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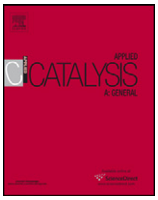

Hydroisomerization of saturated hydrocarbons with novel MCM-41 immobilized Re(V) complex catalysts

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ABSTRACT

The hetero-functionalized phosphines HPN_2, H_2PNO and HPN-Pip containing tricarbonyl Re(V) complexes, *i.e.* $[Re(CO)_3(\kappa^3\text{-}PN_2)]$ (**I**), $[Re(CO)_3Br(\kappa^2\text{-}H_2PNO)]$ (**II**) and $[Re(CO)_3Br(\kappa^2\text{-HPN-Pip})]$ (**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.

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.* SiO_2, Al_2O_3, 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, $–NH_2$, –CN, $–OCH_3$ and –SH) [8,9]. Supported catalysts have several advantages over the homogenous ones such as ease separation form 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 ZrO_2, Al_2O_3 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 $Pt–Re/Al_2O_3$ catalysts has been reported on hydrocarbon reforming [20]. Re was also used with $Ga_2O_3/WO_3/ZrO_2$ 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 HPN_2, H_2PNO 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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2. Experimental

2.1. Catalysts synthesis

2.1.1. Re complexes synthesis

All the Re tricarbonyl complexes were synthesized according to the previously published procedure [27] (Scheme 1). The structures of these complexes were confirmed by NMR, FT-IR, EA and CHN analysis.

(i) Synthesis of $[Re(CO)_3(\kappa^3\text{-}PN_2)]$ (I). HPN_2 (6.5×10^{-2} mmol) in MeOH (2 mL) was added to a solution of $(NEt_4)_2[ReBr_3(CO)_3]$ (6.5×10^{-2} mmol) in MeOH (5 mL) and was heated under reflux for 3 h. The mixture was then allowed to cool to r.t. and water was added until no more white solid precipitated. Solid **I** (yield: 43%) was isolated by filtration and washed with water. **FT-IR** (KBr, ν) 2017, 1887 (CO str), 1590, 1572 and 1544 (CONH str), 750, 695. **^1H NMR** (DMSO-d_6, δ) 7.72 (m, aromatic, 1H), 7.63–7.31 (m, aromatic, 13H), 6.39 (m, CH_2, 1H), 5.49 (br s NH, 1H), 4.40 (m, CH_2, 1H), 3.80 (br s, NH, 1H), 2.26 (m, CH_2, 1H), 2.15 (m, CH_2, 1H). **^{31}P NMR** (DMSO-d_6, δ) 13.9. **EA** Calculated (found) for $C_{24}H_{20}N_2O_4PRe{\cdot}2(H_2O)$: C, 44.10 (44.53); H, 3.70 (3.56); N, 4.29 (4.21).

(ii) Synthesis of $[Re(CO)_3Br(\kappa^2\text{-}H_2PNO)]$ (II). H_2PNO (6.5×10^{-2} mmol) in MeOH (2 mL) was added to a solution of $(NEt_4)_2[ReBr_3(CO)_3]$ (6.5×10^{-2} mmol) in MeOH (5 mL) and the reaction mixture was stirred at r.t. for 18 h. The white precipitate **II** (yield: 68%) was isolated by filtration, washed with a small amount of MeOH, and dried under reduced pressure. **FT-IR** (KBr, ν) 2020, 1938 and 1885 (CO str), 1500 (CONH str), 760, 690. **^1H NMR** (DMSO-d_6, δ) 10.0 (t br s NH, 1H), 7.84 (m, aromatic, 1H), 7.83–7.62 (m, aromatic, 12H), 7.22 (m, aromatic, 1H), 6.7 (m, CH_2, 1H), 4.82 (m, CH_2, 1H), 4.22 (m, CH_2, 1H), 2.35 (m, CH_2, 1H). **^{31}P NMR** (DMSO-d_6, δ) δ 11.6. **EA** Calculated (found) for $C_{24}H_{20}BrNO_5PRe$: C, 41.21 (40.32); H, 2.88 (2.46); N, 2.00 (2.33).

(iii) Synthesis of $[Re(CO)_3Br(\kappa^2\text{-}HPN\text{-}Pip)]$ (III). HPN-Pip (19×10^{-2} mmol) in MeOH (3 mL) was added to a solution of $(NEt_4)_2[ReBr_3(CO)_3]$ (19×10^{-2} mmol) in MeOH (3 mL) and the reaction mixture was stirred at r.t. for 18 h. Solid **III** (yield: 70%) was collected by filtration and washed with diethyl ether. **FT-IR** (KBr, ν) 2019–1880 (CO str), 1610 (CONH str), 760, 715. **^1H NMR** ($CDCl_3$-d_6 δ) 9.48 (t br, NH, 1H), 8.15 (m, aromatic, 1H), 7.64–7.29 (m, aromatic, 12H), 7.07 (m, aromatic, 1H), 6.93–6.81 (m, aromatic, 4H), 3.86 (s, OCH_3, 3H), 3.64 (m, CH_2, 1H), 3.63–3.36 (m, 7H), 2.93 (br s, 2H), 2.81 (m, CH_2, 2H), 2.28 (br s, CH_2, 1H), 2.03 (br s, CH_2, 1H). **^{31}P NMR** ($CDCl_3$-d_6 δ) 14.2. **EA** Calculated (found) for $C_{36}H_{36}BrN_3O_5PRe$: C, 48.71 (48.51); H, 4.09 (4.02); N, 4.73 (4.69).

2.1.2. Synthesis of modified MCM-41

MCM-41 prepared as previously described procedure [28]. A solution of CTAB (2.2 g) in 52 mL, H_2O was added in NH_4OH (26 mL) for 1 h stirring at r.t. and then TEOS (10 mL) was added slowly for 3 h more stirring. The resulting mixture was heated at 110 °C for 3 days in autoclave, washed with distilled water. The final MCM-41 was obtained by the calcinations in air at 550 °C for 8 h. For the preparation of modified MCM-41, a solution of iodopropyl trimethoxysilane (2 g) in toluene (100 mL) was added with MCM-41 (5 g) and reflux overnight. The resulting modified MCM-41 was collected by filtration, washed several times with toluene and dried under atmospheric pressure.

