 and C_6 monocyclic molecules [13,16,40].

With respect to ring opening mechanism over metal catalysts, Gault [8] reported that hydrogenolysis of substituted naphthenes can take place over Pt/Al_2O_3 according to three distinct mechanisms: (1) non-selective mechanism (occurring on highly dispersed platinum) corresponding to an equal chance of breaking any C–C bond of the ring (multiplet mechanism); (2) selective mechanism allowing only the rupture of unsubstituted C–C bonds (dicarbene mechanism); and (3) a “partially selective” mechanism, competing with the dicarbene mechanism (on poorly dispersed Pt catalysts), involving metallocyclobutane species as an intermediate (metallocyclobutane mechanism). In recent studies, the metallocyclobutane mechanism has been frequently invoked to interpret results, involving the cleavage of methyl-substituted C–C bonds that could not be explained by the multiplet or the dicarbene mechanisms [6,16,41].

In addition to the behavior of monofunctional metal and acid catalysts, it was observed that C_6 ring-opening reaction of naphthenes is enhanced by the use of bifunctional catalysts [2,13,16,21,26,29,32,42–46]. This has been interpreted by C_6 to C_5 ring contraction over the acid function and a greater ease of opening C_5 rings over the metal function [16,42,43].

Zirconia was proved to be an attractive support for bifunctional catalysts because of the possibility of fine tuning its acidity by controlled tungsten deposition [47]. We have recently shown that by using tungstated zirconia as supports, after Ir deposition, high performance bifunctional Ir–W catalysts for selective ring opening of methylcyclohexane can be developed [13,45]. However, zirconia is not a typical industrial support and lacks the textural and mechanical properties of more conventional supports such as alumina. Moreover, the shaped industrial catalyst for such a reaction will be produced by extrusion, and alumina is the binder of choice for such a process. Thus, it was of interest to develop an alternative alumina-supported system and compare its performance with the corresponding zirconia-based system. The results showed that identical performance (products distribution, and selectivity) for MCH ring opening can be obtained when alumina is used as a support instead of zirconia [48].

The present work extends previous studies of MCH ring opening over alumina-based catalysts to decalin, a molecule that is more representative of the LCO cut. It involves a detailed investigation of the performance of WO_x-based monofunctional acid catalysts and Ir-based monofunctional metal catalysts for decalin conversion. Specifically, it includes a systematic study of the effect of W surface density (WO_3/Al_2O_3) and iridium loading (Ir/Al_2O_3) on the structure of the catalysts and on their activity and selectivity for decalin ring-opening reaction and a comparison of the results with those obtained for MCH reaction. A reaction network is proposed for both naphthenes and a kinetic model is developed to fit the reactivity results, thus enabling the investigation of structure-catalytic performance relationship. Finally, potential improvement of the cetane number will be evaluated based on the nature and composition of decalin ring-opened products. The present work will serve as a basis for future study aimed at achieving a better understanding of the behavior of bifunctional catalysts.

2. Experimental

2.1. Materials

The γ-Al_2O_3 support (AX 300) was supplied by Criterion. It exhibited, after calcination at 773 K for 2 h, a specific surface area