



Bifunctional MCM-41 aluminosilicate supported Ir with adjusted metal and acid functionality for catalytic ring opening of 1,2-dimethylcyclohexane



Hessam Ziaei-Azad, Abdelhamid Sayari*

Department of Chemistry, Centre for Catalysis Research and Innovation (CCRI), University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

ARTICLE INFO

Article history:

Received 10 June 2016

Revised 14 August 2016

Accepted 21 August 2016

Available online 17 September 2016

Keywords:

Large-pore MCM-41 aluminosilicate

Bifunctional catalysts

Ring opening

Iridium

Brønsted acidity

ABSTRACT

Herein we report H-AlMCM-41 aluminosilica supported Ir materials with adjusted acid/metal function as bifunctional catalysts for selective ring opening (RO) of 1,2-dimethylcyclohexane (1,2-DMCH) at 330 °C and 3 MPa to primary ring opening products (P-ROP), which are defined as C₈ alkanes. Large-pore H-AlMCM-41 materials were synthesized with Si/Al atomic ratios of 20 and 45 and impregnated for the first time with 0.6–1.8 wt% Ir to afford xIr/H-Al-MCM-41(y) bifunctional catalysts (x = Ir content in wt%, y = Si/Al ratio) with moderate Brønsted acidity and relatively strong hydrogenolysis tendency. The optimum catalytic performance was achieved with 1.2Ir/H-AlMCM-41(45), which gave 31% yield of desired alkane products at 71% conversion of 1,2-DMCH. In contrast, zeolite based 0.5Ir/H-Beta-25 as well as the purely metallic 0.7Ir/Na-AlMCM-41(20) catalysts did not exhibit suitable catalytic performance for the production of C₈ alkanes compared to Ir/H-AlMCM-41 catalysts. All materials were thoroughly characterized by N₂ adsorption, solid-state NMR, TEM and FTIR of adsorbed pyridine, and their catalytic behavior was discussed in light of their physicochemical properties.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

After decades of ascending production, the world oil reserves are becoming increasingly heavier and poorer in quality [1]. This change in the oil quality leads to high content of polyaromatics and naphthenic molecules in diesel fuel, which makes it environmentally and economically unacceptable [2,3]. The conventional aromatic saturation process (ASAT) reduces the aromatic content by converting them into naphthenic molecules [4]. However, the resulting naphthenes still have higher density compared to their open-chain paraffinic counterparts of the same carbon numbers, which results in lower blend volume that is not economically favorable [3]. As a result, further upgrading of the naphthenic molecules is necessary for the production of premium quality diesel. Selective ring opening (SRO), which involves the cleavage of naphthenic rings without decreasing the total carbon number of the final products, i.e. without cracking, is an important process for this purpose.

Three types of catalysts have been studied for ring opening (RO) reactions, namely (i) solid acids such as protonated zeolites, H-MCM-41 aluminosilicates and WO₃/Al₂O₃ [5–8], (ii) metallic

catalysts, mainly Pt, Ir, Ru, Pd and Ni supported on non-acidic materials [1,4,6,9–15] and (iii) bifunctional catalysts containing metal(s) supported on acidic materials such as Pt/HY, Pt/H-Beta, Pt/H-mordenite, Pt-Ir/H-Beta, Pt-Ir/HY, Ir/H-Beta, Ir/WO₃/Al₂O₃, Ru-Pd/SiO₂-Al₂O₃, and Ru/MCM-41 [7,16–22]. Solid acid-catalyzed RO proceeds by classical β-scission or protolytic cracking at a tertiary carbon atom, often resulting in excessive cracking, dehydrogenation, coking and unacceptably low selectivity toward ring opening products [4,5]. In contrast, ring opening on metallic catalysts occurs by the hydrogenolysis of endocyclic C–C bonds, which gives rise to alkanes with the same carbon number as the starting material [4]. Several metallic catalysts, in particular Pt-group metals, were studied for this type of reaction since the 1970s, and the literature is unanimous about the superior performance of Ir among the various metals studied [6,9,23]. The rate of ring opening on metals is much lower for six-membered rings compared to five-membered ones due to their higher stability [23]. In addition, the activity and selectivity of metals for RO decrease significantly when external branching on carbon rings increases, especially if branching occurs on different carbon atoms. For instance, a conversion of 73% and RO selectivity of 72% were observed in the RO of methylcyclohexane (MCH) at 300 °C over 0.9% Ir/Al₂O₃, while under similar conditions, the conversion and selectivity were

* Corresponding author.

