

Copyright © 2013 American Scientific Publishers All rights reserved Printed in the United States of America

A Selective Functionalized Mesoporous Silica-Supported Rh Catalyst for Effective 1-Octene Hydroformylation

Jong-Ki Jeon¹, Young Soo Ko¹, and Jin-Heong Yim^{2, *}

¹Department of Chemical Engineering, Kongju National University, Cheonan-si, 331-717, Korea ²Division of Advanced Materials Engineering, Kongju National University, Cheonan-si, 331-717, Korea

Through different functionalization methods, three kinds of Rh-immobilized mesoporous silicas have successfully been prepared to investigate catalytic behavior, including yield and the linear/branched ratio of aldehyde (*L*/*B*) in 1-octene hydroformylation. A conventional post grafting method and two kinds of selective bifunctionalized methods for modification of the mesoporous silica have been applied for this purpose. A relatively high *L*/*B* (> 2.0) was effectively achieved using Rh-immobilized inner pores in the MCM-41 support due to the confinement effects of the Rh complex in the nanospace. Moreover, the Rh-immobilized MCM-41 catalyst, passivated with trimethylchlorosilane (TMCS) only on the external surface, showed fairly good yields of the aldehyde (> 40%).

Keywords: MCM-41, Selective Functionalization, Rhodium Immobilization, 1-Octene Hydroformylation, Linear/Branched Selectivity.

1. INTRODUCTION

The functionalization of mesoporous silica with various organo-silanes has been widely studied for the past twenty years given their enormous application as catalysts, adsorbents and sensors.¹⁻⁴ In general, surface modifications are achieved either direct synthesis (co-condensation)⁵⁻⁹ or a post-grafting method.¹⁰⁻¹³ In addition, several comparative studies have been made focusing upon functional group content, structural stability and reactivity for certain catalytic reactions.¹⁴⁻¹⁷ In the direct synthesis, the large amount of the functional groups was uniformly introduced onto the surface and the ordered structure maintained using specific organotrialkoxysilanes under specific synthetic conditions. Regarding chemical reactivity, the post-grafting method is typically more effective due to distribution of functionalized groups within the silica framework.¹⁶ Moreover, very unique mesoporous materials that selectively modify the surfaces of the intra- and extra-pores have been reported to manipulate chemical anisotropy and enhance efficiency and selectivity for application as adsorbents and catalysts.¹⁸⁻²⁰ The selective functionalization of mesoporous silica was easily accomplished through two different methods using the surface grafting method. The first approach employed calcined mesoporous materials. Shephard et al.¹⁸ reported that the external surface silanol groups were more kinetically accessible than the internal surface in the grafting of alkoxy silane

with bulky substituents such as the phenyl group. Subsequently, the coupling of relatively small organotrialkoxysilanes, fincluding the active species, occurred mainly at the internal surface silanol groups. In the second technique, the grafting was performed without calcinations.¹⁹ The initial external surface grafting with type A organotrialkoxysilane employed as-synthesized mesoporous silica with pores filled with a surfactant template. Following the external grafting, the surfactant template was removed by solvent extraction. Then, the Si-OH group in the templatefree internal pore surface could be effectively reacted with type B organo-silanes containing the desired groups for a specific purpose. These dual functionalized mesoporous materials could potentially improve efficiency and selectivity of catalysis and adsorbents within various chemical processes.

It is possible that the functionalized mesoporous silicas, by the above routes, can be used in hydroformylation reactions through immobilization of metal complexes, including Co, Ru and Rh. Since its discovery in the 1930s, the hydroformylation reaction has driven the commercial production of numerous aldehydes for soaps, detergents and plasticizer alcohols. An alkene is easily converted to a linear and/or branched aldehyde by addition of CO/H_2 under Co or Rh catalysts. The reaction mechanisms for the 1-octene hydroformylation performed with heterogeneous rhodium-immobilized catalysts can be postulated as shown in Figure 1. Between the linear and branched aldehydes, the linear aldehyde is much more commercially useful,²¹ and as such, its selective production would be

^{*}Author to whom correspondence should be addressed.