2.1.3. Synthesis of supported hybrid catalysts

Each of the Re complexes **I**, **II** and **III** (50 mg) was dissolved in dry toluene (50 mL). Then modified MCM-41 (1000 mg) was added to their solutions and the resulting mixture heated under reflux for 6 h. After filtration, each of the isolated solids was washed with toluene and oven dry again. Complex **I** (45.2 mg), complex **II** (44.3 mg) and complex **III** (42.6 mg) were subsequently anchored on modified MCM-41. Any non-anchored Re-complexes were removed by Soxhlet extraction with toluene. The final catalyst **I**/MCM-41 is abbreviated as Catal. **A**, **II**/MCM-41 as Catal. **B** and **III**/MCM-41 as Catal. **C** (Scheme 2).

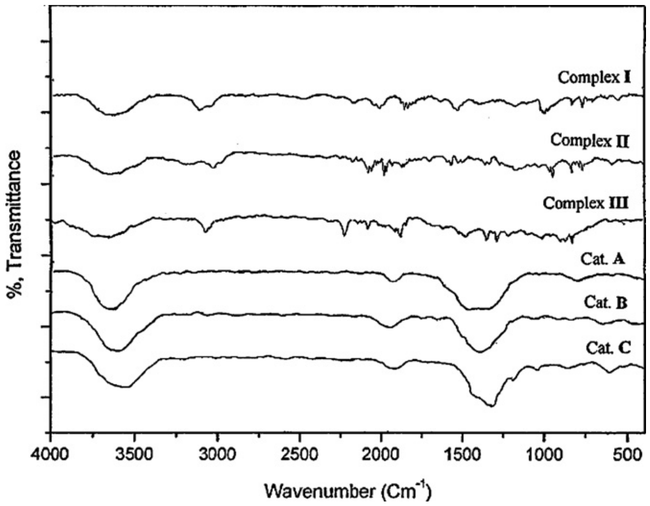


Fig. 1. FT-IR of Re complexes **I–III** and after immobilized on modified MCM-41 as Cat. **A** to Cat. **C**.

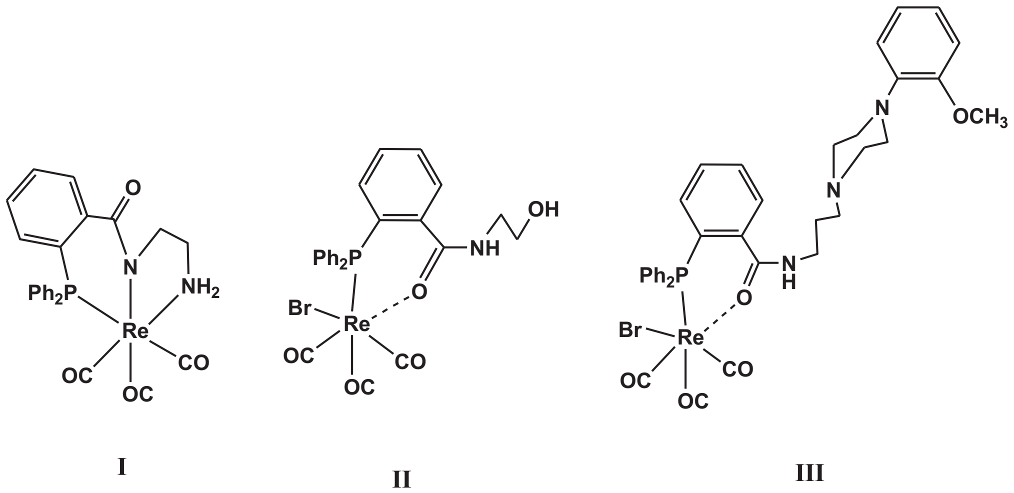
FT-IR (KBr, ν) of all catalysts (Fig. 1): 3815–3305 cm^{-1} and 1410 cm^{-1}, 1060 cm^{-1}, for MCM-41, bands 2000–2020 and 1850 (C=O str), and 1544–1590 (–NH str). **SEM-EDS**: 0.38% of Re of Cat. **B**. **TGA**: weight falls at 276 °C (Cat. **B** and **C**) and at 293 °C (Cat. **A**) and fast weight falls at high temperature until 365 °C for Cat. **A**, Cat. **C** and for 385 °C for Cat. **B**.

2.2. Characterization procedure

The NMR spectra (^1H and ^{31}P) were recorded on a Bruker ARX400 spectrometer at ambient temperature; δ values relative to $SiMe_4$, coupling constants in Hz; FT-IR (4000–400 cm^{-1}) spectra were recorded on a Unicam Research Series spectrophotometer in transmission mode using KBr pellets; ν in cm^{-1}. Elemental analyses (EA) were carried out on a Fisons EA-1108 analyzer. TGA was performed on a TA Instruments Q50 thermogravimetric analyzer. Rhenium concentrations were determined by ICP analysis on a Perkin-Elmer 41000ZL spectrometer. The morphology of the solid supported catalysts was analyzed with a Scanning Electron Microscope (FEI Quanta 400), equipped with an EDS detector (EDAX). For TPD analysis, fresh Cat. **B**, 10 mg was used for the NH_3 treatment (1.0 mL introduced over 10 pulses) under He flow at 150 °C on a Micromeritics Autochem 2910 instrument. GC analyses were carried out on a FISONS GC 8000 gas chromatograph equipped with a FID detector and a DB-WAX capillary column (length: 30 m; internal diameter: 0.32 mm). The products were further identified by GC–MS using a Carlo-Erba Auto/HRGC/MS instrument.