E-mail address: abdel.sayari@uottawa.ca (A. Sayari).

reduced to 42% and 40%, respectively for 1,2,4-trimCH, which has methyl groups on three different carbon atoms [4].

Bifunctional catalysts, which combine acidity and metallic properties, are especially useful for the RO of molecules containing six-membered rings, where the metal activity is reduced. Acidic supports can enhance the skeletal isomerization of a cyclohexyl ring to alkylcyclopentyl ring, which has higher reactivity for subsequent ring opening.

The RO of several naphthenic molecules in the presence of bifunctional catalysts has been investigated. Examples of RO of monocyclic naphthenes include methylcyclohexane (MCH), methylcyclopentane (MCP), n-pentylcyclopentane (PCP) and n-butylcyclohexane (BCH) [4,24–28]. These studies revealed that although bifunctional catalysts can exhibit higher catalytic activities than their metallic counterparts for RO reactions, selectivity values change as well, which may decrease the yield of desired RO products. For instance, in RO of MCP at 290 °C and 30 bar of H₂, 0.9% Ir/USY bifunctional catalyst afforded 27% conversion (X) and 26% selectivity (S) toward RO products (RO yield: 7%), while the metallic catalyst 0.9% Ir/Al₂O₃ converted 16.6% of MCP with 58% selectivity toward RO products, corresponding to higher RO yield of 9.5% [24]. It is reported that supports with strong acidity, such as USY zeolite, increase the conversions in the RO of naphthenic molecules; however, the product selectivity can change in favor of highly branched isomers with cyclic molecules, which are difficult to be opened via hydrogenolysis and/or β -scission [29]. As a result, an appropriate balance of acid and metal functionality is required to achieve highly active and selective RO catalysts.

Bifunctional catalysts are also widely used in the RO of naphthenic molecules with two or more six-membered rings, where monofunctional metallic catalysts show poor activity [6]. Decalin is the most extensively studied molecule in this category. The majority of literature on the RO of decalin focused on conventional bifunctional catalysts such as Pt/HY, Pt/H-Beta, Pt/H-mordenite, Pt-Ir/H-Beta, Pt-Ir/HY, Ir/HY, Ir/H-Beta as well as Ir/WO₃/Al₂O₃, where the catalytic activity is often dominated by the strong Brønsted acidity of the support material [2,7,16–21,30–32]. These catalysts gave rise to high selectivity for skeletal isomerization (ring contraction), but poor selectivity, i.e. <5%, for open-chain products (alkanes) [17]. In contrast, more recent efforts showed that bifunctional catalysts combining high loadings of a strong hydrogenolysis metal such as Ir on a support with low to moderate concentration and strength of Brønsted acid sites may present high selectivity for alkanes even at high conversions [29,33]. These investigations led to unprecedented yields of 44% and 31% for alkanes in the RO of decalin at 86% and 94% conversions over 3.4% Ir/H-Cs-Beta and 2.9% Ir/Na-H-Y bifunctional catalysts, respectively [29,33]. Nonetheless, such materials may suffer fast deactivation in the presence of large naphthenic molecules because of their inhibited pore size.

In terms of acidic supports with low to moderate Brønsted acidity, it is anticipated that periodic mesoporous materials (PMMs) such as SBA-15 and MCM-41 would be suitable supports for RO of naphthenic molecules. Mesoporous silica exhibits no Brønsted acidity, but its acidity can be tuned by incorporating Al or Zr into the silica framework, thus generating weak to moderately acidic sites. Compared to zeolites, PMMs exhibit typically higher surface areas as well as larger pore sizes and pore volumes, which facilitate diffusion of reactants and products and enhance the accessibility of active sites located within the pores [34]. Examples of mesoporous bifunctional catalysts include the following: Pt/Al-SBA-15 for LGO upgrading [3], Ru/H-Al-MCM-41, Pt/H-Al-MCM-41, Pt-Ir/H-Zr-MCM-41 and H-Al-MCM-41 for RO of decalin [5,22,35,36], Pd-Pt, Ru-Pd, Ni and NiW on Si/Zr MCM-41 for RO of naphthalene and tetralin [37–40] as well as Pt-Pd /Al-MCM-41 for RO of alkyl-naphthalenes [41].