J. Nanosci. Nanotechnol. 2013, Vol. 13, No. 4

Jeon et al.

very advantageous. Among the many current metallic catalysts, the rhodium catalyst shows excellent efficiency, bearing several phosphine ligands that elevate activation and selectivity of the linear aldehyde.²¹ Heterogeneous catalyst systems have been studied extensively due to a lack of efficient separation/purification of the product and recycling of the homogeneous catalyst system.^{22–29} For the heterogeneous catalyst supports (Al₂O₃, MgO, ZnO, SiO₂,^{22,24} active carbons and zeolites) have been employed widely in spite of their relatively small pore size. Recently, mesoporous silica materials such as MCM-41,^{23,25,26,28} HMS²⁷ and SBA-15,²⁸ bearing large pore sizes, stable structures, high surface areas and chemical and mechanical stability, were in the limelight as inorganic support materials.

In this work, mesoporous silica MCM-41 was prepared and functionalized with three ways for the purpose of the advanced 1-octene hydroformylation (one *via* nonselective and the others *via* selective functionalization). Primarily, the surface of the MCM-41 was modified by post-grafting with N-(β -aminoethyl) γ -aminopropyl methyldimethoxysilane (AEAPMDMS) (non-selective, Method 1). The secondary selective functionalized process was carried out on the as-synthesized (filled with template) MCM-41. The template-filled MCM-41 was functionalized with trimethylchlorosilane (TMCS), but only on the external surface. Afterwards, the template was removed under reflux in an ethanol/*n*-heptane mixture for internal

grafting. The internal pores were then subsequently modified with AEAPMDMS (selective, Method 2). Lastly, the external and internal surfaces were selectively functionalized after the calcinations. The calcined MCM-41 was pretreated with bulky diethoxydiphenylsilane (Ph₂Si(OEt)₂) to graft a more accessible external surface. Modification of the internal surface (in pores) was then performed with AEAPMDMS (selective, Method 3). Figure 2 depicts the graphical descriptions of the three functionalization methods. Subsequently, the rhodium complexes were tethered on the aminated surface through a coordination bond. 1-Octene hydroformylation was performed using the aforementioned three kinds of catalysts and homogeneous counterparts to investigate catalytic behaviors such like aldehyde yield, TOF and the linear/branched-aldehyde ratio (L/B) in terms of pore size and the environment of the Rh metal complex in the porous solid support. Particularly, linear/branched ratios of the aldehyde are discussed in the context of a confinement effect within the Rh complex in the nanospace.

2. EXPERIMENTAL DETAILS

2.1. Chemicals

For the synthesis of mesoporous silica MCM-41, cetyltrimethylammonium bromide (CTMABr, Aldrich) and a



Fig. 1. Mechanisms for the 1-octene hydroformylation catalized by rhodium-immobilized catalysts: (a) linear and (b) branched aldehyde.²¹

J. Nanosci. Nanotechnol. 13, 3087-3095, 2013



Fig. 2. Conceptual descriptions of the non-selective functionalization method (a): method 1 and the selective functionalization method (b): method 2, (c): method 3.

sodium silicate solution (SiO₂ 20 wt% in H₂O) were used as the surfactant and silica sources, respectively. Sodium hydroxide (Junsei) and acetic acid (Junsei) were used as the base and acid reagents. When the surface functionalization was performed, N-(β -aminoethyl) γ -aminopropyl methyldimethoxysilane (AEAPMDMS, GE Advanced Materials), trimethylchlorosilane (TMCS, Aldrich) and diethoxydiphenylsilane (Ph₂Si(OEt)₂, Aldrich) were used as silane precursors. Toluene (Oriental Chemical Industries), p-toluenesulfonic acid (PTSA, Aldrich) and isopropanol (Samchun Pure Chemical) were also employed. For removal of the surfactant template, ethanol (J. T. Baker), *n*-heptane (Hayashi Pure Chemical Industries, Ltd.) and hydrochloric acid (HCl, 36 wt% in H₂O, Junsei) were used. The samples were then washed with ethanol or methanol (Samchun Pure Chemical). In order to synthesize the rhodium-immobilized catalyst, n-hexane (Junsei Chemical) and tetrarhodium dodecacarbonyl ($Rh_4(CO)_{12}$, Strem Chemicals) were used as the solvent and rhodium derivative, respectively. Hexane was distilled from sodium metal and benzophenone under nitrogen over several hours. Tetrahydrofuran (THF, Aldrich) and 1-octene (Aldrich) were used for the 1-octene hydroformylation

J. Nanosci. Nanotechnol. 13, 3087-3095, 2013

reaction. Triphenylphosphine (TPP, Aldrich) was used as a ligand for 1-octene hydroformylation and a rhodium(II) acetate dimer (99%, Strem Chemicals) was used as the Rh homogeneous catalyst.

