

# A novel MCM-41-supported bi-functional catalyst by immobilizing organoamine and Rh–P complex for one-pot synthesis of 2-ethylhexenal from propene

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## ABSTRACT

We have demonstrated the synthesis of a novel MCM-41-supported bi-functional catalyst containing organoamine and Rh–P complex. We further characterized the catalysts by state-of-the-art analytical techniques including FTIR, UV–vis,  $^{31}\text{P}$  CP MAS NMR, TGA, XRD, BET, TEM, ICP-AES and elemental analysis. The as-synthesized catalyst was applied to the one-pot synthesis of 2-ethylhexenal using propene as raw materials. FTIR, UV–vis,  $^{31}\text{P}$  CP MAS NMR, and TGA results indicate that the active sites, organoamine and Rh–P complex, are successfully immobilized on the surface of catalyst support. The N and Rh content can be adjusted by adding different amounts of organoamine and Rh–P complex during the process of catalyst preparation. The mesoporous structure of the zeolite support remains intact after immobilization. However, the specific surface area and BJH pore size of the mesoporous zeolite support decrease after being grafted with organoamine and Rh–P complex.

The bi-functional catalyst with primary amine has the best catalytic performances for the one-pot synthesis of 2-ethylhexenal since it has better synergistic effect with silanol groups, followed by diamine and then tertiary amine. The Rh content of the catalyst determines the hydroformylation reaction rate of propene, while the self-condensation of *n*-butanal is determined by the balance between organoamine and silanol groups. The results indicate the hydroformylation reaction is the control step of this tandem reaction when the content of Rh in the catalyst is below 0.19%. In contrast, this tandem reaction is controlled by the self-condensation of *n*-butanal with further increasing Rh content. We found that the catalyst containing 1.73% of N (primary amine) and 0.19% of Rh is a suitable choice. And we obtained the best yield of 2-ethylhexenal above 77% in the one-pot synthesis from propene.

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## 1. Introduction

2-Ethylhexanol is an important industrial intermediate and extensively applied to produce washing liquid, plastics, and lubricants. The industrial method to produce 2-ethylhexanol from propene is a three-step process including hydroformylation of propene, self-aldolization of butyraldehyde and hydrogenation of 2-ethylhexenal. There are some limitations in the current process [1–4]. First, the separation of products and catalysts is difficult and expensive in the hydroformylation of propene. Second, liquid base NaOH or KOH acting as a catalyst of aldolization reaction leads to corrosion, separation hurdle of the product, and much alkaline discharge water. In recent years, in order to address the above issues, much more efforts have been committed to develop environment friendly and economical processes [5–21].

For the hydroformylation reaction of propene, many investigations were focused on the immobilization of Rh–P complex on a porous support. The support can be activated carbon [5], silica [2,6,7], magnetic nanoparticle [8], MCM-41 [9–12], SBA-15 [13,14], or polymer [15]. Rh–P complex anchored on activated carbon by covalent bonding showed good catalytic performances, and thermal stability [5]. Abu-Reziq [8] reported a supported magnetic nano catalyst by growing polyaminoamido (PAMAM) dendron on the particle surface. The resultant catalyst had good catalytic performances and was easily separated from reaction system. Mesoporous zeolite was the most frequently used support for the various intrinsic properties, channel structure and size, high surface area, and thermal and chemical stability.

For aldolization reaction, to develop solid-base catalyst is an interesting field in recent years [16–19] since it can reduce waste water discharge and can be easily separated from the reaction system in comparison to liquid alkali catalytic system. Zeolite support has been involved to prepare solid-base catalyst by grafting with organoamine [19–21].

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Bi/multi-functional catalyst has become a research hotspot owing to its unique properties. It can reduce the number of reactors for a tandem reaction or allow the synthesis of two or more products in one pot. Sharma [22] and Srivastava [23] reported a multi-functional catalyst for one-pot synthesis of  $C_{2n+2}$ -aldol derivatives from  $C_n$ -alkenes. More recently, Sharma [24–26] and his co-workers reported a multi-functional catalyst for one-pot synthesis of  $C_8$  aldehydes/alcohols from propene which consisted of  $HRhCO(PPh_3)_3$  and hydrotalcite. It was an eco-friendly catalyst and could carry out the hydroformylation of propene and the self-condensation of *n*-butyraldehyde.

Here, we demonstrated the synthesis of a novel bi-functional catalyst by immobilizing organoamine and Rh–P complex on MCM-41 support. And we further applied this catalyst to the one-pot synthesis of 2-ethylhexenal from propene. Rh–P complex and organoamine are the catalytic sites for the hydroformylation and aldolization reactions, respectively. The resultant catalysts were well characterized by state-of-the-art analytical techniques including FTIR, UV–vis,  $^{31}P$  CP MAS NMR, TGA, XRD, BET, TEM, ICP-AES, and elemental analysis. We also investigate the effects of organoamine type, the N and Rh content on the catalytic performances for the one-pot synthesis of 2-ethylhexenal from propene.