H-Al-MCM-41 is a PMM that exhibits low concentration and strength of Brønsted acid sites. Similar to zeolites, it is possible to adjust the acid content of H-Al-MCM-41 by changing the Si/Al ratio. Unfortunately, the current literature on the use of H-Al-MCM-41 as catalyst support for RO reactions is limited [5,22,35], and the available studies on H-Al-MCM-41 supported metal catalysts did not include iridium, which is the most active metal.

Herein, we report the synthesis and application of Ir-containing bifunctional catalysts supported on large-pore H-Al-MCM-41 mesoporous aluminosilicates with high performance for ring opening of 1,2-dimethylcyclohexane (1,2-DMCH). The pore size of the support materials was increased to ca. 5–7 nm, during a single-step synthesis using a pore-expansion agent along with the structure-directing surfactant. The synthesized materials were characterized by different techniques to analyze their structure and acidity. Although the molecular weight of 1,2-DMCH is somewhat out of the diesel range, we used it here as substrate instead of the more common decalin molecule due to the easier identification and analysis of all the C₈ skeletal isomers as well as the alkane products. At the same time, the presence of two external methyl groups on different positions of the six-membered ring reduces the metallic activity as mentioned earlier, which necessitates the presence of a bifunctional catalyst to achieve high catalytic activity as well as RO selectivity.

2. Experimental

2.1. Materials

Fumed silica (Cab-O-Sil, M5), tetramethylammonium hydroxide (TMAOH, 25 wt% in water from Sigma Aldrich), cetyltrimethylammonium bromide (CTMABr, Fischer Scientific), concentrated ammonia (Fischer), sodium aluminate (NaAlO₂, Strem Chemicals), *N,N*-dimethylhexadecylamine (DMHA, Fluka) and distilled water were used for the synthesis of large-pore MCM-41 aluminosilicates. NH₄-Beta-25 (CP814E) with a SiO₂/Al₂O₃ molar ratio of 25 and a surface area of 680 m²/g was obtained from Zeolyst International. IrCl₃·xH₂O (Strem Chemicals) was used as the source of Ir. 1,2-dimethylcyclohexane from TCI as well as nitrogen and hydrogen gases of ultra-high purity (99.999%) from Linde was used for catalytic reactions.

2.2. Material synthesis

Two batches of large-pore Na-ALMCM-41 mesoporous aluminosilicate with nominal Si/Al atomic ratios of 15 and 30 were synthesized reproducibly by a method previously reported by our group for the synthesis of pore-expanded mesoporous MCM-41 silica with minor modifications [34,42]. DMHA was used as a pore-expansion agent. The as-synthesized Na-ALMCM-41 was calcined in a furnace by heating under flowing nitrogen to 550 °C using a 1 °C/min ramp, followed by switching to air at 550 °C for 5 h to remove any remaining organic material. The calcined Na-ALMCM-41 was further transformed into NH₄-ALMCM-41 by overnight ion-exchange with 1 M ammonium nitrate or ammonium chloride solution at room temperature. Subsequently, it was converted to H-ALMCM-41 by calcination in flowing air at 500 °C for 5 h. Zeolite β was used for comparison. Commercial NH₄-Beta-25 was transformed into the protonated form by a multi-step calcination process: 2 h at 120 °C, heating at 10 °C/min to 500 °C and 5 h at 500 °C under dynamic air flow using a temperature-controlled furnace.

Iridium was added to the protonated support materials by the incipient wetness impregnation technique using the required amount of IrCl₃·xH₂O aqueous solution to obtain a nominal metal

Download English Version:

<https://daneshyari.com/en/article/6455918>

Download Persian Version:

<https://daneshyari.com/article/6455918>

[Daneshyari.com](https://daneshyari.com)