2.2. Synthesis of Mesoporous Materials by the Post Synthesis Method—Method 1

The synthesis of mesoporous silica MCM-41 was performed using a previously published procedure.²⁶ The calcined MCM-41 (0.5 g) was immersed in 75 mL of toluene (a non-polar solvent) and stirred at 50 °C for 0.5 h. *p*-Toluenesulfonic acid (3.5 mg) and 1.0 mmol of AEAP-MDMS (organo-silane) were then added. The mixture was heated to reflux temperature (~ 120 °C) and stirred for 2 h. The mixture was then allowed to cool to ambient temperature and the solid product filtered and washed with ethanol three times. The isolated solid was dried at 100 °C for 12 h.¹³ For the rhodium immobilization, 1.0 g of the amine-functionalized mesoporous silica MCM-41 was dispersed in hexane. The Rh₄(CO)₁₂ (0.037 g) in hexane was then added under N₂. The mixture was stirred at room temperature for 5 h under N₂. The colorless solvent was then drawn off through a syringe under N_2 and the resulting solid washed three times with hexane. The solid powder (brown in color) was vacuum dried at ambient temperature²³ (henceforth designated MCM-41/AEAPMDMS/Rh).

2.3. Synthesis of Mesoporous Materials by the Selective Functionalization Method—Method 2

The sample of mesoporous silica MCM-41 was achieved by a general process and the surfactant template left unremoved (without calcinations). As-synthesized (filled with template) MCM-41 (2.04 g) was dispersed in a mixture of isopropanol and 12.0 N HCl (70:70 = g:g). Then, 3.26 g of trimethylchlorosilane (TMCS) was added and stirred at 80 °C for 2 h. After 2 h, the isolated solid was washed with methanol, a mixture of methanol/deionized water and deionized water until the chloride was not detected. In order to remove the template, 1.5 g of the dried powder product was added to the ethanol and *n*-heptane mixture (50 wt%) with 0.58 g of hydrochloric acid. The system was refluxed at 70 °C for approximately two days (external grafting).

To graft the internal surface, 1.0 g of TMCS was dispersed in 75 mL of toluene and stirred at 50 °C for 0.5 h. Afterwards, 0.007 g of *p*-toluenesulfonic acid and 2.0 mmol of AEAPMDMS were added to the system and the mixture refluxed at 120 °C for 2 h. The material was filtered, washed with ethanol three times, and dried at 100 °C for 12 h.

The Rh complex was then immobilized on the internal surface of the mesoporous materials using the same procedure whereby 1.1 g of MCM-41/TMCS/AEAPMDMS was immersed in hexane and 0.037 g of $Rh_4(CO)_{12}$ in hexane was added. The mixture was then stirred for 5 h under ambient temperature. Finally, the hexane was removed, washed with hexane three times, and dried under vacuum (designated MCM-41/TMCS/AEAPMDMS/Rh).

2.4. Synthesis of Mesoporous Materials by the Selective Functionalization Method—Method 3

Mesoporous silica MCM-41 was prepared according to the above method and then calcined. The as-calcined MCM-41 (3.0 g) was then dispersed in 80 mL of toluene and stirred at 50 °C for 0.5 h. After sufficient immersion, 0.021 g of *p*-toluenesulfonic acid and 6.0 mmol of $Ph_2Si(OEt)_2$ were added sequentially and the mixture stirred at 120 °C for 2 h. The isolated solid product was washed with ethanol three times and dried at 100 °C for 12 h (external grafting).

For the internal grafting process, 3.0 g of MCM- $41/Ph_2Si(OEt)_2$ was added to 80 mL of toluene. After 0.5 h of stirring at 50 °C, 0.021 g of *p*-toluenesulfonic acid and 6.0 mmol of AEAPMDMS were added and the mixture refluxed at 120 °C for 2 h. The solid product was filtered and washed with ethanol three times. Then, the selective

functionalized mesoporous silica MCM-41 was dried at 100 °C for 12 h.