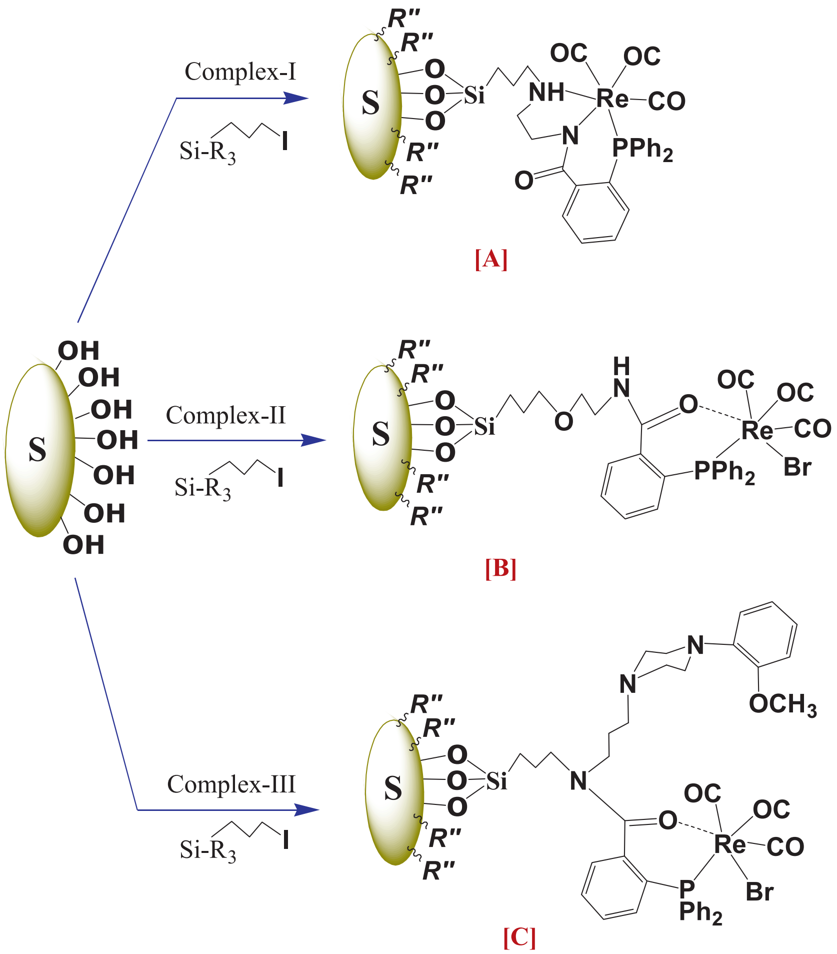
2.3. Catalyst tests and product analysis

A stainless steel rocking type micro-batch reactor (22 cm^3 capacity), equipped with a gas inlet and a pressure gauge, was used for the hydroisomerization reactions. The inner temperature of the reactor was monitored by a thermocouple. In each experiment, the reactor was charged with the n-alkane and the catalyst, closed, the air removed and H_2 was introduced. At the end of the reaction, the solid catalyst was separated from the liquid product by filtration, washed several times with acetonitrile and dried at 60 °C for 8 h and collected for further recycling studies. The



Scheme 1. Structures of hetero-functionalized phosphines HPN_2, H_2PNO and HPN-Pip containing Re(V) complexes.

reaction products were quantitatively analyzed by GC (30 µL of hexanone added as internal standard to 1.0 mL of the filtered final reaction solution) and product was identified by GC–MS. The product yield was calculated as the total moles of formed product per mole of substrate. The selectivity was calculated as mole of isomer per mole of total yield of products. Total TON was calculated as moles of isomer per mole of anchored Re complex on MCM-41.



Where, ***S*** *= MCM-41 support,* ***R*** *= OCH_3,* ***R''*** *= other anchored units,*
Supported catalysts = **[A]**, **[B]** and **[C]**

Scheme 2. Single site anchoring of Re(V) complexes on MCM-41 as supported hybrid catalysts.

3. Results and discussion

3.1. Synthesis and characterization of Re complex catalysts

The aim of the present study was to use the potentially active tricarbonyl Re(V) complexes as reusable and selective catalysts for the *n*-alkanes hydroisomerization reaction at relatively mild temperature. Therefore, hetero-functionalized phosphines HPN_2 and H_2PNO containing tricarbonyl Re complexes such as $[Re(CO)_3(\kappa^3\text{-}PN_2)]$ (**I**), $[Re(CO)_3Br(\kappa^2\text{-}H_2PNO)]$ (**II**) and $[Re(CO)_3Br(\kappa^2\text{-}HPN\text{-}Pip)]$ (**III**) were synthesized according to reported procedure [27,29] (Scheme 1). Complexes **I**, **II** and **III** are good examples of rhenium tricarbonyl complexes $[Re(CO)_3]$ stabilized with functionalized phosphines containing PON_2 (**I**) and PNO (**II**, **III**) donor atom sets. In complex **I**, the ligand is tridentate and monoanionic, coordinating to the Re through the phosphorus atom and two nitrogen atoms of the amide and amine groups. In complexes **II** and **III**, the ligand is neutral and bidentate, coordinating through the phosphorus atom and oxygen atom of CO–Re of the amide function. The stretching vibrations of CO were clearly observed between 2019 and 1880 cm^{-1} in FT-IR.

These Re complexes were immobilized by a covalent bond resulting from the substitution of the terminal reactive iodine on the modified MCM-41 support. The nucleophilic amine and amide groups of complexes **I** and **III** and the hydroxyl group of complex **II** were utilized to bonding them to support. To the best of our knowledge, these supported Re catalysts are being described for the first time. The FT-IR spectra of catalysts **A**–**C** show two broad shoulders between 3815 and 3305 cm^{-1} and between 1410 and 1060 cm^{-1}, due to the modified MCM-41 support. The presence of Re(V) complexes on the support matrix was confirmed by the additional bands of $C{=}O$ at 2000–2020 and 1850 and –NH bands at 1544–1590.

