

# The Heteropolyacids Enhanced Preparation of the Functionalized HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/MCM-41 Materials for Isobutene Hydroformylation

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**Abstract:** The supported catalyst HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/HPA-MCM-41 had been prepared by impregnating water-soluble organometallic complex HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> onto the mesoporous Si-MCM-41 carrier functionalized by the heteropolyacids. The catalysts were characterized with the N<sub>2</sub> adsorption/desorption, FT-IR and XRD technologies. The isobutene hydroformylation to isovaleraldehyde was selected as a model reaction. The supported catalysts HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/HPA-MCM-41 had exhibited significant catalytic performances besides the advantage of easy separation of catalysts from product mixture, compared with the homogeneous catalyst; the highest selectivity of isovaleraldehyde over catalyst using mesoporous Si-MCM-41 carrier was achieved, compared with that of those carried by SiO<sub>2</sub>, ZSM-5 and β-zeolite. The heteropolyacids was very promoting for enhancing the activity with a high selectivity.

**Keywords:** Mesoporous Molecular Sieves; Si-MCM-41; Isobutene; Hydroformylation

## 1. Introduction

Isobutene hydroformylation is very interesting because the product isovaleraldehyde is an important industrial intermediate in the production of detergents and many other chemicals [1]. It has been known that cobalt and rhodium catalysts are the most active in this process at the industrial level [2-3], while the relevant industrial products of hydroformylation are produced by homogeneous systems over the past 20 years. The research work has been active in these fields by now [4-5].

However, compared with homogeneous catalysts, heterogeneous catalysts can offer the potential advantages, such as easy separation and purification of products, reusable recycling of catalysts from the reaction mixture, and the possible continuous or multiple processing of fine chemicals. Many approaches for immobilization of homogeneous complex to solve this problem have been explored [5-9]. Thus, the novel and efficient supported Rh complex catalysts have become the popular topic, which behave several advantages [8-9]. Heterogeneous catalysts were extensively applied in hydroformylation of olefin, Rh<sub>4</sub>(CO)<sub>12</sub> had been successfully anchored to Si-MCM-41 materials and Si-MCM-48 mesoporous materials. For 1-hexene hydroformylation, such Rh-P complexes were attached to amino-group functionalized Si-MCM-41 and Si-MCM-48 [10]. The heterogeneous catalysts showed higher catalytic activity comparable to the corresponding homogeneous ones; the high product selectivity was due to the larger cone angle of the ligands over Rh-PPh<sub>3</sub> in the homogeneous systems, the angle was also observed in the heterogeneous ones.

The aim of the current work was synthesizing and characterizing the functionalized Si-MCM-41 supported Rh complex catalysts and investigating the effects of different carriers on catalytic performance of isobutene hydroformylation. In

this paper, the heteropolyacids (H<sub>3</sub>[P(W<sub>3</sub>O<sub>10</sub>)<sub>4</sub>]·nH<sub>2</sub>O) was used to modify the Si-MCM-41 carrier. The isobutene hydroformylation was selected as a model reaction to investigate the important catalytic application of the heterogeneous catalysts.

## 2 Experimental

### 2.1 Catalysts preparation

Si-MCM-41 was prepared by hydrothermal method according to the literature [11].

All of the solvents used for reactions were analytical grade and treated by standard methods. All manipulations were carried out under argon atmosphere. HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> was synthesized according to the following procedures. Typically, 1.200 g (4.6 mmol) TPPTS was dissolved in 30 mL anhydrous ethanol at 78 °C under reflux, then 200 mg RhCl<sub>3</sub>·3H<sub>2</sub>O was added. The resulting mixture was stirred for 30 min, and then 3 mL formaldehyde was added into the above mixture. After the color of mixture solution became yellow, the 0.285 g sodium borohydride (NaBH<sub>4</sub>) dissolved in ethanol solution was added to the above mixture solution. The obtained mixture was stirred for another 1 h before the precipitate was filtered. The obtained powder was washed with ethanol (C<sub>2</sub>H<sub>5</sub>OH) and vacuum-dried at 80 °C overnight to obtain the HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> complex.

