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One-pot synthesis to engineer a Co-KIT-6 catalyst for the ring opening of methylcyclopentane[☆]

Synthèse par voie directe d'un catalyseur Co-KIT-6 pour l'ouverture de cycle du méthylcyclopentane

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ARTICLE INFO

Article history:

Received 8 September 2017

Accepted 30 October 2017

Available online xxxx

Keywords:

Co-KIT-6

Methylcyclopentane

Ring opening

n-H

Endocyclic C–C bond rupture

ABSTRACT

Co-KIT-6 mesoporous materials with *la3d* symmetry and Si/Co ratios of 50, 25, and 10 were prepared using hydrothermal one-pot synthesis. The Co-KIT-6 mesoporous materials were characterized by X-ray diffraction, N₂ adsorption–desorption isotherms, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared, and X-ray photoelectron spectroscopy. The physicochemical characterization results show that all of the samples have well-ordered cubic mesostructures and that the structural integrity is preserved for n_{Si}/n_{Co} ratios as high as 10. It was found that most of the cobalt ions exist as isolated framework species, but for Co-KIT-6 with an n_{Si}/n_{Co} ratio of 10, the presence of extra-framework species/small cobalt oxide clusters cannot be excluded. The ability of these catalysts was tested by examining the conversion of the reaction of methylcyclopentane with hydrogen at atmospheric pressure and temperatures between 200 and 450 °C. The catalytic results show that their catalytic activity increases significantly with increasing cobalt content. The active sites, tetrahedrally coordinated Co and isolated atomic Co sites, were responsible for the endocyclic C–C bond rupture between substituted secondary–tertiary carbon atoms, whereas the small clusters serve as active sites for the successive C–C bond rupture. The ring-opening selectivity can be improved by increasing the density of isolated cobalt atom sites at low reaction temperatures.

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R É S U M É

Les matériaux mésoporeux Co-KIT-6, avec une symétrie *la3d* et des rapports Si/Co de 50, 25 et 10, ont été préparés par voie directe en utilisant la synthèse hydrothermale. Les matériaux mésoporeux Co-KIT-6 ont été caractérisés par sorption d'azote, DRX,

Mots clé:

Co-KIT-6

Méthylcyclopentane

[☆] This article is part of the thematic issue dedicated to the scientific work of François G. Gault.

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<https://doi.org/10.1016/j.crci.2017.10.007>

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Please cite this article in press as: S. Debbih-Boustila, et al., One-pot synthesis to engineer a Co-KIT-6 catalyst for the ring opening of methylcyclopentane, *Comptes Rendus Chimie* (2017), <https://doi.org/10.1016/j.crci.2017.10.007>

Ouverture du cycle

n-H

Rupture endocyclique de liaison C–C

microscopies MET et MEB, FT-IR et XPS. Les résultats de la caractérisation physicochimique montrent que tous les échantillons ont une mésostructure cubique bien ordonnée et que l'intégrité structurale est conservée pour des rapports $n_{Si}/n_{Co} > 10$. On a constaté que la plupart des ions cobalt existent comme atomes isolés. En revanche, pour Co-KIT-6 avec un rapport n_{Si}/n_{Co} de 10, la présence d'espèces extra-charpentes/petits amas d'oxyde de cobalt ne peut être exclue. Les performances catalytiques de ces catalyseurs ont été testées en examinant la réaction de conversion du méthylcyclopentane (MCP) avec de l'hydrogène, à la pression atmosphérique et des températures entre 200 et 450 °C. Les résultats catalytiques montrent que leur activité catalytique augmente significativement avec l'augmentation de la teneur en cobalt. Les sites actifs, le Co tétraédriquement coordonné et les sites de Co atomiques isolés, sont responsables de la rupture de la liaison C–C endocyclique entre les atomes de carbone secondaire–tertiaire substitués, tandis que les petits amas de Co servent de sites actifs pour les ruptures successives des liaisons C–C. La sélectivité pour l'ouverture de cycle peut être améliorée en augmentant la densité des sites d'atomes isolés de cobalt, à basse température de réaction.

