Hydroformylation of alkyl alkenes catalyzed by rhodium supported on MCM-41: The effect of $H_3PW_{12}O_{40}$ on the catalytic activity and recycling

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Abstract

Heteropolyacids impregnated with rhodium(I) or (III) complexes were prepared and used as supported catalysts in the hydroformylation of alkyl alkenes. Two general types of catalysts were prepared and tested: rhodium(I) or (III) in the presence and in the absence of the heteropolyacid $H_3PW_{12}O_{40}$, $25H_2O$ (adopted as HPW_{12}) supported on MCM-41 (30 Å). 1-Octene was chosen as a model substrate. Different types of supported catalysts were tested in the hydroformylation of 1-octene and other alkyl alkenes. The effects of the temperature and the type of solvent on the reaction were studied. The results showed that the supported catalysts containing the heteropolyacid $H_3PW_{12}O_{40}$, $25H_2O$ (HPW_{12}) along with rhodium(I) or (III) gave higher catalytic activity. In addition, the recycling of the supported catalysts was studied and the results showed again the important effect of the presence of HPW_{12} on the recycling of the rhodium catalysts.
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1. Introduction

Linear adehydes are important industrial intermediates in the production of detergents and many other chemicals [1]. Hydroformylation or Oxo process is an old and important industrial process for the production of oxygenates including aldehydes from olefins and syngas. It has been known that cobalt and rhodium catalysts are the most active in this process at the industrial level [1–3]. While the industrially relevant products of hydroformylation were produced by the homogeneous systems over the past 20 years, the research work has continued actively to improve the catalysts activity and recycling [1–3]. The immobilization or heterogenization of homogeneous catalysts on inorganic support materials was actively investigated and can be achieved by various methods [4–6]. Rh/Al_2O_3 catalyst with high rhodium dispersion was active in the hydroformylation of styrene but it suffered from leaching [4]. Hydroformylation of styrene over $Rh/SiO_2·Al_2O_3$ has

been studied in the presence of the chiral diphosphines (−)-Chiraphos and (−)-DIOP. The catalytic activity decreased significantly in the presence of the diphosphines although high levels of both chemo- and regioselectivity towards the chiral aldehyde were maintained [7]. Amphiphilic Rh/phosphonate-phosphine catalysts were found widely superior to Rh/TPPTS in the two-phase hydroformylation of 1-octene [8]. The supported Co/SiO_2 and Co/C catalysts were studied in the hydroformylation of 1-hexene. The silica supported cobalt catalyst exhibited the highest catalytic activity [9]. The $[Rh(\mu\text{-Cl})(COD)]_2$ complex impregnated on activated carbon showed high stability and activity in the hydroformylation of 1-octene [10]. Silica-tethered rhodium thiolate catalysts prepared by the condensation of $[Rh_2[\mu\text{-S}(CH_2)_3Si(OCH_3)_3]_2(CO)_4$ or $[Rh_2[\mu\text{-S}(CH_2)_3Si(OCH_3)_3]_2[Ph_2P(CH_2)_3Si(OC_2H_5)_3]_2 (CO)_2$ on silica gel were found to exhibit high activity for hydroformylation of 1-octene in the presence of phosphine or phosphite ligands [11]. Immobilization of a dinuclear rhodium(II) acetato complex with bridging *ortho*-metalated phosphine ligands on MCM-41 resulted in useful catalysts for hydroformylation of styrene and 1-decene [12]. A polysilicate immobilized rhodium complex was found to be a selective hydroformylation catalyst showing an

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overall selectivity for the linear aldehyde of 94.6% with 1-octene at 80 °C and 50 atm of CO/H_2 (1:1) [13]. Functionalization of MCM-41 with 3-aminopropyltrimethoxysilane (APTS), and subsequent encapsulation and anchoring of $HRh(CO)(PPh_3)_3$ in the mesoporous material was reported as an active catalysts for the hydroformylation of 1-octene [5].

$Rh_4(CO)_{12}$ have been successfully anchored to MCM-41(PPh_2), MCM-41(NH_2) and MCM-41(SH), the effect of the three donor ligands on the catalytic hydroformylation of cyclohexene were compared [14]. In recent years, the immobilization of $Rh-PPh_3$ complexes onto amino-functionalized MCM-41 and MCM-48 as efficient heterogeneous catalyst for higher olefin hydroformylation has been reported by several groups [15,16].

Another approach to immobilizing homogeneous catalysts on solid supports has been reported, in which the Wilkinson's hydroformylation catalyst complex was tethered through heteropolyacid to zeolites [17,18] and MCM-41 [5], this result to an excellent stability, reusability and even improved activity.

We have recently reported new supported catalysts systems involving rhodium(I) or rhodium(III) for the hydroformylation of aryl alkenes [19]. The new heterogenized catalysts were at least as active as the homogeneous species and capable of being re-used many times with little los in activity and selectivity.

2. Experimental

2.1. General

All chemicals, otherwise stated, including solvents and alkenes were highly pure (>99%) and were purchased from Sigma–Aldrich Company. The solvents used in the experiments, such as THF, hexane, cyclohexane, CH_2Cl_2, benzene, 1,4-dioxane, methyl ethyl ketone (MEK), acetone, 1,2-dimethoxyethane (DME), methanol, ethanol and others were HPLC grade and were stored under nitrogen over activated 3 Å molecular sieves. Anisole, tetraetoxysilane (TEOS), *n*-hexadecyltrimethyl ammonium (or cetyltrimethyl ammonium) bromide, ammonium hydroxide, tetramethyl ammonium bromide (25% by weight solution in water), triphenylphosphite [P(OPh)$_3$] and $H_3PW_{12}O_{40}$, $25H_2O$ were used without any further purification. The rhodium complexes $RhCl_3 \cdot 3H_2O$,

$[Rh(COD)Cl]_2$, $[Rh(CO)_2Cl]_2$ and $RhHCO(PPh_3)_3$ (Strem Company) were used without purification.

2.2. Preparation of catalysts

2.2.1. Preparation of MCM-41

MCM-41 having pore size 30 Å, used as a support for the impregnation of the catalysts, was synthesized according to the method described in literature [20].

The MCM-41 samples were analyzed by X-ray diffraction using JOEL JDX-3530 diffractometer with Cu Kα radiation ($\lambda = 0.15405$ nm). Diffraction data were recorded between 1 and 30° 2θ in steps of 0.02° with a count time of 1 s at each point. We assume that the pore wall thickness is 10 Å.