The obtained 2.0 g new carrier Si-MCM-41 was impregnated and refluxed with a solution of 110 mg HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> (dissolved in 40 mL ethanol) under Argon. Whereafter, the mixture solution was stirred and refluxed at 78 °C for 18 h. After the reaction, the solvent was removed by evacuation when cooled to the room temperature. The solid sample was further treated under vacuum at 80 °C overnight. The obtained supported heterogeneous catalyst then was carefully preserved under Argon before use.

## 2.2 Characterization of samples using different techniques

XRD patterns of the calcined samples were carried on an X-ray diffraction (Philips X'pert pro MPD) equipped with a graphite monochromator for Cu-K $\alpha$  (40 kV, 40 mA) radiation. The specific surface area, total pore volume, and average pore diameter were measured by the N<sub>2</sub> adsorption/desorption method with a Quantachrome Nova1000e static volumetric instrument at liquid nitrogen temperature.

## 2.3 Catalytic evaluation tests in the isobutene hydroformylation

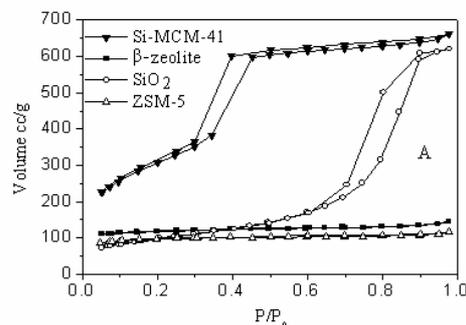
A typical heterogeneous hydroformylation was carried out in a 100 mL stainless steel autoclave, and the reaction system was mechanically stirred. 0.6 g catalyst and 40 mL isobutene together in 40 mL anhydrous dimethylbenzene were transferred into the reactor, and the autoclave was sealed and replaced with 2.5 MPa Nitrogen for three times and 2.5 MPa syngas (equimolar CO and H<sub>2</sub>) for one time. Subsequently, the pressure of syngas in the autoclave was increased to 2.5 MPa. The reaction system was maintained at 100 °C and stirred mechanically at 700 rpm for 5 h. During the experiment, an equimolar mixture of CO: H<sub>2</sub> was fed to the reactor, keeping the total pressure constant. After the reaction then cooling to room temperature, the excess CO and H<sub>2</sub> were slowly vented. The analysis of products was performed using SC-200 gas chromatography with a TCD detector.

## 3. Results and discussion

### 3.1 Texture analysis with N<sub>2</sub>-adsorption/desorption

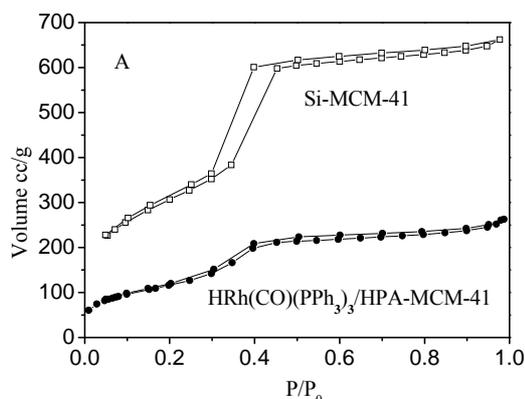
Nitrogen sorption isotherm of Si-MCM-41,  $\beta$ -zeolite, SiO<sub>2</sub> and ZSM-5 carriers was showed in **Fig. 1**. The isotherm of Si-MCM-41 materials could be classified as a typical type Langmuir IV isotherm [11], which was typical characterization of mesoporous materials, ZSM-5 and  $\beta$ -zeolite materials were microporous materials, and the SiO<sub>2</sub> was the macroporous materials. The ZSM-5 and  $\beta$ -zeolite materials surface area and average pore diameter was 300 and 361 m<sup>2</sup>.g<sup>-1</sup>, 2.4 and 2.5 nm respectively; their small pore diameter would limit the product formation of isobutene hydroformylation. The SiO<sub>2</sub> pore diameter distribution was broad. Its surface area and average pore diameter was 349 m<sup>2</sup>.g<sup>-1</sup> and 11.0 nm. Si-MCM-41 materials surface area and average pore diameter was 1104 m<sup>2</sup>.g<sup>-1</sup> and 3.7 nm. The surface area of mesoporous Si-MCM-41 materials was 3 times higher than that of ZSM-5,  $\beta$ -zeolite and SiO<sub>2</sub> material. From the pore diameter distribution, the distribution of Si-MCM-41 was more uniform than that of the SiO<sub>2</sub> materials using BJH method. ZSM-5 and  $\beta$ -zeolite materials had the similar distribution using HK method, however, the smaller pore diameter of ZSM-5 and  $\beta$ -zeolite was limited in hydroformylation reaction compared with the mesoporous Si-MCM-41. The catalysts using mesopore Si-MCM-41 material with narrow pore diameter distribution was the most preponderant in isobutene hydroformylation reaction than catalysts using other three supports. The narrow pore diameter distribution was beneficial for selectivity of the product. The higher surface area of materials, the better dispersion of active component of catalyst. So, the selectivity over catalysts with uniform pore diameter distribution (Si-MCM-41) was better than that of other material with the broad pore diameter distribution. Therefore, Si-MCM-41 material with high 96.4% selectivity of