For the purposes of Rh immobilization, the same process was performed. The detailed conditions were as follows: 2.5 g of MCM-41/Ph₂Si(OEt)₂/AEAPMDMS, 0.0925 g of Rh₄(CO)₁₂ in hexane, 5 h stirring at room temperature under N₂ (henceforth designated MCM-41/Ph₂Si(OEt)₂/AEAPMDMS/Rh).

2.5. 1-Octene Hydroformylation

Hydroformylation of 1-octene was performed according to a previous method. The prepared catalyst, internal and external (or selectively internal) rhodium-immobilized aminated mesoporous materials, was added to a SUS-316 autoclave reactor containing 75 mL of THF and 4.68 g of 1-octene. Then, 0.044 g (or 0.022 g) of TPP was added to the mixture as the ligand. Subsequently, the autoclave was flushed with N₂. The syn-gas (CO/H₂ = 1) in the reactor was pressurized up to 300 psi and depressurized to atmospheric pressure three times. After the reactor was heated to 140 °C, the syn-gas was introduced to bring the total pressure to 300 psi. The system was maintained at 140 °C for 0.5 h and the syn-gas filled from a reservoir in order to maintain a pressure of 300 psi. The homogeneous rhodium catalyst was also used for 1-octene hydroformylation for comparison with the heterogeneous system. The rhodium acetate dimer, as the homogeneous Rh catalyst, was diluted with methanol. Then the calculated mixture was added to the reaction system. All experimental steps were identical to those described above and are listed in Table III. Final products were analyzed by gas chromatography (GC).

2.6. Characterizations

Nitrogen adsorption-desorption isotherms were obtained using a Micrometrics ASAP 2020 at -196 °C. Prior to analysis, the samples were degassed at 350 °C (or 200 °C) for 3 h. The surface area was calculated according to the Brunauer-Emmett-Teller (BET) equation and the pore volume obtained from the *t*-plot method. Small-angle powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 X-ray diffractometer. The samples were scanned from 0.3° to 5.0° (2 θ) with a step size of 0.01° at 300 mA and 40 kV. Transmission electron microscopy (TEM) was carried out on a Tecnai G2 F30 (FEI company) operated at an acceleration voltage of 300 kV. The nitrogen and carbon contents of the rhodium-immobilized materials were determined by elemental analysis (EA) using a Flash EA 1112 series (CE Instruments). The amount of the anchored rhodium on the materials was calculated by an inductively coupled plasma-atomic emission spectrometer (ICP-AES) using an Optima 4300DV (PERKIN ELMER) after HF treatment. The 1-octene hydroformylation products were analyzed using a GC-2014 (Shimadzu).

3. RESULTS AND DISCUSSION

3.1. Studies of the Functionalized Materials and Rh Immobilization

Using the different modification methods (Fig. 2), the non-selective and selective functionalized materials were synthesized and the rhodium complexes anchored on the aminated surface. Each material was characterized by means of BET, XRD, TEM, EA and ICP-AES measurements to confirm the crystalline pore structure of the MCM-41-based materials and Rh immobilization.

The textural parameters, including pore volume, surface area and pore size, are listed in Table I. The surface areas and pore sizes of the materials decreased with functionalization and the Rh immobilization caused by attaching the silanes to the pore surface and partial pore blocking. The surface areas of the MCM-41-based catalysts synthesized using methods 1, 2 and 3 were 787, 675 and 617 m² g⁻¹, respectively. The selective functionalized materials without calcinations (method 2) showed the biggest pore sizes as compared to others because the shrinking of the silica framework can not be occurred during calcinations. The pore size of the samples for method 2 was the biggest, 2.54 nm. In method 3, modified with Ph₂Si(OEt)₂ and AEAPMDMS, the decrease in surface area was the most extreme among other methods. This phenomenon can be attributed to the introduction of bulky phenyl groups on the extra-pores. However, the degree of pore size decrease was similar over all samples because the internal pores of every material were selectively attached with AEAPMDMS. In addition, the pore volumes decreased upon modification in all samples.