2.2.2. Preparation and characterization of rhodium(I) and rhodium(III) impregnated with and without $H_3PW_{12}O_{40}$ on MCM-41

The MCM-41materials with pore size of 30 Å were chosen as an inorganic support due to their relative simple method of preparation and also due to their large pore size and high specific surface area.

2.2.3. Synthesis of 2% of Rh(I) or Rh(III)/10% of $HPW_{12}/MCM-41$ in methanol (M)

$RhCl_3 \cdot 3H_2O$ [or Rh(I) complexes] alone or with the cocatalyst was impregnated on the MCM-41 using methanol (M) as a solvent. In a typical procedure, 11.4 mg $RhCl_3 \cdot 3H_2O$ and 56.8 mg of $H_3PW_{12}O_{40} \cdot 25H_2O$ (HPW_{12})] were stirred in 10 ml of methanol for 30 min at room temperature under nitrogen atmosphere. Five hundred milligrams of MCM-41 were than added to the solution and the mixture was stirred for 24 h. The solvent was removed under vacuum and washed thoroughly with methanol and the solid sample was dried at 90 °C for 2 h and stored in the refrigerator. The catalysts prepared are summarized in Table 1 (Cat. 1–Cat. 2, Cat. 5–Cat. 6, Cat. 9–Cat. 10).

2.2.4. Synthesis of 2–5% of Rh(I) or Rh(III)/HPW_{12}/MCM-41 in ethanol (E)

The tethered catalyst was prepared following the procedure reported by Augustine et al. [21]. In a typical procedure, 33 μmol

Table 1
Supported catalysts obtained by impregnation of rhodium(III) or rhodium(I) with or without heteropolyacid (HPW_{12})

Cat. No.	Catalyst	Rhodium catalyst (%)	Cocatalyst (%)	Solvent (S)
Cat. 1	**Rh32MCM-M**	$Rh^{III}Cl_3 \cdot 3H_2O$ (2%)	–	Methanol (M)
Cat. 2	**Rh32W10MCM-M**	$Rh^{III}Cl_3 \cdot 3H_2O$ (2%)	$H_3PW_{12}O_{40}$ (10%)	Methanol (M)
Cat. 3	**Rh35MCM-E**	$Rh^{III}Cl_3 \cdot 3H_2O$ (5%)	–	Ethanol (E)
Cat. 4	**Rh35W10MCM-E**	$Rh^{III}Cl_3 \cdot 3H_2O$ (5%)	$H_3PW_{12}O_{40}$ (10%)	Ethanol (E)
Cat. 5	**Rh^A12MCM-M**	$[Rh^I(COD)Cl]_2$ (2%)	–	Methanol (M)
Cat. 6	**Rh^A12W10MCM-M**	$[Rh^I(COD)Cl]_2$ (2%)	$H_3PW_{12}O_{40}$ (10%)	Methanol (M)
Cat. 7	**Rh^A12MCM-E**	$[Rh^I(COD)Cl]_2$ (2%)	–	Ethanol (E)
Cat. 8	**Rh^A12W10MCM-E**	$[Rh^I(COD)Cl]_2$ (2%)	$H_3PW_{12}O_{40}$ (10%)	Ethanol (E)
Cat. 9	**Rh^B12MCM-M**	$HRh^ICO(PPh_3)_3$ (2%)	–	Methanol (M)
Cat. 10	**Rh^B12W10MCM-M**	$HRh^ICO(PPh_3)_3$ (2%)	$H_3PW_{12}O_{40}$ (10%)	Methanol (M)
Cat. 11	**Rh^B15MCM-E**	$HRh^ICO(PPh_3)_3$ (5%)	–	Ethanol (E)
Cat. 12	**Rh^B15W10MCM-E**	$HRh^ICO(PPh_3)_3$ (5%)	$H_3PW_{12}O_{40}$ (10%)	Ethanol (E)

Table 2
Rhodium supported catalysts in the heterogeneous hydroformylation of 1-octene[a]

Entry	Catalyst	Conversion[b] (%)	Product distribution[c] $B_1/B_2/B_3/L$ (%)	Octenes (%)	
				1-Octene	Other octene isomers
1	**Rh$3$2MCM**-*M*	64	35/1/0/64	90	10
2	**Rh$3$2W10MCM**-*M*	94	37/5/8/50	17	83
3	**Rh$3$5MCM**-*E*	66	26/0/0/74	55	45
4	**Rh$3$5W10MCM**-*E*	88	33/1/0/66	87	13
5[d]	**Rh$3$2W10MCM**-*M*	35	31/2/3/64	22	78
6	**Rh^A$1$2MCM**-*M*	77	35/2/4/59	10	90
7	**Rh^A$1$2W10MCM**-*M*	96	37/3/6/54	11	89
8	**Rh^A$1$2MCM**-*E*	75	34/3/4/58	13	87
9	**Rh^A$1$2W10MCM**-*E*	95	38/2/5/55	9	91
10	**Rh^B$1$2MCM**-*M*	79	36/3/4/57	8	92
11	**Rh^B$1$2W10MCM**-*M*	96	34/8/3/55	5	95
12	**Rh^B$1$5MCM**-*E*	92	35/10/4/51	8	92
13	**Rh^B$1$5W10MCM**-*E*	94	33/9/4/54	7	93
14[e]	**Rh^B$1$5MCM**-*E*	80	37/10/6/47	10	90
15[e]	**Rh^B$1$5W10MCM**-*E*	87	37/11/8/44	6	94

[a] Reaction conditions: 1-octene (5.0 mmol), THF (5 ml), 600 psi (CO/H_2 = 1/1), 80 °C, 16 h.

[b] Determined by GC.

[c] Determined by GC and ^1H NMR.

[d] P(OPh)$_3$ (0.010 mmol) was added.