The SEM morphological study of catalyst **B**, which was found to be most active, is shown in Fig. 2 (at 20,000× magnification). The SEM picture of modified MCM-41 is presented in Fig. 2(a). In Fig. 2(b) the dark-gray regions indicate the clusters of complex **II** immobilized on the cylindrical MCM-41 matrix. The presence of the Re complex was also confirmed by the EDS detector coupled to the SEM, showing 0.38% of Re on the surface of MCM-41. The thermal stability of the supported catalysts was evaluated by TGA (Fig. 3). Initially, small weight losses (*ca.* 100–120 °C) of these catalysts were observed, most likely due to the absorbed atmospheric moisture; after this, a slow decomposition of the anchored metal complex was observed until 276 °C (Cat. **B** and **C**) and 293 °C (Cat. **A**). Rapid weight losses were observed above theses temperatures (until 365 °C for Cat. **A**, Cat. **C** and for 385 °C for Cat. **B**). An absolute decay (*ca.* 5.5%) of these supported catalysts was observed between 470 and 490 °C. Thus suggests that the supported catalysts are stable in the range of the reaction temperatures studied.TPD analysis was also used for the treatment of weak acid sites with ammonia (NH_3) to penetrate into all pores of the Cat. **B** and gives the quantity and strength of the acid sites. As seen in Fig. 4, Cat. **B** sample showed a broad desorption signal in the region of 280 °C (359.7 $\mu mol\ NH_3\ g^{-1}$), indicating a wide distribution of the surface acid strength [30,31]. The ammonia-TPD results were thus in accordance with our FT-IR results, obtained one additional very small band at 3495 cm^{-1}. These results are indicative of overall increase not only in the acid site concentration, but also in the strength of these sites as a result of Re complex **II** incorporation. It was further conform with the BET analysis of only support (MCM-41) shown to have 870 cm^2/g surface area with pore volume 0.69 cm^3/g, which after anchoring Re complexes **I**–**III**, the surface area of the support catalysts were significantly reduced from 557 to 655 cm^2/g and pore volume from 0.53 to 0.64 cm^3/g (Table 2).

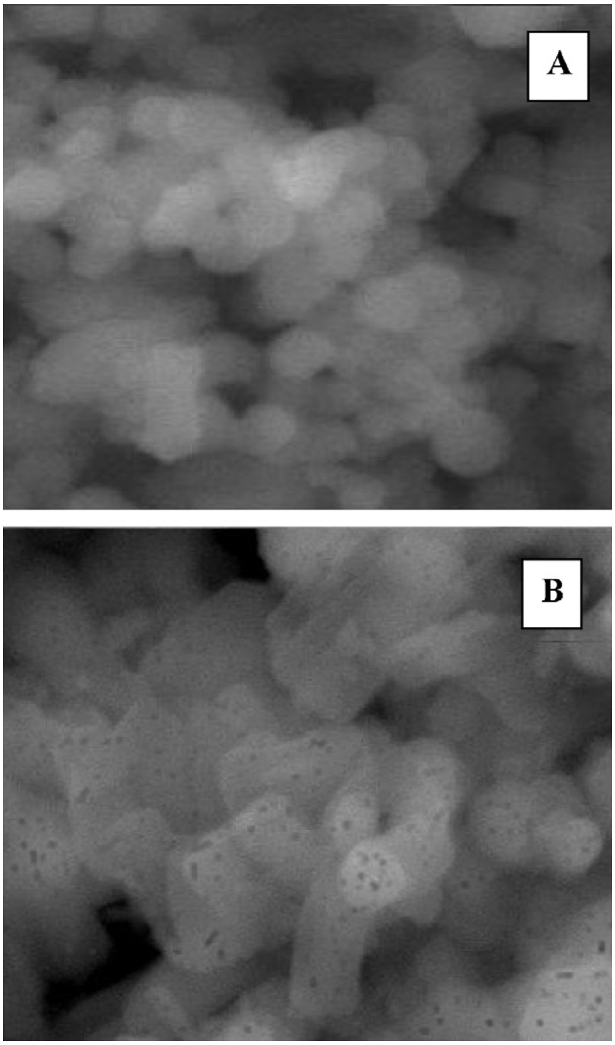


Fig. 2. Scanning electron microscopy morphological study (20,000× magnification) of (a) modified MCM-41 and (b) MCM-41 immobilized Cat. **B**.

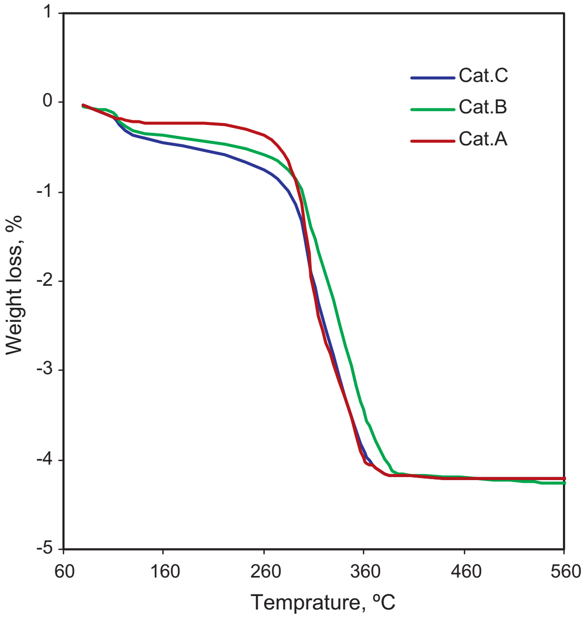


Fig. 3. TGA analysis results of single site immobilization of Re complexes over MCM-41 Cat. **A** to **C**.

Table 1
Reformation study of n-alkanes catalyzed by modified MCM-41 supported Re(V) complex catalysts.[a]

Substrate	Catalyst	TONs[c] ($\times 10^3$)	Yield (%)[b]						
			2-MP	3-MP	MCP	2,2-DMB	2,3-DMB	By-products	Overall[d]
n-Hexane	Cat. **A**	2.11	8.9	4.8	–	1.1	1.0	3.7	19.5
	Cat. **B**	3.32	14.7	6.9	4.7	1.9	1.9	1.1	31.2
	Cat. **C**	2.63	11.3	5.2	4.2	1.3	1.2	2.1	25.3
Substrate	Catalyst	TONs[c] ($\times 10^3$)	Yield (%)[b]						
			2-MH	3-MH	2,3-DMP	2,2-DMP	3,3-DMP	By-products	Overall[d]
n-Heptane	Cat. **A**	1.96	7.8	5.1	2.3	0.8	0.6	0.2	16.8
	Cat. **B**	3.18	9.4	8.6	3.9	2.6	1.4	1.8	27.7
	Cat. **C**	2.56	7.5	6.2	2.7	1.9	1.0	0.1	19.4

[a] Reaction conditions: catalyst = 25 mg, $p(H_2)$ = 2 atm, n-hexane = 3.0 mL; 140 °C for 12 h and n-heptane = 3.0 mL; at 220 °C for 18 h).
[b] Overall yield = main isomerized products + by-products.
[c] TONs = mmol of main isomers per mole of metal complex on support for catalysis.
[d] Molar % product yield = mole of isomerized product selectivity per mole of n-alkane.