 Table I.
 Structural properties of the non-selective (method 1) and selective (method 2 and method 3) functionalized MCM-41-based catalysts.

		BET			
Catalyst	$\frac{\text{SAXS}}{d_{100}}$	$\frac{V_{\rm tot}}{(\rm cm^3 g^{-1})}$	$\frac{S_{\rm BET}}{(\rm m^2~g^{-1})}$	Pore size (nm)	
Method 1					
MCM-41	2.18	0.98	1016.11	2.95	
MCM-41/AEAPMDMS	2.18	0.50	878.96	2.42	
MCM-41/AEAPMDMS/Rh	2.18	0.43	787.01	2.44	
Method 2					
MCM-41/TMCS	2.13	0.87	912.01	2.89	
MCM-41/TMCS/ AEAPMDMS	2.12	0.62	758.06	2.68	
MCM-41/TMCS/ AEAPMDMS/Rh	2.13	0.49	674.96	2.54	
Method 3					
MCM-41	2.20	1.08	1099.48	3.03	
MCM-41/Ph ₂ Si(OEt) ₂	2.20	0.58	933.96	2.56	
MCM-41/Ph ₂ Si(OEt) ₂ / AEAPMDMS	2.20	0.43	688.05	2.40	
MCM-41/ Ph ₂ Si(OEt) ₂ / AEAPMDMS/Rh	2.20	0.39	616.68	2.40	

J. Nanosci. Nanotechnol. 13, 3087-3095, 2013



Fig. 3. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distributions of the non-selective and selective functionalized MCM-41-based catalysts.

The nitrogen adsorption–desorption isotherms and the pore size distributions are represented in Figure 3. For all samples, of the MCM-41-based catalysts manufactured by the three methods, the isotherms were type IV hysteresis loops according to the IUPAC categorization, characteristic of mesoporous hexagonal structures. In addition, the type IV hysteresis loops remained unchanged during functionalization and Rh immobilization (not shown in this article). The amount of the absorptions was highest in method 1 (Fig. 3(a)).

The MCM-41-based materials represented pore sizes in the range of $2.4 \sim 2.6$ nm, with sharp distribution curves. After functionalization and Rh immobilization, the monodispersion curves of the pore sizes remained significantly unaffected with a slight shift to the lower pore diameters (not presented in this paper) (Fig. 3(b)). As explained previously, the peak of the maximum pore sizes of the samples for method 2 showed the biggest pore due to the absence of the silica framework shrink during the calcinations.

The small-angle powder X-ray diffraction (XRD) patterns of the prepared MCM-41-based catalysts in this work are shown in Figure 4. The as-synthesized MCM-41



Fig. 4. XRD patterns of the functionalized MCM-41-based catalysts by (a) method 1, (b) method 2 and (c) method 3.

(Fig. 4(a)) had three obvious peaks corresponding to (100), (110) and (200) diffractions of the hexagonal symmetry. In the as-calcined MCM-41, the intense peak is present at $2\theta = 2.2^{\circ}$ (100) and the two weak peaks are at $2\theta = 3.8^{\circ}$ (110) and 4.4° (200). After selective functionalization with method 2 and Rh immobilization, the three well-resolved peaks remained for the MCM-41-based materials. Despite the slight reduction of the characteristic peak intensities upon treatment, it seems that the ordered hexagonal structures were preserved bearing the surface modifications and Rh immobilization. In method 3, as well as in method 2, a similar tendency developed for the MCM-41-based catalysts (Fig. 4(c)). The XRD patterns of all samples were very similar after additional surface treatment, and the peak intensity declined slightly upon modification. The d_{100} spacings of all the materials were not significantly shifted by the decrease in pore size (Table I).