[e] 110 °C, 3 h.

of HPW$_{12}$ dissolved in 20 ml of ethanol and 500 mg of MCM-41, the mixture was stirred at room temperature for 16 h, the resulting solid was filtered and washed with ethanol to remove the free HPA and finally dried at 100 °C for 6 h. The solid was suspended in 20 ml of dry ethanol and 30 μmol of HRhCO(PPh$_3$)$_3$ (or [Rh^I(COD)Cl]$_2$ or Rh^{III}Cl$_3$·3H$_2$O) was added and refluxed (at 80 °C) under stirring for 18 h. The light grey solid product was then washed with ethanol repeatedly to remove the unanchored species, dried at 80 °C and used as such for the reaction. The catalysts prepared are summarized in Table 1 (Cat. 3–Cat. 4, Cat. 7–Cat. 8, Cat. 11–Cat. 12).
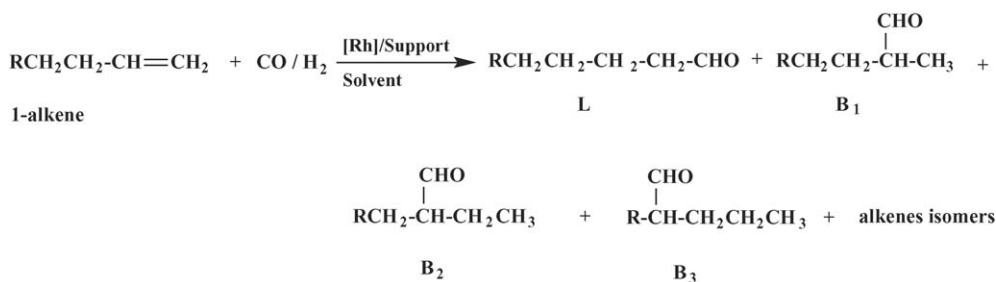
3. Results and discussions

3.1. Hydroformylation of 1-octene by Rh-HPW$_{12}$-MCM-41 system

3.1.1. Effect of the type of the supported catalyst

The hydroformylation of 1-octene was examined by Rh(I) and Rh(III) supported catalysts, prepared by the impregnation of Rh^{III}Cl$_3$·3H$_2$O, HRh^{I}CO(PPh$_3$)$_3$ or [Rh^I(COD)Cl]$_2$ with HPW$_{12}$ on MCM-41 in methanol (*M*) or ethanol (*E*) as a solvent (Eq. (1), Table 2).

The results obtained with 1-octene, considered as a model substrate, showed clearly the higher catalytic activity of the supported catalysts that incorporate both rhodium(III) complex and HPW$_{12}$. The conversion obtained with the catalyst **Rh$3$2MCM-M**, containing no hetropolyacid, was 64% compared to 94% with **Rh$3$2W10MCM-M** (Table 2, entries 1 and 2). The same trends were observed with the catalysts **Rh$3$5MCM-E** and **Rh$3$5W10MCM-E** obtained by the impregnation in ethanol as a solvent (Table 2, entries 3 and 4). We have previously reported that the hydroformylationof of styrene can be enhanced by the addition of water to the system catalyzed by **Rh$3$2W10MCM-M** [19]. With 1-octene, when water (25 μl) was added to the liquid phase along with **Rh$3$2W10MCM-M**, the reaction was seriously inhibited and the conversion of 1-octene dropped from 94 to 26% after 16 h. Furthermore, the addition of monophosphine (PPh$_3$), or diphosphine (dppb) ligand to **Rh$3$2W10MCM-M** totally inhibited the reaction while monophosphite ligands contributed to the serious decrease of the conversion of the reaction. For example, when triphenylphosphite P(OPh)$_3$ was used, the conversion of 1-octene dropped from 94 to 35% (Table 2, entry 5).

The presence of water may enhance the conversion of **Rh(I)(CO)$_2$** into **Rh^0(CO)$_m$** and subsequently into rhodium cluster **Rh$_6$(CO)$_{16}$** via **Rh$_4$(CO)$_{12}$** [22]. PPh$_3$ may lead

RCH$_2$CH$_2$-CH=CH$_2$ + CO / H$_2$ $\xrightarrow[\text{Solvent}]{\text{[Rh]/Support}}$ RCH$_2$CH$_2$-CH$_2$-CH$_2$-CHO + RCH$_2$CH$_2$-CH(CHO)-CH$_3$ +

1-alkene   L   B$_1$

RCH$_2$-CH(CHO)-CH$_2$CH$_3$ + R-CH(CHO)-CH$_2$CH$_2$CH$_3$ + alkenes isomers

B$_2$ B$_3$

(1)

to stable and not active rhodium-phosphine or diphosphine intermediates [1].

Higher catalytic activity of rhodium(I) supported catalysts was observed compared to rhodium(III) catalysts in terms of conversion at the same experimental conditions (Table 2, entries 6–15). The rhodium(I) based supported catalysts, prepared by impregnating Rh(I) with or without HPW_{12} on MCM-41, were also used in the hydroformylation of 1-octene. The conversion of 1-octene obtained with the catalysts **$Rh^A12W10MCM$-*M***, **$Rh^A12W10MCM$-*E***, **$Rh^B12W10MCM$-*M*** and **$Rh^B12W10MCM$-*E*** were excellent (94–96%) and higher than the conversions obtained with their counterparts lacking HPW_{12}, namely **Rh^A12MCM-*M***, **Rh^A12MCM-*E***, **Rh^B12MCM-*M*** and **Rh^B12MCM-*E***. These results showed once again the advantages of the use of the hetropolyacid HPW_{12} on the catalytic activity of these systems in the hydroformylation of 1-octene. However, **$Rh^B15W10MCM$-*E*** with 5% rhodium gave excellent conversion of 1-octene and similar selectivity in aldehydes (Table 2, entry 15).

The optimization of the reaction conditions required the study of the effects of the type of catalyst, the temperature, the reaction time and the type of solvent.

