



Selective ring opening of methylcyclopentane over Pt/ γ -Al₂O₃, Ir/ γ -Al₂O₃ and Pt-Ir/ γ -Al₂O₃ catalysts with hydrogen at atmospheric pressure

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ABSTRACT

Pt/ γ -Al₂O₃, Ir/ γ -Al₂O₃ and Pt-Ir/ γ -Al₂O₃ were prepared by incipient wetness impregnation and co-impregnation methods. The catalysts were characterised by the classical physico-chemical techniques of SEM, TEM, XRD, N₂-sorption, H₂-TPR and elemental analysis. The metallic particles were highly dispersed on the support, assuming the presence of an icosahedral Mackay structure, which is a limited only by (111) face. The performances of the catalysts were investigated in the conversion of methylcyclopentane (MCP) with hydrogen at atmospheric pressure at temperatures between 180 and 400 °C. At low temperature, only Ir/ γ -Al₂O₃ showed the ability to open MCP with an atom economy (S_{RO} = 100%) and without by-products from cracking and ring enlargement reactions. Ir/ γ -Al₂O₃ opened the MCP ring at the secondary–secondary positions. The Pt/ γ -Al₂O₃ and Pt-Ir/ γ -Al₂O₃ catalysts opened MCP starting at 220 °C, in the secondary–tertiary positions, with atom economy (S_{RO} = 100%). The synergistic effect between Ir and Pt was observed in our conditions, but the Pt and Ir particles existed also as individual entities on the support. At high temperature, all the catalysts were inactive in MCP ring opening. Cracking reactions became more pronounced with increasing temperature and parallel decreases in ring opening selectivities. The formation of benzene was observed at high temperatures only on Pt/ γ -Al₂O₃.

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1. Introduction

A challenge for the 21st century is the control of technological processes in the chemical, petrochemical, and pharmaceutical industries to develop atom-economical, environmental friendly processes without by-products [1–4]. In the petrochemical industry, the ring opening of methylcyclopentane (MCP) can be performed with atom economy (100% selectivity) on noble metal catalysts. This reaction is key factor for increasing the cetane number of diesel fuel [5–9] and producing fuel of high quality with minimal harmful emissions. The noble metals capable of opening MCP with atom economy are Pt, Rh, Ru, and Ir [10–13], 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. The differences in the product distribution of the ring opening of MCP on metals is ascribed to the intrinsic nature of the metals, the dispersion of the metal on the support, the nature of the support, the mode of adsorption of

hydrocarbons on the metals and the experimental conditions [10]. For example, Pt catalysts can open MCP by breaking either the substituted or the unsubstituted C–C bond of MCP [10]. 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 favoured due to a π allyl mechanism, which requires a flat adsorption of three neighbouring 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 behaviour was observed on Ir catalysts, which were found to be insensitive to the dispersion of particles (2-MP and 3-MP products only) [10,12,14–17]. In addition, Ir catalysts exhibited the tendency to break the endocyclic C–C bonds of MCP on unsubstituted secondary–secondary carbon atoms [10,14,16,17]. 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 [15] broke the endocyclic C–C bond of MCP on the substituted C–C bonds when the catalysts became

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