



Hydroisomerization of saturated hydrocarbons with novel MCM-41 immobilized Re(V) complex catalysts

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ABSTRACT

The hetero-functionalized phosphines HPN₂, H₂PNO and HPN-Pip containing tricarbonyl Re(V) complexes, *i.e.* [Re(CO)₃(κ³-PN₂)] (**I**), [Re(CO)₃Br(κ²-H₂PNO)] (**II**) and [Re(CO)₃Br(κ²-HPN-Pip)] (**III**) were covalently bonded to modified and MCM-41 to obtain novel supported hybrid catalysts. Remarkable high catalytic effects were observed with these catalysts in the hydroisomerization of *n*-alkanes at low temperature. The catalyst **II**/MCM-41 provided the highest TONs 3.32×10^3 with 37% yield for *n*-hexane and 3.18×10^3 with 30% yield for *n*-heptane. Under optimized condition, good selectivities for *n*-hexane (85%) and for *n*-heptane (91%) were obtained. The TGA was used to evaluate the stability of catalysts and reusable for several cycles. A possible carbenium-based mechanism been used to explain product formation.

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1. Introduction

Coordination chemistry of Re complexes has attracted a lot of interest owing to their potential role in several biological processes [1,2] and various types of catalytic reactions of commercial significance [3,4]. In fact, heterogenized metal and supported metal complex catalysts have been found to act efficiently in multiple chemical transformations of hydrocarbons [5]. A variety of materials (*i.e.* SiO₂, Al₂O₃, MCM-41, SBA-15 and clays) have been used for supported metal catalysts, including Re catalyst [6–8]. The anchoring of the metal complexes on support has been achieved mainly through the interaction between the surface silanol groups of the support and terminal groups of metal complexes (*e.g.* –Cl, –NH₂, –CN, –OCH₃ and –SH) [8,9]. Supported catalysts have several advantages over the homogenous ones such as ease separation from product, high selectivity, lower toxicity and reutilization possibility [10,11].

Isomerization (or hydroisomerization) is one of the reformation processes employed to provide high-octane-number for gasoline [12,13]. The usual reforming processes have been carried out in which isomerization of alkanes to isoalkanes and alkylcyclopentane to aromatics, *etc.* [14]. Supported Pd and Pt metals have been

widely used on ZrO₂, Al₂O₃ and/or WO_x supports as the catalyst for hydrocarbons isomerization [15,16]. Natural zeolite supported Pd catalysts have been also used for *n*-hexane isomerization, with conversion varying between 17 and 80% [17]. Another example with Pd catalysts have provided conversion between 39 and 57% at 260 °C, mainly yielding 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,3-dimethylbutane (2,3-DMB), and 2,2-dimethylbutane (2,2-DMB) [18]. Beta-type zeolite-Pt catalyst has also been used to produce mono- and multi-branched isomers of *n*-heptane [19].

Few publications are available so far describing supported Re catalysts for hydrocarbons hydroisomerization, despite being cheaper than Pd and Pt. The effect of Re concentration on the activity and stability of Pt–Re/Al₂O₃ catalysts has been reported on hydrocarbon reforming [20]. Re was also used with Ga₂O₃/WO₃/ZrO₂ as catalyst in *n*-hexane isomerization [21]. The acidic pillared clay support has been used with Pt/Re for the hydroisomerization of *n*-pentane, *n*-hexane, and *n*-heptane under different conversion conditions [22]. Moreover, some other supported metal catalysts (Ni, Co and Zr) have been also applied to hydrocarbons reformation processes [23–26].

In this study, we report the preparation of hetero-functionalized phosphines HPN₂, H₂PNO and HPN-Pip [Pip = 4-(3-aminopropyl)-1-(2-methoxyphenyl)piperazine] containing tricarbonyl Re(V) complexes covalently bonded to modified MCM-41 as supported catalysts. These catalysts were tested in the hydroisomerization of *n*-hexane and *n*-heptane. These were found to have high turnover numbers (TONs) and high selectivity.

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