3.2. Hydroformylation of 1-octene by Rh-HPW12-MCM-41 system

3.2.1. Effect of the temperature

The temperature of the reaction of hydroformylation of 1-octene has a strong effect on the conversion and the selectivity. The reaction was studied using the supported catalyst systems **$Rh32W10MCM$-*M*** and **$Rh^B12W10MCM$-*M*** formed by the impregnation of Rh(III) and R(I) complexes with HPW_{12} on MCM-41 in methanol (*M*) (Figs. 1–3). The reaction was conducted for 16 h with **$Rh32W10MCM$-*M*** and **$Rh^B12W10MCM$-*M*** and for 6 h with the rhodium(I) supported catalyst **$Rh^B12W10MCM$-*M***. The results showed that maximum conversion in the reaction of hydroformylation of 1-octene
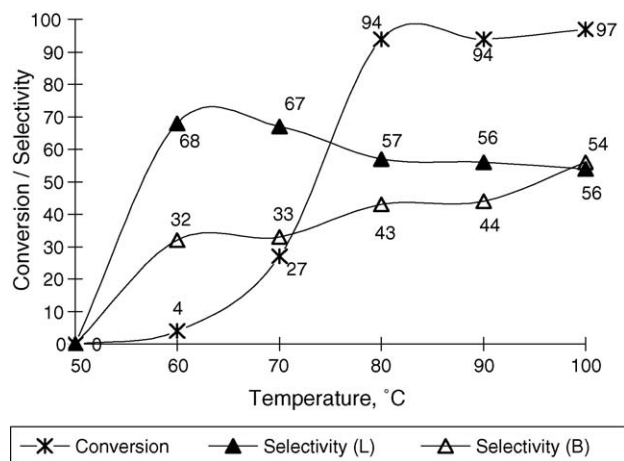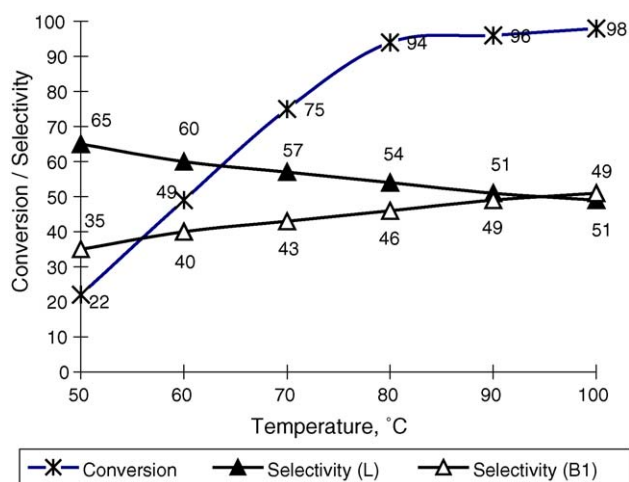
Fig. 2. Hydroformylation of 1-octene by **$Rh^B12W10MCM$-*M***. Effect of the temperature on the conversion and the selectivity. Reaction conditions: **$Rh^B12W10MCM$-*M*** (10 mg), 1-octene (5.0 mmol), THF (5 ml), CO (300 psi), H_2 (300 psi), 16 h.

catalyzed by **$Rh32W10MCM$-*M*** (Fig. 1) was 94% at 80 °C after 16 h. It is important to note that no reaction was observed at 50 °C and the conversion at 60 °C was only 4% with 67% selectivity toward the linear aldehyde (**L**). As the temperature of the reaction was increased, the conversion increased and the selectivity dropped. The addition of water inhibited the reaction of hydroformylation of 1-octene and the conversion at 80 °C dropped from 94% to 26%. In addition, the use of $P(OPh)_3$ showed also negative effect on the reaction and the conversion dropped to 35%. However, **$Rh^B12W10MCM$-*M*** showed higher catalytic activity compared to **$Rh32W10MCM$-*M*** especially at temperatures below 80 °C (Fig. 2). Excellent conversion (94%) was obtained at 80 °C and reached 96% at 90 °C. Similar to the previous observation, the selectivity of the reaction towards linear aldehydes decreased with the increase of the temperature (Fig. 2). The same reaction was studied with **$Rh^B12W10MCM$-**
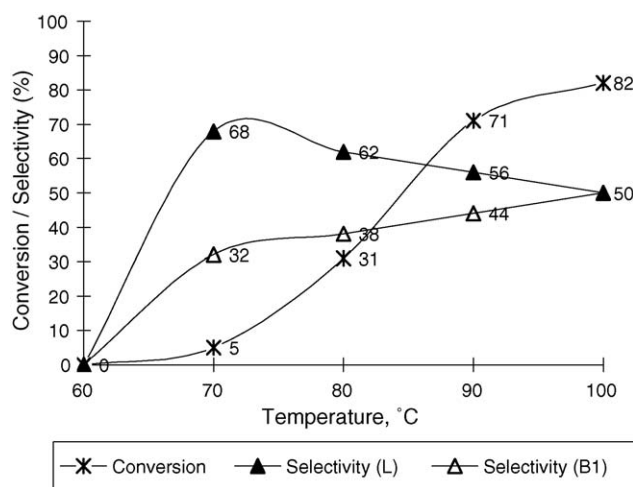
Fig. 1. Hydroformylation of 1-octene by **$Rh32W10MCM$-*M***. Effect of the temperature on the conversion and the selectivity. Reaction conditions: **$Rh32W10MCM$-*M*** (10 mg), 1-octene (5.0 mmol), THF (5 ml), CO (300 psi), H_2 (300 psi), 16 h.

Fig. 3. Hydroformylation of 1-octene by **$Rh^B12W10MCM$-*M***. Effect of the temperature on the conversion and the selectivity. Reaction conditions: **$Rh^B12W10MCM$-*M*** (10 mg), 1-octene (5.0 mmol), THF (5 ml), CO (300 psi), H_2 (300 psi), 6 h.

Table 3
Hydroformylation of 1-octene by **Rh*3*2W10MCM-M**; effect of the reaction time vs. temperature[a]

Run	Time (h)	Conversion[b] (%)	T (°C)	Product distribution[c] $B_1/B_2/B_3/L$ (%)	1-Octene (%)	Octene isomers (%)
1	2	2	80	30/0/0/70	98	2
2		8	100	27/0/0/73	54	46
3	4	6	80	32/0/0/68	88	12
4		32	100	35/4/7/54	18	82
5	6	12	80	36/2/4/58	76	24
6		58	100	34/6/8/52	4	96
7	8	28	80	36/3/5/56	32	68
8		76	100	34/7/9/50	4	96
9	12	68	80	36/4/6/54	24	76
10		90	100	33/8/10/49	5	95
11	16	88	80	37/5/8/50	17	83
12		98	100	32/10/12/46	4	96

[a] Reaction conditions: **Rh*3*2W10MCM-*M*** (10 mg), 1-octene (5.0 mmol), THF (5 ml), 600 psi ($CO/H_2 = 1/1$).

[b] Determined by GC.

[c] Determined by GC and ^1H NMR.

M for the effect of the temperature for 6 h only (Fig. 3). The conversion at 80 °C was 31% only. The conversion increased to reach 71 and 82% at 90 and 100 °C, respectively. It appears that rodium(I) supported catalysts were much active even at lower temperatures and shorter reaction time, while the selectivity was only slightly affected by the temperature and the type of rhodium catalyst.