isovaleraldehyde was promising in isobutene hydroformylation reaction.



**Fig. 1** Nitrogen sorption isotherm of Si-MCM-41, SiO<sub>2</sub>,  $\beta$ -zeolite and ZSM-5 materials.

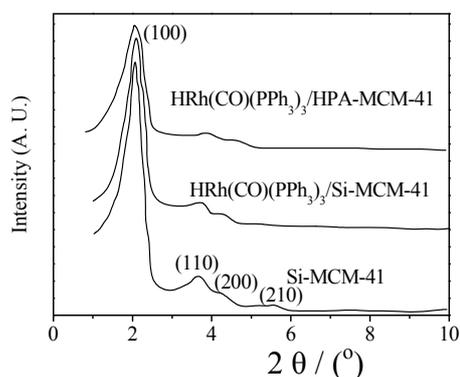
Nitrogen sorption isotherm of the Si-MCM-41, HPA-MCM-41 supported HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> was showed in **Fig. 2**. N<sub>2</sub> adsorption experimental results showed that the structural ordering of mesoporous Si-MCM-41 was kept even it was functionalized with HPA and utilized for the immobilization of Rhodium-phosphine complex, but modifications resulted in the decrease of pore size, total pore volume and surface area. The surface area and pore diameter of this material changed from 1104 m<sup>2</sup>/g and 3.7 nm for the initial Si-MCM-41 support to 444 m<sup>2</sup>/g and 3.6 nm when the HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> was supported on HPA-MCM-41, which illustrated that the HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> interacted with the surface hydroxyl and deposited on the surface of inner pores of functionalized Si-MCM-41 mesoporous material. The remaining rate of the surface area and pore diameter was 40.2% and 97.3%, respectively. From the isotherm of these materials, the mesopore structure remained perfectly. From the pore diameter distribution, the HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/HPA-MCM-41 materials has the similar narrow distribution as Si-MCM-41 materials. The uniform pore diameter was beneficial for the high selectivity for hydroformylation.



**Fig. 2** Nitrogen sorption isotherm of Si-MCM-41 and HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/ HPA-MCM-41 with Heteropolyacid (HPA) addition.

### 3.2 Structure characterization using XRD technique

The crystallinity of the Si-MCM-41 support was monitored by X-ray powder diffraction. The XRD results (**Fig. 3**) showed the typical Bragg reflections of the hexagonal Si-MCM-41 at small angles, including a strong peak around  $2.075^\circ$  and three weak peaks around  $3.605^\circ$ ,  $4.175^\circ$ , and  $5.645^\circ$ , which can be indexed as (100), (110), (200) and (210) reflections of Si-MCM-41 respectively, suggesting perfect long-range order in this material [12]. Clearly, well-resolved (100), (110) and (200) diffraction peaks of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/HPA-MCM-41 were observed, which indicated that the mesopore-structure was kept intact even HPA modified Si-MCM-41 supported HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> materials. The good order of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/HPA-MCM-41 material was maintained which can be seen from Fig. 3. The diffraction peaks of the supported HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> catalyst became broader and the peak intensities decreased, which indicated the order of the Si-MCM-41 was weakened after the active component HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> was anchored on Si-MCM-41 mesoporous support. This result was in agreement with that of N<sub>2</sub> adsorption.