Figure 5 shows HR-TEM images of MCM-41-based catalysts prepared by method 1 (Fig. 5(a)), method 2 (Fig. 5(b)) and method 3 (Fig. 5(c)). All three catalysts indicated the ordered hexagonal structures over the perpendicular and axis faces. Unfortunately, the Rh particles were not observed in the TEM images because the rhodium complexes existed in their atomic forms in the mesostructure, like this lab's previous research.²⁸

The contents of amine, carbon and rhodium, determined by the EA and ICP-AES, are exhibited in Table II. The existence of organic groups on the surface was confirmed with EA through nitrogen and carbon estimates. The catalysts synthesized by the three modification methods possessed nitrogen and carbon, which were absent in the mesoporous silica framework. The non-modified MCM-41 included neither nitrogen nor carbon. Actually, the respective nitrogen and carbon contents of the MCM-41 were 0.00 and 0.08 wt%. A carbon content of 0.08 wt% was estimated because a portion of the surfactant template remained after the calcinations. In method 1, the nitrogen content of the MCM-41-based catalyst was 4.98 wt%. In the case of methods 2 and 3, however, the amount of the nitrogen was 3.96 and 3.62 wt%, respectively. The carbon content was from three to six times higher than nitrogen. This is reasonable because the functional groups possessed levels of carbon three to nine times than nitrogen. The Rh contents were in the range of 1.1~1.4 wt% for all modified samples.

3.2. Studies of the 1-Octene Hydroformylation

The homogeneous and three types of the MCM-41-based heterogeneous catalysts were applied toward the 1-octene hydroformylation. The catalytic properties of conversion, branched and linear aldehyde yield, L/B ratio and turn over frequency (TOF) are represented in Table III. The homogeneous catalyst has shown conversion (~98%) and TOF (2189 hr⁻¹) higher than that of the heterogeneous systems. This was not unexpected as it is well

J. Nanosci. Nanotechnol. 13, 3087–3095, 2013



Fig. 5. HR-TEM images of the MCM-41-based catalysts prepared by three methods: (a) method 1, MCM-41/AEAPMDMS/Rh, (b) method 2, MCM-41/TMCS/AEAPMDMS/Rh and (c) method 3, MCM-41/Ph₂Si(OEt)₂/AEAPMDMS/Rh.

Table II. Functional groups (nitrogen and carbon) content and rhodium Un The MCM-41/AEAPMDMS/Rh, the non-selective funccontent of the catalysts.

Catalyst	N content (wt%) ^a	C content (wt%) ^a	Rh content (wt%) ^b		
MCM-41	0.00 ± 0.00	0.08 ± 0.01	0.00		
MCM-41/AEAPMDMS/Rh	4.98 ± 0.02	15.32 ± 0.15	1.10		
MCM-41/TMCS/	3.96 ± 0.03	15.12 ± 0.02	1.12		
AEAPMDMS/Rh					
MCM-41/Ph ₂ Si(OEt) ₂ /	3.62 ± 0.00	21.62 ± 0.04	1.42		
AEAPMDMS/Rh					

Notes: ^aBy elemental analysis (EA); ^bBy ICP-AES with hydrofluoric acid (HF) treatment.

known that the homogeneous system has a conversion and TOF superior to the heterogeneous system. Meanwhile, the conversion, aldehyde yield and TOF declined gradually in the MCM-41-based heterogeneous systems.

tionalized material, showed a somewhat reduced conversion and TOF of 96% and 1950 hr^{-1} , with a total aldehyde yield similar to the homogeneous system at 26%. Additionally, in the selective functionalized system, conversion and TOF decreased in the heterogeneous systems.

The ratio of linear to branched aldehydes (L/B) was in a range of $1.6 \sim 3.6$ for all samples. The L/B of the aldehydes produced with the Rh homogeneous and MCM-41/AEAPMDMS/Rh (non-selective) systems was 1.6 and 1.7, respectively. However, significantly, when selective functionalized materials were used for 1-octene hydroformylation, the L/B rapidly increased to 2.2 and 3.6. In particular, the MCM-41/Ph₂Si(OEt)₂/AEAPMDMS/Rh system showed a L/B of 3.6. It seems that the selectively passivated materials with amine and Rh complexes

Table III. Catalytic properties of Rh₄(CO)₁₂-immobilized heterogeneous catalysts at the 30 min reaction time in the 1-octene hydroformylation.