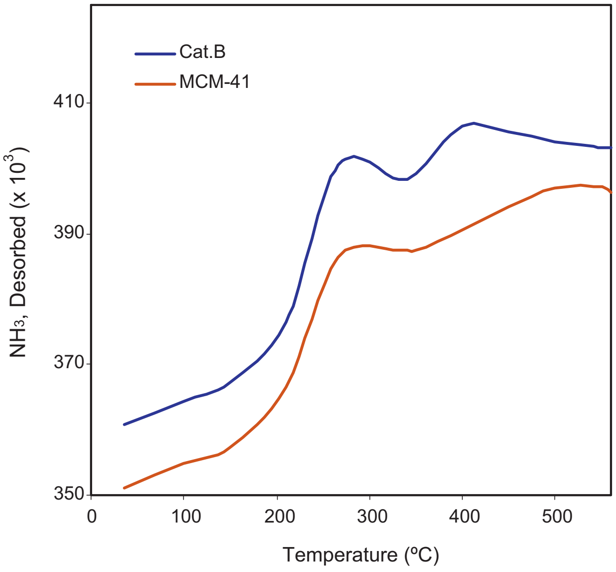


Fig. 4. Temperature programmed desorption analysis (TPD) of the absorption NH_3 of Cat. **B** and MCM-41.

3.2. Hydroisomerization of n-alkanes by Re-catalysts

The modified MCM-41 supported hetero-functionalized phosphines HPN_2, H_2PNO and HPN-Pip containing tricarbonyl Re(V) complexes as solid catalysts (Cat. **A**, Cat. **B** and Cat. **C**) and their soluble derivatives **I**, **II** and **III**, were tested under homo- and heterogeneous conditions for n-alkanes hydroisomerization. These reactions were performed under relatively mild and solvent free conditions in a SS rocking type batch reactor. In the n-hexane and n-heptane hydroisomerization mainly mono- and di-branched isomers of lower alkanes were observed. In the case of n-hexane a small amount of cyclic product was also obtained (Table 1). The color of both substrates changed from colorless to light yellow. The catalysts colors also turned from light yellow to light brown. The reaction mixture was quantitatively analyzed by GC and the identity of the products was confirmed by GC/MS.

Table 2
BET surface area analysis of modified MCM-41 supported Re(V) complex catalysts.

Catalyst	Surface area (cm^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
Support	870	2.53	0.69
Cat. **A**	557	2.49	0.53
Cat. **B**	605	2.46	0.58
Cat. **C**	653	2.43	0.64

Unsupported Re complexes **I** (1.4×10^{-2} mmol), **II** (1.4×10^{-2} mmol) and **III** (1.1×10^{-2} mmol) showed less catalytic activity in the hydroisomerization of both n-alkanes compared to the corresponding supported catalysts under the same conditions (Table 1). Complex **II** gave higher overall yield (10.3% for n-hexane and 9.3% for n-heptane) when compared with those of Complex **I** (8.6% for n-hexane and 7.5% for n-heptane) and **III** (9.7% for n-hexane and 8.8% for n-heptane) under analogous conditions. These soluble derivatives of Re complexes were decomposed during the course of the reaction. When the reaction was performed only with MCM-41, the obtained yields were much lower, *i.e.* 5.4% for n-hexane and 5.0% for n-heptane, under similar conditions. In a blank experiment (absence of catalyst and support), less than 4.6% overall yield was achieved for both these n-alkanes.

Hydroisomerization results with these catalysts are summarized in Table 1. Unexpectedly, very high TONs, from 2100 to 3300, with overall yields (*ca.* 16–31%) were observed with immobilized Re complex on MCM-41 (Cat. **A** to Cat. **C**). Among them, Cat. **B** showed the best yields: 31.2% for n-hexane and 27% for n-heptane. Lower yields were obtained with Cat. **A** (19.5% for hexane and 16.8% for heptane) and catalyst **C** (25.3% for n-hexane and 19.4% for n-heptane). Even this catalyst also performed high TONs: from 2.1×10^3 to 3.3×10^3 for n-hexane and 1.9×10^3 to 3.1×10^3 for n-heptane. The above results showed that the best TONs and best yields were achieved by Cat. **B** in the n-alkanes hydroisomerization. The presence of Br groups is seen to improve the catalytic efficiency. Catalyst **A** without bromine performed the lowest yield in both the n-alkanes reactions. These results suggest that not only Re is responsible for improving the catalytic activity but some other features also play a role in the catalytic hydroisomerization, *e.g.* the mesoporous MCM-41 support and the structure of complex **II** (less hindrance with Br and PPh_2).

3.2.1. Optimization of the hydroisomerization process

As seen from Table 1, it is apparent that Cat. **B** is the most effective catalyst for both the n-alkanes hydroisomerization reactions. Subsequently, temperature is raised from 80 to 260 °C, for reaction time rang from 4 to 30 h and catalyst amount from 5 to 45 mg. The hydroisomerization results of both the alkanes and recycle tests are summarized in Figs. 5–7.