3.3. Hydroformylation of 1-octene by supported catalyst

3.3.1. Effect of the reaction time versus temperature

The hydroformylation of 1-octene was also carefully studied against reaction time and temperature (Tables 3 and 4). The effects of the reaction time and the temperature were investigated with **Rh*3*2W10MCM-*M*** as a catalyst at 80 and 100 °C for the reaction time of 2–16 h (Table 3). The conversions were very low (<28%) at 80 °C for the periods 2–8 h. However, a significant increase in the conversion (68%) was observed after 12 h and a maximum conversion (94%) was achieved after 16 h. At 100 °C, the rate of the reaction of hydroformylation of 1-octene increased compared to the previous conditions. The selectivity of the reaction was not much affected by the temperature and the ratio of L/B was almost maintained between 1.4 and 1.6.

However, the hydroformylation of 1-octene by the rhodium(I) supported catalyst Rh*B*12W10MCM-M showed much faster reactions at 80–100 °C reflected by the higher conversions compared to reactions catalyzed by **Rh*3*2W10MCM-*M*** (Table 4). The conversions at 100 °C reached 82, 90 and 94% at 6, 8 and 12 h, respectively. It is very important to note that the isomerization of 1-octene increased with the time and the temperature. For example, at 80 °C, the amounts of 1-octene not isomerized were 46, 17, 15, 13 and 11% between 4 and 16 h of reaction (Table 4, entries 3, 5, 7, 9 and 11). At 100 °C, the rate of isomerization was much higher and the amounts of 1-octene not isomerized were 2–5% only after 6–16 h (Table 4, entries 2, 4, 6, 8, 10 and 12). Rhodium(I) complexes are well known as catalysts enhancing the isomerization processes of alkenes [1].

Table 4
Hydroformylation of 1-octene by **Rh*B*12W10MCM-*M***; effect of the reaction time vs. temperature[a]

Run	Time (h)	Conversion[b] (%)	T (°C)	Product distribution[c] $B_1/B_2/B_3/L$ (%)	1-Octene (%)	Octene isomers (%)
1	2	12	80	33/0/0/69	92	8
2		57	100	35/3/5/58	3	97
3	4	48	80	31/0/0/67	46	54
4		74	100	36/6/8/50	2	98
5	6	70	80	34/1/2/63	17	83
6		82	100	37/8/11/45	3	97
7	8	82	80	35/2/2/61	15	85
8		90	100	36/7/12/45	4	96
9	12	90	80	36/2/3/59	13	87
10		94	100	35/10/12/43	5	95
11	16	96	80	37/3/6/54	11	89
12		98	100	37/9/12/42	4	96
13[d]	6	58	80	36/1/2/61	20	80
14[d]		78	100	35/7/10 48	2	98

[a] Reaction conditions: **Rh*B*12W10MCM-*M*** (10 mg), 1-octene (5.0 mmol), THF (5 ml), 600 psi ($CO/H_2 = 1/1$), 80 °C.

[b] Determined by GC.

[c] Determined by GC and ^1H NMR.
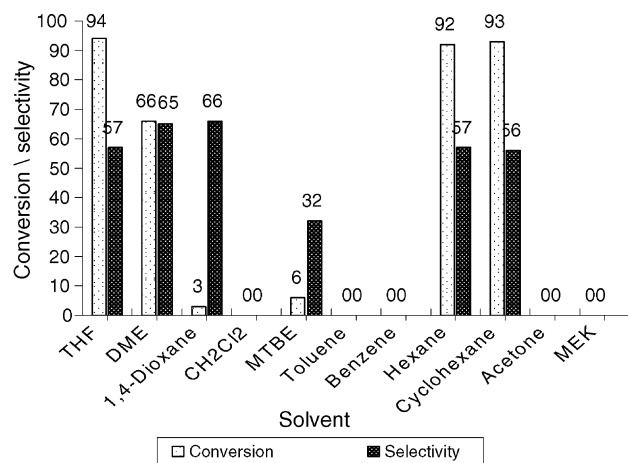
[d] P(OPh)$_3$ (0.010 mmol) was added.

Fig. 4. Hydroformylation of 1-octene by **Rh3**2**W**10**MCM**-*M*. Effect of the type of solvent on the conversion and the selectivity in the linear aldehyde. Reaction conditions: catalyst **Rh3**2**W**10**MCM**-*M* (10 mg), 1-octene (5.0 mmol), CO (300 psi), H_2 (300 psi), 80 °C, 16 h.

Fig. 5. Hydroformylation of 1-octene **Rh**[B]**1**2**W**10**MCM**-*M*. Effect of the type of solvent on the conversion and the selectivity in the linear aldehyde. Reaction conditions: catalyst **Rh**[B]**1**2**W**10**MCM**-*M* (10 mg), 1-octene (5.0 mmol), CO (300 psi), H_2 (300 psi), 80 °C, 6 h.

The results obtained on the correlation of the reaction time versus temperature showed clearly the various options toward either very high conversion at higher temperature (100 °C) versus the high selectivity at lower temperature (80 °C) by fixing the reaction time at 6 h. Any increase in the reaction time will have an impact on both the conversion and the selectivity. Some additional experiments showed that the type of the heteropolyacid and the type of the rhodium(I) catalyst do not affect much this important correlation.

3.4. Hydroformylation of 1-octene by supported catalyst

3.4.1. Effect of the type of solvent

The type of solvent has a definite impact on the course of the reaction of the hydroformylation of 1-octene. Various solvents such as THF, DME, dioxane, acetone, MTBE, CH_2Cl_2, benzene, toluene, hexane and cyclohexane have been used in this study (Figs. 4 and 5). Supported catalysts based on rhodium(III) and rhodium(I) were used. The results showed that there was no clear correlation of catalytic activity of the system with the polarity of the solvent. For instance, excellent conversions were obtained in THF, hexane and cyclohexane, and no reaction
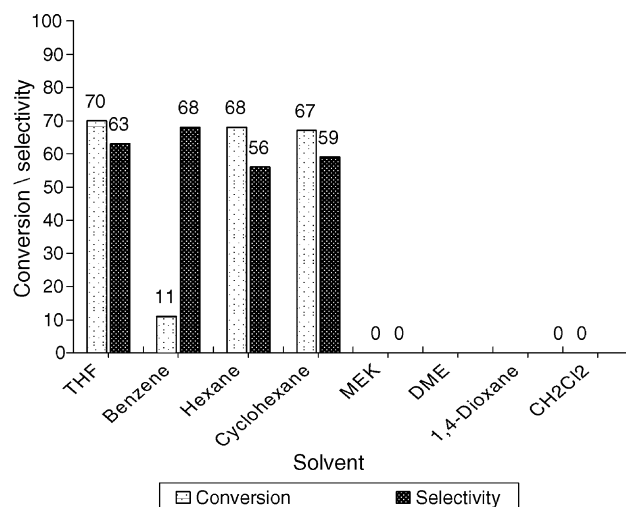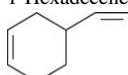
or very poor conversions were observed with acetone, methyl ethyl ketone (MEK), CH_2Cl_2, MTBE, dioxane, benzene and toluene. These observations were made for both types of catalysts **Rh3**2**W**10**MCM**-*E* and **Rh**[B]**1**2**W**10**MCM**-*E*. However, the reaction was much faster with **Rh**[B]**1**2**W**10**MCM**-*E* in THF, hexane and cyclohexane as a solvent.