Catalyst	Yield (%)			Total aldebude	Linear/		
	Conversion (%)	<i>b</i> -C9-aldehyde ^{<i>d</i>}	<i>l</i> -C9-aldehyde ^e	yield (%)	branched (L/B)	TOF $(hr^{-1})^f$	
Rh homogeneous ^a	98.45	10.06	16.52	26.57	1.60	2189.22	
MCM-41/AEAPMDMS/Rh ^b	96.96	9.70	16.56	26.26	1.71	1950.86	
MCM-41/TMCS/AEAPMDMS/Rh ^c	89.66	15.03	34.11	49.14	2.27	1803.58	
MCM-41/Ph ₂ Si(OEt) ₂ /AEAPMDMS/Rh ^c	93.91	5.13	18.66	23.79	3.64	688.69	

Notes: a Catalysts 0.00165 g (8.01 × 10⁻⁶ mol), 1-octene 4.68 g, THF 75 ml, TPP 0.044 g, reaction: 140 °C, 300 psi, 0.5 hr; b Catalysts 0.083 g (~ 8.06 × 10⁻⁶ mol), TPP 0.022 g, 1-octene 4.68 g, THF 75 ml, reaction: 140 °C, 300 psi, 0.5 hr; 'Catalysts 0.165 g (~ 16 × 10⁻⁶ mol), TPP 0.044 g, 1-octene 4.68 g, THF 75 ml, reaction: 140 °C, 300 psi, 0.5 hr; a^{-c}The amount of catalysts was calculated by ICP-AES (the Rh content ~1.0 wt%); ^dBranched aldehyde; ^fMol-aldehyde/mol-Rh ·hr.



Fig. 6. (a) Turn over frequency (TOF) and (b) ratio of linear and branched aldehyde (L/B) on the 1-octene hydroformylation over the rhodium homogeneous and heterogeneous catalyst systems.

in the intra-pores show a higher selectivity for linear aldehydes in the 1-octene hydroformylation. The reason for this phenomenon has not yet to be clearly elucidated, but is predicted to be due to the confinement effects of the Rh complexes in the mesopores. It is well known that due to steric effects, the bulky phosphine ligands enhance catalyst activity and productivity of the linear aldehyde over the branched aldehyde.²¹ In particular, on the mesopore (pore size $2.0 \sim 3.0$ nm), the steric bulky triphenylphosphine ligand greatly improved the selectivity of the less hindered linear aldehydes over the branched aldehyde. Concerning this unique result, extensive mechanistic studies will be made by this group. The TOF and L/B graphs as a function of the catalyst are shown in Figure 6.

Among the selective functionalized catalysts, the selective functionalized material (by method 2) with TMCS and AEAPMDMS in the extra- and intra-pores, denoted MCM-41/TMCS/AEAPMDMS/Rh, displayed the highest total aldehyde yield (49%) with a fairly high TOF (1803 hr⁻¹). The total aldehyde yield (49%) of the material functionalized with TMCS, in the extra-pores, was higher than that of the homogeneous system by two orders of magnitude.

4. CONCLUSIONS

The Rh-tethered mesoporous silica MCM-41-based catalysts have been synthesized using three methods, including post grafting and two kinds of selective functionalization techniques. The 1-octene hydroformylation was then effectively performed via these catalyst systems. In the case of the Rh-immobilized catalysts whose internal pore was selectively anchored, the ratio of the linear aldehyde to branched aldehyde increased remarkably up to L/B = 2.27and 3.64. This may be due to a confinement effect of the Rh complex located in the inner mesopore space. Especially, the sample selectively bifunctionalized with TMCS (the extra-pore) and AEAPMDMS (the intra-pore), using method 2, showed a high TOF (1803 hr⁻¹) and a total aldehyde yield (49%) with only a 0.5 h reaction time.

Acknowledgments: This work was supported by a Korea Science and Engineering Foundation (KOSEF) grant, funded by the Korea government(MOST) (No. R01-2007-000-20144-0).