In illustrative tests relatively mild conditions for n-hexane provide 31.2% yield at 140 °C for 12 h, while n-heptane provides 27.7% yield at 220 °C for 18 h (under H_2). The branched products of n-hexane have been identified as 2-MP, 3-MP, 2,2-DMB, 2,3-DMB and MCP, where the latter is obtained as a minor product. On the

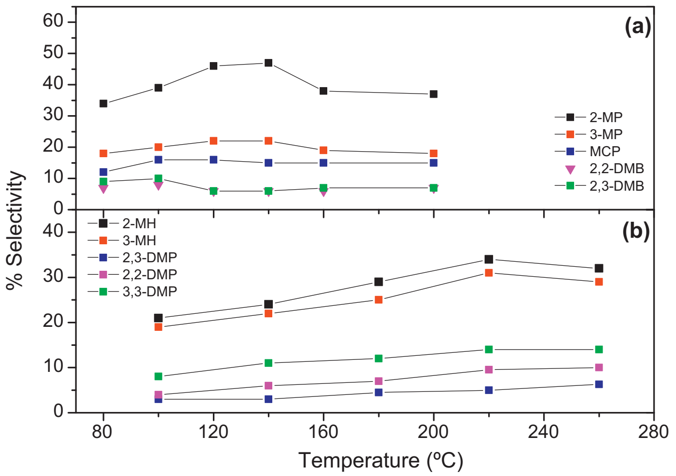


Fig. 5. Temperature effect on the percentage selectivity of the isomerized products of *n*-hexane (a) and *n*-heptane (b), in the presence of the Cat. **B** (constant conditions: catalyst; 25 mg, $p(H_2)$; 2 atm, *n*-alkane; 3.0 mL; 12 h for *n*-hexane and 18 h for *n*-heptane).

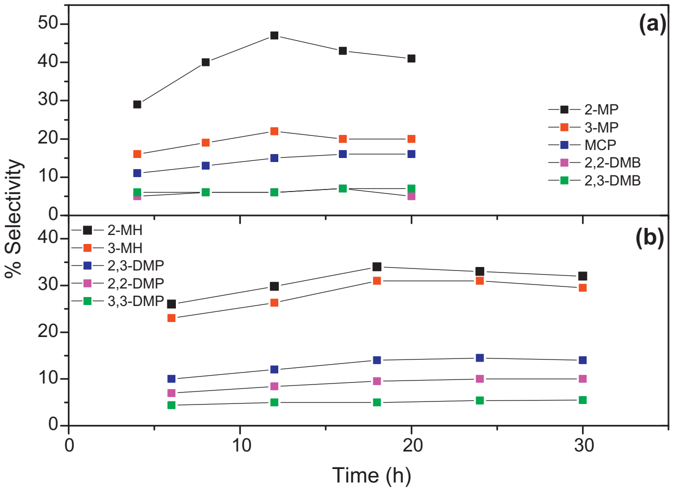


Fig. 6. Time effect on the percentage selectivity of the isomerized products of *n*-hexane (a) and *n*-heptane (b), in the presence of Cat. **B** catalyst (constant conditions: catalyst; 25 mg, $p(H_2)$; 2 atm, *n*-alkane; 3.0 mL; at 140 °C for *n*-hexane and at 220 °C for *n*-heptane).

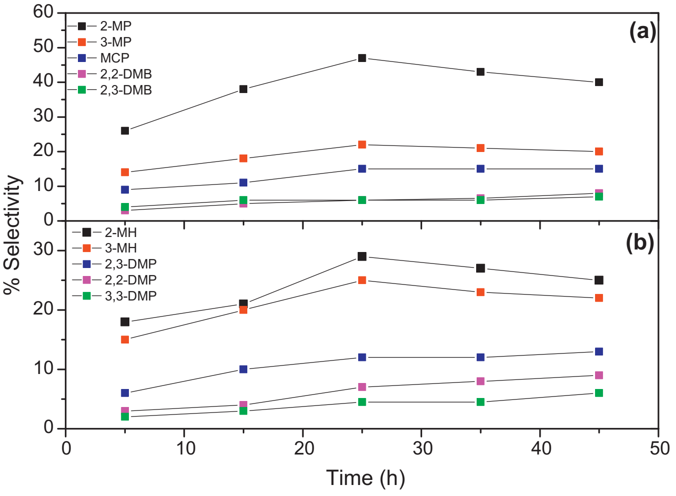


Fig. 7. Cat. **B** amount effect on percentage selectivity of the isomerized products of *n*-hexane (a) and *n*-heptane (b) (constant conditions: $p(H_2)$; 2 atm, *n*-alkane; 3.0 mL; 12 h for *n*-hexane at 140 °C and 18 h for *n*-heptane at 220 °C).