We have not yet been able to fully understand and explain such a solvent behavior and we are investigating these results.

3.5. Hydroformylation of various terminal alkyl alkenes by Rh[B]12W10MCM-E

The study of the optimization made with 1-octene showed that **Rh**[B]**1**2**W**10**MCM**-*M* is the active catalyst where the highest conversion was obtained at 80 °C and 16 h. Therefore, the hydroformylation of different terminal alkyl alkenes was realized using the catalyst system **Rh**[B]**1**2**W**10**MCM**-*E* in THF as a solvent at 80 °C and 16 h. The results are summarized in the Table 5. We have observed that alkene with shorter alkyl chain, such as 1-heptene, was slightly less reactive than 1-octene

Table 5
Hydroformylation of various terminal alkyl alkenes[a]

Entry	Substrate	Conversion[b] (%)	Product distribution[c] (%)		Alkenes[b] (%)	
			B_1/L	$B_2 + B_3 + B_4$	1-Alkene	Alkenes isomers
1	1-Heptene	72	35/63	2	21	79
2	1-Octene	96	37/54	9	11	89
3	1-Dodecene	80	36/56	8	33	67
4	1-Tetradecene	89	36/51	13	35	65
5	1-Hexadecene	84	35/52	13	39	61
6		56	16/84	–	–	–

[a] Reaction conditions: **Rh**[B]**1**2**W**10**MCM**-*M* (10 mg), 1-octene (5.0 mmol), THF (5 ml), 80 °C, CO (300 psi), H_2 (300 psi), 16 h.
[b] Determined by GC using anisole as internal standard.
[c] Determined by GC and ^1H NMR.

Table 6
Hydroformylation of 1-octene by **Rh^{B}15W10MCM**-*E*; recycling of the catalyst[a]

No. of cycles	Time (h)	Conversion[b] (%)	Product distribution[c] (%)			
			L	B$_1$	B$_2$	B$_3$
1	3	87	44	37	11	8
2	3	85	50	34	9	6
3	6	84	42	38	12	9
4	6	55	60	34	4	2
5	12	87	41	39	12	9
6	12	64	48	37	9	6
7	16	83	44	38	10	8
8	16	52	49	38	8	5

[a] Reaction conditions: catalyst (50 mg), 1-octene (5.0 mmol), cyclohexane (5 ml), 600 psi (CO/H$_2$ = 1/1), 110 °C.
[b] Determined by GC.
[c] Determined by GC and ^{1}H NMR.

Table 7
Hydroformylation of 1-octene by **Rh^{B}15MCM**-*E*; recycling of the catalyst[a]

No. of cycles	Time (h)	Conversion[b] (%)	Product distribution[c] (%)			
			L	B$_1$	B$_2$	B$_3$
1	3	80	47	37	10	6
2	3	85	40	38	12	9
3	3	70	51	37	9	6
4	12	98	38	38	12	10
5	20	45	59	35	4	2

[a] Reaction conditions: catalyst (50 mg), 1-octene (5.0 mmol), cyclohexane (5 ml), 600 psi (CO/H$_2$ = 1/1), 110 °C.
[b] Determined by GC.
[c] Determined by GC and ^{1}H NMR.

under the same experimental conditions (Table 5, entry 1). The conversion was 72% but the selectivity toward the aldehydes L + B$_1$ was very high (98%). Other long chain alkyl alkenes, such as 1-dodecene, 1-tetradecene and 1-hexadecene were converted to aldehydes (Table 5, entries 3–5), and the selectivity toward L + B$_1$ was also high (87–92%). 4-Vinylcyclohexene was hydroformylated by the catalyst **Rh^{B}12W10MCM**-*E* (Table 5, entry 6). The reaction took place only on the terminal double bond (vinyl group) while the internal double bond (cyclohexene) stayed intact. The reaction was slower and the best conversion obtained after 16 h was 56%. The explored supported system that includes rhodium and heteropolyacid is also capable of converting various terminal alkyl alkenes with short and long

alkyl chains into aldehydes. The reaction still lacking the high selectivity toward the linear aldehydes, but excellent overall results in terms of catalytic activity, conversion and total selectivity were obtained.

3.6. Study of the catalyst recycling

The study of the recycling of the supported catalysts was realized in a similar manner to the hydroformyaltion of styrene [19]. The hydroformylation of 1-octene was carried out with 50 mg of **Rh^{B}15W10MCM**-*E* or **Rh^{B}15MCM**-*E* using cyclohexane as a solvent. The results are summarized on Tables 6 and 7. Different recycling abilities were shown with **Rh^{B}15W10MCM**-*E* or **Rh^{B}15MCM**-*E*. The catalyst **Rh^{B}15W10MCM**-*E* has been recycled about eight times with acceptable to high conversions. The reaction time was different for the recycling experiments (Tables 6 and 7). The conversions of 87 and 85% were obtained