References and Notes

- 1. A. Stein, B. J. Melde, and R. C. Schroden, *Adv. Mater.* 12, 1403 (2000).
- K. Ariga, A. Vinu, Y. Yamauchi, Q. Ji, and J. P. Hill, Bull. Chem. Soc. Jpn. 85, 1 (2012).
- 3. Y. Ren, Z. Ma, and P. G. Bruce, Chem. Soc. Rev. 41, 4909 (2012).
- J. L. Vivero-Escoto, Y.-D. Chiang, K. C.-W. Wu, and Y. Yamauchi, Sci. Technol. Adv. Mater. 13, 013003 (2012).
- 5. L. Mercier and T. J. Pinnavaia, Chem. Mater. 12, 188 (2000).
- M. C. Burleigh, M. A. Markowitz, M. S. Spector, and B. P. Gaber, J. Phys. Chem. B 105, 9935 (2001).
- J. A. Melero, G. D. Stucky, R. van Griekena, and G. Morales, J. Mater. Chem. 12, 1664 (2002).
- A. S. M. Chong, X. S. Zhao, A. T. Kustedjo, and S. Z. Qiao, *Micropor. Mesopor. Mater.* 72, 33 (2004).
- 9. X.-M. Wang, X.-Z. Du, C.-L. Li, and X. Cao, *Appl. Surf. Sci.* 254, 3753 (2008).
- 10. X. S. Zhao and G. Q. Lu, J. Phys. Chem. B 102, 1556 (1998).
- V. Zelenak, M. Badanicova, D. Halamova, J. Cejka, A. Zukal, N. Murafa, and G. Goerigk, *Chem. Eng. J.* 144, 336 (2008).

J. Nanosci. Nanotechnol. 13, 3087–3095, 2013

Jeon et al.

- 12. W. Xiao and D. Xiao, Talanta 72, 1288 (2007).
- N. Garcia, E. Benito, J. Guzman, P. Tiemblo, V. Morales, and R. A. Garcia, *Micropor. Mesopor. Mater.* 106, 129 (2007).
- 14. M. H. Lim and A. Stein, Chem. Mater. 11, 3285 (1999).
- B. Rac, A. Molnar, P. Forgo, M. Mohai, and I. Bertoti, J. Mol. Catal. A 244, 46 (2006).
- A. Calvo, M. Joselevich, G. J. A. A. Soler-Illia, and F. J. Williams, Micropor. Mesopor. Mater. 121, 67 (2009).
- 17. J. A. Bae, S. H. Hwang, K.-C. Song, J.-K. Jeon, Y. S. Ko, and J.-H. Yim, J. Nanosci. Nanotech. 10, 290 (2010).
- D. S. Shephard, W. Zhou, T. Maschmeyer, J. M. Matters, C. L. Roper, S. Parsons, B. F. G. Johnson, and M. J. Duer, *Angew. Chem. Int. Ed.* 37, 2719 (1998).
- 19. F. de Juan and E. R.-Hitzky, Adv. Mater. 12, 430 (2000).
- 20. C.-M. Yang, H.-A. Lin, B. Zibrowius, B. Spliethoff, F. Schuth, S.-C. Liou, M.-W. Chu, and C.-H. Chen, *Chem. Mater.* 19, 3205 (2007).

- R. H. Crabtree, The Organometallic Chemistry of the Transition Metals, Wiley, New York (1988).
- 22. J. L. G. Fierro, M. D. Merchan, S. Rojas, and P. Terreros, J. Mol. Catal. A: Chemical 166, 255 (2001).
- 23. L. Huang, J. C. Wu, and S. Kawi, J. Mol. Catal. A: Chemical 206, 371 (2003).
- 24. M. Marchetti, S. Paganelli, and E. Viel, *J. Mol. Catal. A: Chemical* 222, 143 (2004).
- 25. Y. Yang, C. Deng, and Y. Yuan, J. Catal. 232, 108 (2005).
- 26. B. E. Ali, J. Tijani, M. Fettouhi, M. E.-Faer, and A. A.-Arfaj, *Appl. Catal. A* 283, 185 (2005).
- **27.** N. Sudheesh, S. K. Sharma, R. S. Shukla, and R. V. Jasra, *J. Mol. Caral. A: Chemical* 296, 61 (2008).
- 28. J. A. Bae, K.-C. Song, J.-K. Jeon, Y. S. Ko, Y.-K. Park, and J.-H. Yim, *Micropor. Mesopor. Mater.* 123, 289 (2009).
- 29. X. S. Zhao, G. Q. M. Lu, and G. J. Millar, *Ind. Eng. Chem. Res.* 35, 2075 (1996).

Received: 31 October 2012. Accepted: 28 November 2012.

Delivered by Ingenta to: Nanyang Technological University IP: 46.161.56.57 On: Sun, 05 Jun 2016 06:48:13 Copyright: American Scientific Publishers