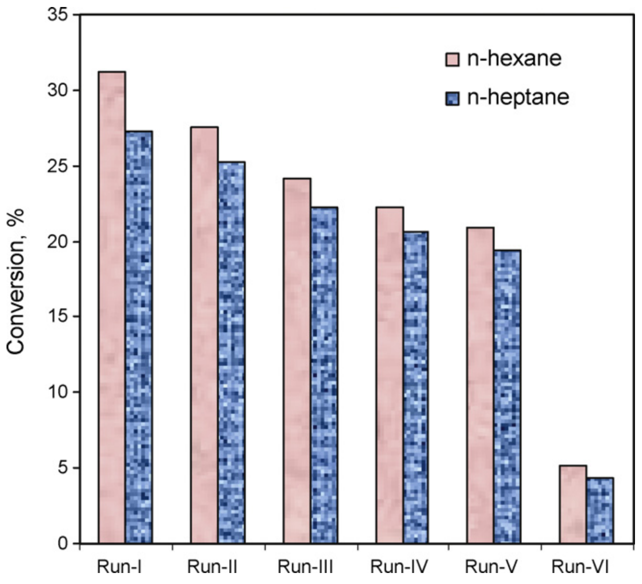
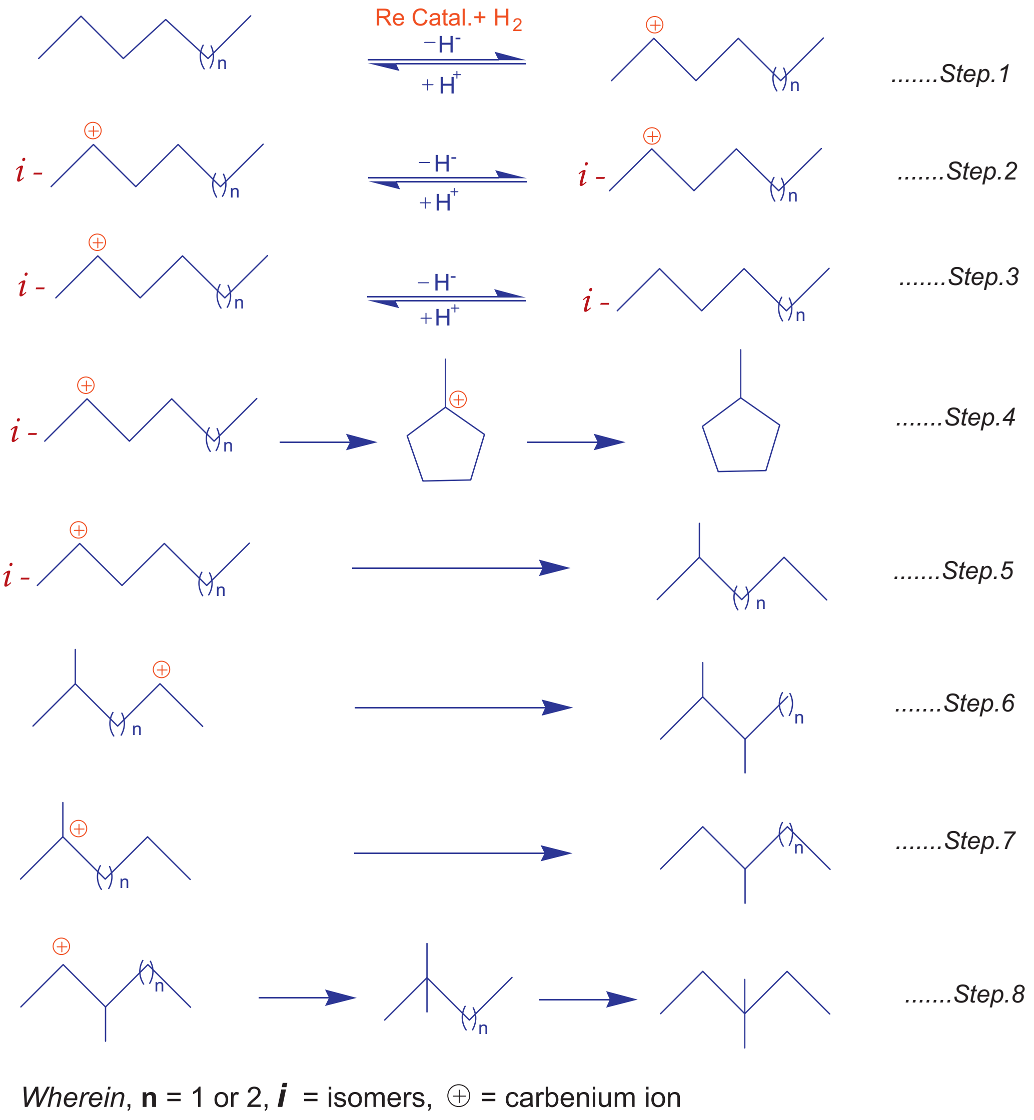


Fig. 8. Recycle testes of Cat. **B** in the course of *n*-alkanes hydroisomerization (conditions as in Table 1).

other hand, *n*-heptane gives 2-MH, 3-MH, 2,2-DMP, 3,3-DMP and 2,3-DMP. Formation of these products confirms that there is no cracking, dehydrocyclization or dehydrogenation reactions and the results are consistent with those reported [19,21].

The effect of temperature on yield and selectivity of *n*-alkanes hydroisomerization with Cat. **B** was examined between 80 and 260 °C (Fig. 5). The reactions were carried out under H_2, keeping the amount of catalyst (25 mg) and the reaction time (12 h for *n*-hexane and 18 h for *n*-heptane) constant. The similar increasing trends were observed for both *n*-alkanes. The overall yield and the concentration of the main isomers (2-MP, 2- and 3-MH) were initially low at 80 °C for *n*-hexane (7.1% overall yield) and 100 °C for *n*-heptane (4.4% overall yield). Highest yields were observed at 160 °C for *n*-hexane (yield 35.3%) and 260 °C for *n*-heptane (yield 29.8%). Above this temperature, the overall yields did not change significantly. Higher temperatures had a detrimental effect on the *n*-alkanes selectivity of the main isomers. The dependence of selectivity on the temperature is shown in Fig. 5, indicating that the best selectivity toward the main isomers 2-MP was 47% achieved at 140 °C for *n*-hexane, while it was 34% for 2-MH and 31% of 3-MH for *n*-heptane at 220 °C.

The effect of reaction time (varying from 4 to 30 h) on the yield and selectivity of *n*-alkanes have been reported in Fig. 6. The overall yield of the main branched products increases slowly up to 4 h with yield 4.1% for *n*-hexane and yield 2.7% for *n*-heptane at 6 h. Beyond this time, the overall yield raised rapidly up to 31.2% at 12 h for *n*-hexane and 27.7% at 18 h for *n*-heptane. After it remained practically constant. The high overall yield values of 34.5% for *n*-hexane and 30% for *n*-heptane were observed after 20 h and 30 h, respectively. However, longer reaction times led to the formation of polymerized black material which decreased the selectivity of main products. Higher selectivity toward the main isomers (2-MP, 47%; 3-MP, 22%) for reforming of *n*-hexane, Fig. 6(a) and the lower selectivity of di-branched isomers (2,2-DMB, 6%; 2,3-DMB, 6%) were observed after 12 h. One cyclic isomer (MCP, 15%) was also found. Similarly maximum selectivity toward the main branch isomers (2-MH, 34%; 3-MH, 31%) of *n*-heptane were obtained. The lower amount of di-branched isomers (2,2-DMP, 9.5%; 2,3-DMP, 14%; 3,3-DMP, 5%) was observed after 18 h reaction time, without formation of any cyclic product, Fig. 6(b).



Scheme 3. Proposed reaction mechanism for *n*-alkanes hydroisomerization (wherein, **n** = 1 or 2, **i** = isomers, ⊕ = carbenium ion).