at 3 h of reaction time (Table 6, entries 1 and 2). The conversions decreased at the same reaction time in the further cycles. However, if the reaction time was prolongated to 6 h, the conversions increased to 84% (Table 6, entry 3). The catalytic activity of the catalyst decreases with number of cycles and more time was required to get the high conversions. For example, the conversions of 87 and 64% were obtained at the fifth and sixth cycles but after 12 h of reaction (Table 6, entries 5 and 6). The seventh and eighth cycles required more time as well (Table 6, entries 7 and 8). The products of the hydroformylation of 1-octene are nonaldehyde (linear L), 2-methyl octanaldehyde (branched B$_1$), 2-ethyl heptanaldehyde (branched B$_2$) and 2-propyl hexanaldehyde (branched B$_3$). The selectivity for the linear isomer ranges from 41 to 60% and that of predominant branched isomer (2-methyl octanaldehyde) ranges from 34 to 39%. The combined selectivity for the other two branched isomers ranges from 6 to 21% as shown in Table 6.
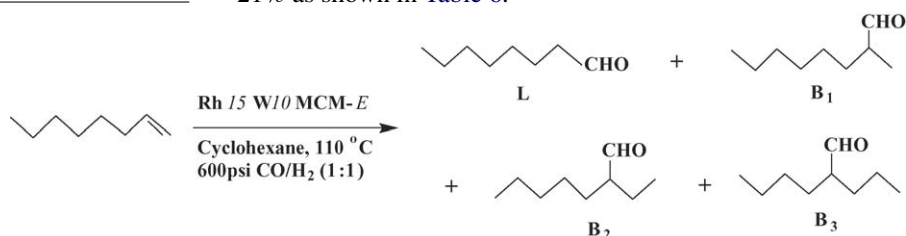
In order to assess the effect of HPA in the recyling process, we have made a comparative study by using the HPA free system (**Rh15MCM**-*E*) under the same experimental conditions adopted for **Rh^{B}15W10MCM**-*E* (Table 7). The conversion of 1-octene by the end of fifth cycle has dropped to about 45% even after running the reaction for 20 h compared to 98% in case of **Rh15W10MCM**-*E* after 12 h of reaction time.

These results showed again the advantage of using HPW$_{12}$ along with rhodium catalysts anchored on MCM-41 in the process of the catalyst recycling.

It is important to note that the recycling process with **Rh^{B}15W10MCM**-*E* or **Rh^{B}15MCM**-*E* in hexane showed similar trends to the process in cyclohexane as a solvent. Although, the use of THF in this experiment leads to excellent conversion of 1-octene but most of rhodium catalyst was leached out from the support and the catalyst could not be recycled.

The crystallinity of the MCM-41 support was monitored by X-ray powder diffraction. The X-ray patterns of recycled sup-
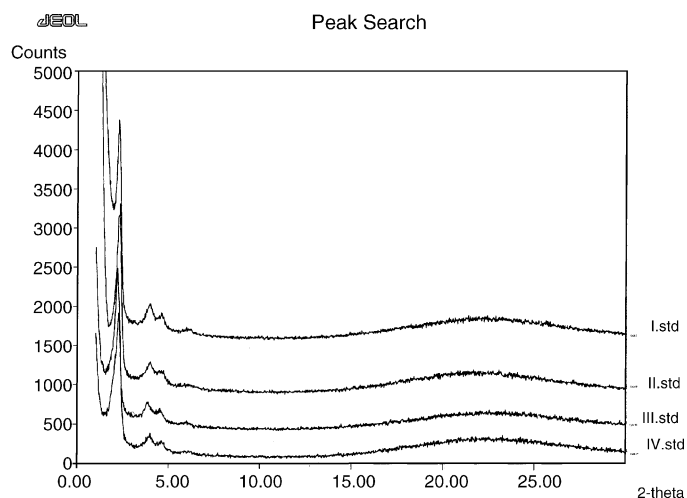
Fig. 6. The X-ray powder diffraction patterns of recycled supported catalyst **Rh^{B}15W10MCM**-*E* for four cycles.
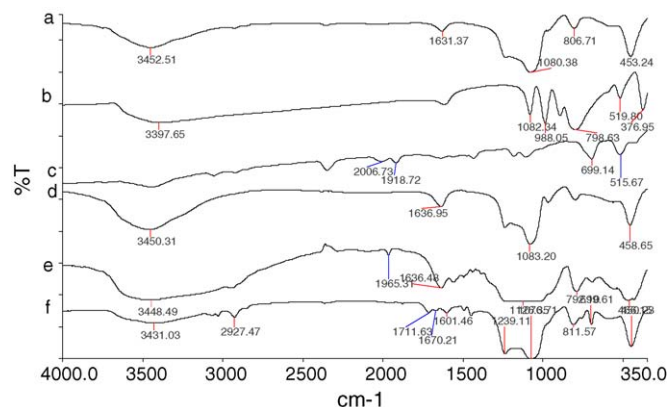

Fig. 7. FT-IR spectra of different materials (a) MCM-41; (b) HPW$_{12}$; (c) HRhCO(PPh$_3$)$_3$; (d) MCM-41/HPW$_{12}$; (e) **Rh^{B}15W10MCM**-*E*; (f) recycled supported catalyst **Rh^{B}15W10MCM**-*E* after six cycles.

ported catalysts **Rh^{B}15W10MCM**-*E* are shown in Fig. 6. The crystallinity of the MCM-41 support was maintained even after four cycles in the study of the catalyst recyling. These results showed the high stability of the system under the experimental conditions.

The supported catalysts were monitored by FT-IR spectrometry. The spectra of the systems that include MCM-41, HPW$_{12}$, HRhCO(PPh$_3$)$_3$, HPW$_{12}$ supported on MCM-41, **Rh^{B}15W10MCM**-*E*, and the recycled supported catalyst