## 2. Experimental

### 2.1. Materials

MCM-41 zeolite in powder form was purchased from Shanghai Novel Chemical Technology Co., Ltd (PR China). 3-Aminopropyltriethoxysilane (APTS), 3-(*N,N*-dimethylaminopropyl) triethoxysilane (NDMAPTES), 3-trimethoxysilylpropylethylenediamine (TSPEDM), toluene, anhydrous ethanol, *n*-hexane and anhydrous chloroform were purchased from Aladdin-Reagent Co., Ltd (PR China). The structures of three types of organoamine were shown in Scheme 1. All reagents were used as received without any further purification. Rh–P complex ( $HRhCO(PPh_3)_3$ ) was self-synthesized as reported [27,28].

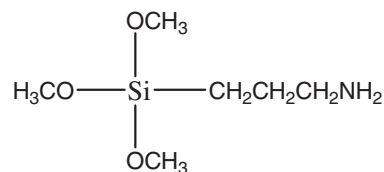
### 2.2. Preparation of the bi-functional catalysts

#### 2.2.1. Functionalization of MCM-41 by organoamine

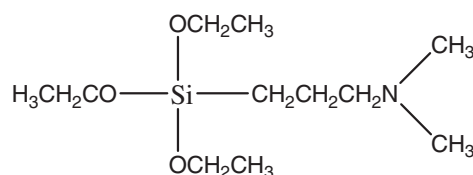
Functionalization of MCM-41 was carried out by following the procedure reported by Mukhopadhyay [29] and Stein [30]. MCM-41 powder in certain amount was suspended in boiling toluene and then required organic silicane was added dropwisely. The reaction was kept under refluxing state for 16 h. Then, the power was filtered, cleaned with anhydrous toluene and followed by Soxhlet-extracted once with  $CHCl_3$  to remove the attached organoamine with physisorption. The obtained sample was then dried at 80 °C for 12 h. Since the amine type has a great effect on the catalytic performances of catalysts, the catalysts grafted with different amines were synthesized, as shown in Table 1. The as-synthesized sample was coded as MCM-41-NR<sub>1</sub>R<sub>2</sub> (R<sub>1</sub> = H, CH<sub>3</sub>; R<sub>2</sub> = H, CH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>). The functionalization process can be depicted by Scheme 2 [13,31].

#### 2.2.2. Anchoring Rh–P complex

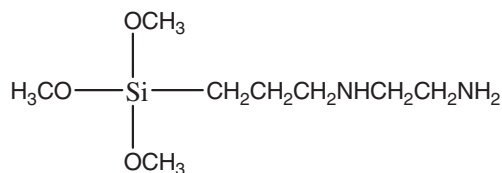
Anchoring Rh–P complex was performed as follows. Rh–P complex and MCM-41-NR<sub>1</sub>R<sub>2</sub> sample in required amount were orderly added to ethanol solution and stirred for 24 h at room temperature. The light yellow solid powder was filtered and then washed for several times with ethanol followed by Soxhlet-extracted once to remove the attached Rh–P complex on the support by physisorption, then dried in vacuum to get bi-functional catalyst samples. It was coded as MCM-41-NR<sub>1</sub>R<sub>2</sub>-Rh–P. The procedure was



APTS



NDMAPTES



TSPEDM

Scheme 1. The structure of amines.

described in Scheme 3 [13,29]. The detailed parameters for preparing different catalysts and the labels were summarized in Table 1.

### 2.3. Characterizations

#### 2.3.1. FTIR and UV–vis

Fourier transform infrared (FTIR) spectra of Rh–P complex, MCM-41, MCM-41-NR<sub>1</sub>R<sub>2</sub> and MCM-41-NR<sub>1</sub>R<sub>2</sub>-Rh–P catalysts were recorded with a Perkin–Elmer Spectrum Nicolet 5DX Fourier transform infrared spectrophotometer system in 500–4000  $\text{cm}^{-1}$  using KBr pellets. Ultraviolet visible (UV–vis) spectra of the samples were recorded with a Varian Cary 500 UV–VIS–NIR spectrophotometer. The scan wavelength ranged from 800 nm to 200 nm.

#### 2.3.2. $^{31}P$ CP MAS NMR and TGA

$^{31}P$  CP MAS (cross-polarized, magic angle spinning) NMR spectra of Rh–P complex and MCM-41-NR<sub>1</sub>R<sub>2</sub>-Rh–P were recorded with a Bruker-Avance-400 spectrometer. Thermogravimetric analysis (TGA) of Rh–P complex, MCM-41, MCM-41-NR<sub>1</sub>R<sub>2</sub> and MCM-41-NR<sub>1</sub>R<sub>2</sub>-Rh–P was carried out using a Mettler TGA/SDTA 851 e equipment under  $N_2$  atmosphere ( $50 \text{ mL min}^{-1}$ ) at  $10 \text{ }^\circ\text{C min}^{-1}$ .

#### 2.3.3. XRD

The powder X-ray diffraction (XRD) patterns of MCM-41, MCM-41-NR<sub>1</sub>R<sub>2</sub> and MCM-41-NR<sub>1</sub>R<sub>2</sub>-Rh–P samples were recorded with DMAX-111C system equipped with XRK 900 reaction chamber, using Cu-K $\alpha$  radiation ( $\lambda = 0.15405 \text{ nm}$ ). The observable  $2\theta$  range was from  $0.5^\circ$  to  $5^\circ$  at a scan rate of  $1^\circ \text{ min}^{-1}$ .

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