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1. Introduction

For the petrochemical industry, the ring opening of methylcyclopentane (MCP) can be performed with atom efficiency (100% selectivity) on noble metal catalysts. This reaction is a key factor for increasing the cetane number of diesel fuel [1–6] and producing fuel of high quality with minimal harmful emissions. The ring opening of MCP is one of the most-used model reactions for exploring the structural sensitivity of hydrocarbon conversion catalyzed by noble metals [1–7]. More exactly, taking into account that each dearomatization reaction followed by a hydrogenation step leads to a cyclopentane, the MCP chemistry is very important [8]. Although MCP is not a component of diesel fuel, the ring opening of MCP must first be understood because it serves as a *model molecule* and provides the basis for understanding the behavior of all other molecules [1–8]. The noble metals capable of opening MCP with atom efficiency are Pt, Rh, Ru, and Ir [4–7,9–11], although it is very important to stress that not all of these metals exhibit ring-opening products with high cetane numbers. The ring-opening products of MCP are branched (2-methylpentane, 2-MP; 3-methylpentane, 3-MP) and linear paraffins (*n*-hexane, *n*-H), with the latter having the higher cetane number and therefore being the desired product. Pt catalysts can open MCP by breaking either the substituted or the unsubstituted C–C bond of MCP [9]. The difference between the two directions of opening is governed by the dispersion of Pt metal on the Al₂O₃ support. On highly dispersed Pt/Al₂O₃ ($d < 2$ nm), the rupture of substituted C–C bonds is favored due to a π -allyl mechanism, which requires a flat adsorption of three neighboring carbon atoms interacting with a single metal site on the catalyst surface. Thus, the products obtained from opening of MCP on highly dispersed catalyst were 2-MP, 3-MP, and *n*-H. On poorly dispersed Pt/Al₂O₃ ($d > 2$ nm) the preferential rupture of the unsubstituted C–C bond takes place. This can be attributed to a dicarbene mechanism where two endocyclic carbon atoms are involved with adjacent metal

atoms. In this case, the reaction products are only 2-MP and 3-MP, not *n*-H. Opposite behavior was observed on Ir catalysts, which were found to be insensitive to the dispersion of particles (2-MP and 3-MP products only) [9,11–15]. In addition, Ir catalysts exhibited the tendency to break the endocyclic C–C bonds of MCP on unsubstituted secondary–secondary carbon atoms [9]. In this case, the ring opening of MCP is mainly via a dicarbene mechanism in which the intermediate products adsorb perpendicularly to the metal surface. Nevertheless, these results are not absolute because other catalytic results on Ir catalysts of different dispersions [13] broke the endocyclic C–C bond of MCP on the substituted C–C bonds when the catalysts became covered with carbon species [16–18]. In this case, a plausible explanation was the presence of carbon species that could suppress the dicarbene mechanism. Contrary to alumina support making the breakage of endocyclic C–C bonds on substituted positions possible, the prevailing dicarbene mechanism was observed on Ir catalysts when silica was used as the support [19]. The aim of this study was to find a Pt–Ir/Al₂O₃ bimetallic catalyst with the ability to convert molecules with low cetane numbers, such as MCP, to higher value cetane number molecules (e.g., 2-MP, 3-MP, and *n*-H) at low temperature and with good atom efficiency for diesel fuel applications.

However, new generation ring-opening catalysts are a necessity due to increasing stringent regulations. Many approaches have been pursued to achieve this challenging task, among which the testing mesoporous catalysts with much interest is an important one [8,20–24]. The discovery of mesoporous materials has attracted intense interest because of their high-specific surface area, uniform pore size distributions, and their highly valuable potential applications in catalysis, separation, and adsorption [25–32]. Cobalt-mesoporous catalyst sieves have received intense interest because of their high potential to catalyze various reactions. Is a necessity to prepare uniformly distributed and preferably isolated sites on silica surfaces, which is crucial for high activity and

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