The effect amounts of Cat. **B** have been also studied by varying it from 15 mg to 45 mg, has been reported in Fig. 7. The maximum overall yields 37% for *n*-hexane and 30% for *n*-heptane were obtained with 45 mg of the catalyst **B**. The product distribution for *n*-hexane was observed as 14.9% for 2-MP, 7.4% for 3-MP, 7.6% for 2-MH, and 6.4% for 3-MH. Similarly for 5 mg of catalyst the yield was low as well as product distributed (0.7% for 2-MP, 0.4% for 3-MP, 0.6% for 2-MH, and 0.5% for 3-MH. The best selectivity of the main products, *i.e.* 2-MP, 2-MH and 3-MH were obtained with 25 mg of catalyst (see Fig. 7). The selectivities toward the mono-branched products of *n*-alkanes decreased slowly while the other di-branched products increase with increasing amount of catalyst.

3.2.2. *Catalyst recycling and leaching tests*

The recycling experiments were carried out with the most active catalyst **B** (Fig. 8) to see how many times the catalyst can be used. The overall yields of *n*-alkanes then decried after 2nd cycle, relatively to the first runs, from 32.2 to 27.5% for *n*-hexane and from 27.7 to 25.2% for *n*-heptane, showing that the reaction system still presents a significant catalytic activity. Thus, the catalytic experiments were extended further more experiments up to 6th cycles (each time 12 h for *n*-hexane and 18 h for *n*-heptane). Both *n*-alkanes the yield dropped slowly until the fifth run; after which is loosed all its catalytic strength (5.6% for *n*-hexane and 4.4% for *n*-heptane).

Illustrative leaching tests of Cat. **B** were also performed in ICP and found fresh catalyst **B** has 0.26 wt% of Re. After second run, 0.24 and 0.23 wt% of Re were observed for *n*-hexane and *n*-heptane, respectively. No Re content was found after the 5th catalytic cycles of the used catalysts. We believe that metal loss was not the sole responsible factor for the decrease the catalytic activity. Some other factors such as possible structural modification of the catalyst (metal complex structure), could have occurred as suggested by change of color. One could also have deposition of polymerized material on the catalyst surface, which could lead to pore-blocking given to catalyst deactivation. The low surface area of used Cat. **B** was confirmed in the BET analysis (after 12 h, 487 cm^2/g for *n*-hexane and after 18 h, 468 cm^2/g for *n*-heptane).

3.3. *Mechanism*

Several mechanisms have been reported for the hydroisomerization of hydrocarbons [24,32,33]. Mainly carbenium ions (or carbocations) are responsible for the alkane's skeletal rearrangement. Therefore, the most important step is the formation of carbenium ions and their rearrangement on the heterogenized catalyst surface. Although the mechanistic details are not yet clear precisely [32–35], one can consider that *n*-hexane and *n*-heptane reactions from alkylcarbenium ions first. In our system, they are initially formed by reaction of *n*-alkanes with H_2 in presence of Re catalyst (Scheme 3, *steps* 1 *and* 2). The acidic nature of the catalyst (see above TPD analysis) also favors the formation of carbenium ions [34]. Once the alkylcarbenium ions are formed, this ion undergoes either through cyclization forming adsorbed cyclic species (*step* 4) or a simple bond shift/bond cleavage forming mono branch (*step* 5) or di-branched species (*steps* 6–8).

In this regard, the α-, ά- and γ-adsorbed species are formed on the support and the main mono-branched (*steps* 5 and 7) and di-branched isomers are formed (steps. 6 and 8) [32,34]. The 2-MP, 2-MH, 3-MP and 3-MH isomers of *n*-alkanes are obtained by a single bond shift. The di-branched isomers of *n*-alkenes, *i.e.* 2,2-DMB, 2,2-DMP, 3,3-DMP, 2,2-DMB and 2,3-DMP are obtained by two bonds shift (or cleavage of two bonds). A small amount of the cyclic isomer (MCP) could be formed by the cyclization of *n*-hexane reaction (*step* 4). In our experiments, the mono-branched species are formed as primary product with high selectivity in both *n*-hexane as well as *n*-heptane while di-branched isomers are formed in lesser amounts. One of the important reasons of this to occur is that mono-branch isomers could be formed by single bond cleavage from the parent *n*-alkane. Science the branch isomers occurs with one more single-bond-cleavage, on mono branch products. Di-branch isomers are obtained lesser amount. The presence of H_2 is not expected to change this mechanism of reaction [32–35].

4. Conclusions

In summary, the main objective of the current study is to use potentially active tricarbonyl Re complexes as recyclable solid catalysts for *n*-alkanes hydroisomerization under relatively mild conditions. Therefore, we have prepared $[Re(CO)_3(\kappa^3\text{-}PN_2)]$ (**I**), $[Re(CO)_3Br(\kappa^2\text{-}H_2PNO)]$ (**II**) and $[Re(CO)_3Br(\kappa^2\text{-HPN-Pip})]$ (**III**) complexes. These Re(V) complexes were anchored on the modified MCM-41 using iodopropyl trimethoxysilane as spacer. These supported catalysts (Cat. **A**, Cat. **B** and Cat. **C**) and their soluble derivatives (**I**, **II** and **III**) have been tested for reformation of *n*-hexane and *n*-heptane in presence of H_2 in batch reactor without additives. Very high TONs (from 2.1×10^3 to 3.3×10^3) were obtained by these supported catalysts, unsupported complexes **I**–**III** were shown to have considerably lower activity under analogous reaction conditions. Supported Cat. **B** showed highest catalytic activity giving overall yield 31.2% with 85% selectivity for *n*-hexane and 28% overall yield with 91% selectivity for *n*-heptane. These results were obtained at 140 °C, 12 h reaction time for *n*-hexane and 220 °C, 18 h reaction time for *n*-heptane. When 25 mg of Cat. B was used with 2 atm pressure of H_2. The mono-branched isomers (2-MP, 3-MP, 2-MH and 3-MH) were formed in larger amount by single bond shift while the di-branched isomers formed in lower amount. Catalyst recycles and leaching tests with ICP indicated that the Cat. **B** does not leach out up to five cycles. The TGA showed that these catalysts were stable at the temperatures used for hydroisomerization reactions. In conclusion, our catalysts give branched alkanes from their linear counterparts improving the burning efficiency of fuel.

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