Rh^{B}15W10MCM-*E* after six cycles (Fig. 7a–f). The pure HPW$_{12}$ spectra with Keggin structure showed the following four important IR bands: 1082 (P–O), 988 (W=O), 800 (W–O–W) and 525 cm^{-1} (W–O–P) (Fig. 7b) [23]. It was also observed that the framework bands of Si-MCM-41 are 1235, 1084, 966, 801, 564 and 456 cm^{-1} [24] and overlap with those of HPW$_{12}$ [25]. The described IR spectra confirmed that the framework of MCM-41 remained intact even after six cycles.
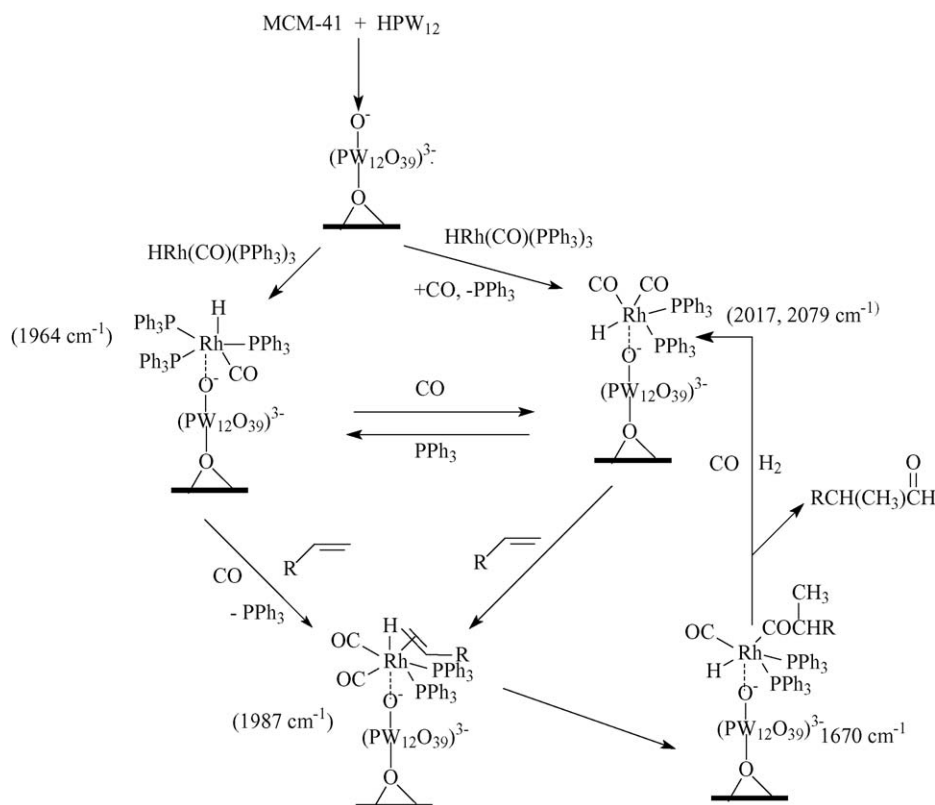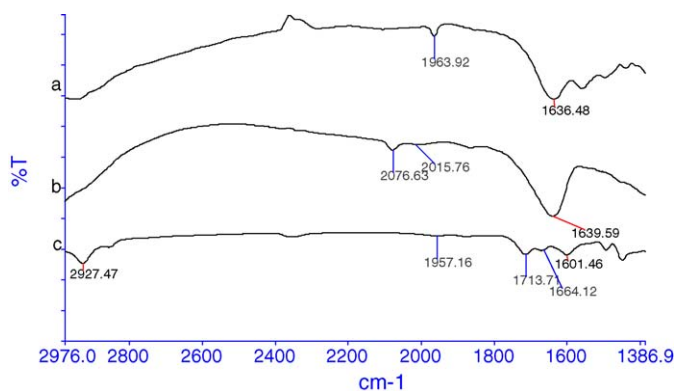

Scheme 1. Proposed reaction mechanism.

Fig. 8. FT-IR spectra of catalyst materials. (a) **Rh^{B}15W10MCM**-*E*; (b) **Rh^{B}15W10MCM**-*E* treated with CO/H$_2$ at 600 psi and 110 °C for 2 h; (c) recycled supported catalyst **Rh^{B}15W10MCM**-*E* after six cycles.

4. Proposed reaction mechanism for heterogeneoushydroformylation of alkenes

Keggin ions, $X^{n+}W_{12}O_{40}^{(8-n)-}$, where X is phosphorous or silicon have T_d symmetry and feature tetrahedral XO_4 unit, at each vertex of which are three edge-shared MO_6 octahedra. The four M_3O_{13} trimetric groups are bonded to one another by a corner sharing of oxygen atoms [12]. The charge in the $X^{n+}W_{12}O_{40}^{(8-n)-}$ anions is delocalized so that the oxygen atoms lying on the surface of the cluster are weakly nucleophilic. Oxygen alkylation is expected. Rh(I) cation, exemplified by $(Ph_3P)_2Rh(CO)^+$, may be stabilized in the solid state by the lattices provided by the negatively charged molecular metal oxide clusters [8].

The proposed reaction mechanism of the hydroformylation of alkyl alkenes is presented in the Scheme 1.

The exact chemistry of the tethered moiety is not yet understood. Weak coordinate-covalent interaction similar between oxygen atoms of HPA and the Rh-atom of the $HRh(CO)(PPh_3)_3$ complex have been reported. This sort of ionic interaction fastens the Rh-complex tightly to the oxygen atoms of HPA tethered to the zeolite Y or MCM-41 matrix, thus restricting the complex from leaching out in the liquid phase.

The FT-IR is most widely method used to characterize the supported rhodium through the study of the CO vibrational mode. The IR absorptions of CO and P-Rh in the pure Rh(I) carbonyl complex $HRh(CO)(PPh_3)_3$ are 1921 and 515 cm^{-1}, respectively (Fig. 7c) [5,26]. However, the supported catalyst **Rh^{B}15W10MCM**-*E*, freshly prepared by the impregnation of $HRh(CO)(PPh_3)_3$ and HPW_{12} on MCM-41, showed a CO band of Rh–CO shifted to 1965 cm^{-1} (Fig. 8a). When the same supported catalyst was treated with 600 psi of CO/H$_2$ for 2 h at 110 °C, two absorptions appeared at 2017 and 2079 cm^{-1}, which correspond probably to the two gem-dicarbonyl (Fig. 8b). This observation is explained by the replacement of PPh$_3$ ligand by CO. Similar assignments were also made in previous reports [19,27,28].

However, the same catalyst **Rh^{B}15W10MCM**-*E* showed at end of several cycles new additional absorptions at 1714 and 1671 cm^{-1}. These two peaks are tentatively attributed to CO

stretching in Rh–CO–Rh bridging and in the supported acyl rhodium species, respectively (Fig. 8c) [29,30].

5. Conclusion

The hydroformylation of alkyl alkenes by the supported catalysts showed clearly that the rhodium(I) based catalyst **Rh^{B}12W10MCM**-*E* was more active than **Rh32W10MCM**-*E* in term of conversion at the same experimental conditions. The results showed no clear correlation between the catalytic activity and the polarity of the solvent. Excellent conversions were obtained in THF, hexane and cyclohexane, and no reaction or very poor conversions were observed with acetone, MEK, CH$_2$Cl$_2$, MTBE, dioxane, benzene and toluene.

The addition of P(OPh)$_3$ in the reaction of the hydroformylation of 1-octene did not show any effect on the conversion, selectivity and the kinetics of the reaction and enhanced the leaching out of rhodium from the support.

The catalyst recycling showed clearly the role of the heteropolyacid on the catalytic activity of the impregnated rhodium(I) catalyst. **Rh^{B}15W10MCM**-*E* or **Rh^{B}15MCM**-*E* catalyzed efficiently the hydroformylation of 1-octene in cyclohexane as a solvent. However, the HPA containing system **Rh^{B}15W10MCM**-*E* showed better recyling ability.

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