**Fig. 3** X-ray diffraction patterns of Si-MCM-41, HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/MCM-41 and HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/HPA-MCM-41.

### 3.3 Catalytic performance of hydroformylation

#### 3.3.1 Effect of different supports on catalytic performance of hydroformylation

The effect of different supports on catalytic performance of isobutene hydroformylation was listed in **Table 1**. The experimental results indicated that the supported HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> catalyst using mesoporous Si-MCM-41 as carrier exhibited significant catalytic performances, compared with other catalyst using SiO<sub>2</sub>, commercial ZSM-5 and  $\beta$ -zeolite carriers. It was observed that the conversion was 18.10% over the Si-MCM-41 supported catalysts; the value was lower than that of using SiO<sub>2</sub> support (30.6%). However, the isovaleraldehyde selectivity of catalyst using SiO<sub>2</sub> support was only 80.7%. By contrast, a good selectivity value of 96.4% in isovaleraldehyde was obtained over the catalyst using Si-MCM-41 support, which was higher than that of other supported catalysts (respectively 85.5% for ZSM-5 and 94.8% for  $\beta$ -zeolite of isovaleraldehyde selectivity). These results were probably due to the different pore diameter distribution and surface area of different supports.

**Table 1** Effect of different supports on catalytic performance of isobutene hydroformylation

Catalysts	Conv. (%)	Yield (%)	Sel. (%)	ASTY (mol/mol-Rh.h)
HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub> /SiO <sub>2</sub>	30.6	24.8	80.7	129.4
HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub> /ZSM-5	21.2	18.1	85.5	94.7
HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub> / $\beta$ -zeolite	13.8	13.1	94.8	68.3
HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub> /Si-MCM-41	18.1	17.4	96.4	109.7

Conditions: 40 ml solvent of xylene, P=2.5 MPa, T=100 °C, Reaction time=5 h, Catalyst amount = 200 mg, isobutene quantity = 2.0 g

#### 3.3.2 Effect of HPA modified catalysts on isobutene hydroformylation

HPA was selected to modify the mesoporous Si-MCM-41 support for the preparation of novel efficient supported Rh catalysts. The results indicated that the novel catalysts modified by HPA showed better catalytic performances than unmodified catalyst using Si-MCM-41 support (**Table 2**). The isobutene conversion was reached 35.1%, which was twice of the value of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/MCM-41; the selectivity of isovaleraldehyde was 96.1% and the ASTY value was 208.2 mol/(mol-Rh.h). By contrast, the HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/MCM-41 catalyst presented a selectivity of isovaleraldehyde of 96.4% and ASTY of only 109.7 mol/(mol-Rh.h), which indicated that the HPA addition was favorable for isobutene hydroformylation, the catalytic reactivity of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/HPA-MCM-41 was 1.12 times higher than that of the HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> homogeneous catalyst besides its advantage of easy separation of catalyst from product mixture. These results showed the advantages of the use of the heteropolyacids on the catalytic activity in the hydroformylation of isobutene.

**Table 2** Effect of HPA modified catalysts on isobutene hydroformylation

Catalysts	Conv. (%)	Yield (%)	Sel. (%)	ASTY (mol/mol-Rh.h)
HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	30.5	29.0	95.1	187.1
HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub> /MCM-41	18.1	17.4	96.4	109.7
HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub> /HPA-MCM-41	35.1	33.7	96.1	208.2

## 4. Conclusions

The supported catalysts using mesoporous Si-MCM-41 carrier exhibited significant catalytic performances besides the advantage of easy separation of catalysts from product mixture, compared with the homogeneous catalyst; the highest selectivity of isovaleraldehyde over catalyst using mesoporous Si-MCM-41 carrier was achieved, compared with that of those carried by SiO<sub>2</sub>, ZSM-5 and  $\beta$ -zeolite. The novel HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/HPA-MCM-41 catalysts showed a high ASTY of 208.2 mol/(mol-Rh.h). HPA was efficient for enhancing the selectivity and activity of the Si-MCM-41 sup-

ported Rh catalyst in the isobutene hydroformylation to isovaleraldehyde.

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