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Article

Rh-PPh₃-polymer@mesosilica composite catalyst for the hydroformylation of 1-octene

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ABSTRACT

Rh-PPh₃-polymer@mesosilica composites were prepared by the polymerization of mixtures of divinylbenzene (DVB) and 4-vinyl-triphenylphosphine monomer in the nanopores of mesoporous silicas followed by coordination with Rh(acac)(CO)₂ (acac = acetylacetonate). These catalysts were characterized by XRD, N₂ sorption, TEM, FT-IR, and TG, and could efficiently catalyze the hydroformylation of 1-octene with higher activity than a pure polymer catalyst because of their high surface area and large pore volume, which were beneficial for the exposure of active sites and mass transport. Through the control of pore size and pore connectivity by using different mesoporous silica (MCM-41, SBA-15, and FDU-12), the activity and selectivity can be controlled. Rh-PPh₃-polymer@FDU-12 with a cage-like mesostructure showed lower activity but slightly higher selectivity than the catalyst with a 2-D hexagonal mesostructure (Rh-PPh₃-polymer@SBA-15 or Rh-PPh₃-polymer@MCM-41). By varying the polymer content in the nanopores of the mesosilica, the activity and selectivity (92%–96%) can also be tuned. The solid composite catalyst can be recycled without loss of activity, but a decrease in selectivity was observed.

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1. Introduction

The hydroformylation of alkenes represents one of the most widely used homogeneously catalyzed reactions in industry. The aldehyde products are valuable intermediates in the synthesis of bulk chemicals like alcohols, esters, and amines [1–6]. Different catalysts have been developed based on cobalt or rhodium complexes [3,7–9]. Rhodium complexes generally show much higher activity and aldehyde selectivity than cobalt complexes under mild conditions. However, until very recently, all commercial hydroformylation of long chain alkenes used cobalt-based catalysts because of the high cost of noble metals

and the difficulty in the separation of thermally sensitive rhodium-based catalysts from the low volatility products [3]. Therefore, the immobilization of rhodium complexes on a solid support is an important issue for practical application because of the advantages of heterogeneous catalysis, such as easy purification of the product and recovering and recycling of the catalyst [10].

Several strategies have been developed for the immobilization of rhodium complexes, such as covalent tethering, electrostatic interaction, encapsulation, and so on [11–21]. The covalent tethering of homogeneous rhodium complexes on a chemically modified inorganic solid support containing donor func-

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tions often gives superior stability to those prepared by other methods. Rhodium complexes anchored on silica gel and mesoporous silica (SBA-15, MCM-41, or MCM-48) have been reported previously [10,22]. Although the immobilized catalysts are easily recyclable, they often exhibited lower activity than their corresponding homogeneous catalysts due to the altered microenvironment of the metal complexes and mass transfer limitation in the solid catalysts. Tethering metal complexes in a network of an organic polymer support provides another approach for the immobilization of homogeneous catalysts [23,24]. However, polymer supported catalysts often have the problem of swelling in an organic solvent. Polymer@silica composite materials, which combines the advantages of both an organic polymer (e.g., flexibility, ductility, and processibility) and an inorganic material (e.g., rigidity and thermal stability), have potential as an efficient solid support for the immobilization of metal complex catalyst [25,26].

Here, we report the synthesis of Rh-PPh₃-polymer@mesosilica composite catalysts by engineering the polymerization of divinylbenzene (DVB) and 4-vinyl-triphenylphosphine monomer in the nanopores of a mesoporous silica followed by coordination with Rh(acac)(CO)₂ (acac = acetylacetonate) for the hydroformylation of 1-octene. The influence of polymer content, pore structure, and pore size of the support on the catalytic performance of the composite catalysts was investigated.

2. Experimental

2.1. Chemicals and materials

All chemicals were used as received unless otherwise stated. Pluronic P123 copolymer (EO₂₀PO₇₀EO₂₀) and pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆) were purchased from Sigma Aldrich. Tetraethylorthosilicate (TEOS, AR) and hexadecyltrimethylammonium bromide (CTAB) were purchased from Shanghai Chemical Reagent Company of the Chinese Medicine Group. The metal precursor Rh(acac)(CO)₂ was purchased from Energy Chemical Company. Divinylbenzene (DVB, 80%) was purchased from Aladdin Reagent Company. Toluene was distilled from sodium benzophenone ketyl under argon. 4-Vinyl-triphenylphosphine was synthesized according to the literature method [27]. SBA-15, MCM-41, and FDU-12 were synthesized according to a reported method [28–30].

2.2. Preparation of PPh₃-polymer@mesosilica composite materials

DVB was purified on an alumina column to remove the polymerization inhibitors. The mesoporous silica materials FDU-12, SBA-15, and MCM-41 were used after vacuum degassing at 120 °C for 3 h. Typically, DVB (*M_w* = 130; 21 mg), 4-vinyl-triphenylphosphine (*M_w* = 288; 144 mg) monomer mixtures and 2,2'-azobisisobutyronitrile (AIBN, 3% relative to total vinyl group) were added to 1.0 g of activated mesoporous silica following the wet impregnation procedure using *N,N*-dimethylformamide (DMF) as solvent [31]. After impregnation with

the solution, the sample was subjected to a freeze-vacuum-thaw procedure to remove air and reach equilibration at the same time to achieve a uniform distribution. Then, the sample was heated to perform the polymerization reaction at 90 °C for 20 h. The resulting samples were thoroughly washed with dichloromethane and ethanol several times to remove unreacted monomers and oligomers, followed by drying under vacuum. The samples prepared with FDU-12, SBA-15, and MCM-41 were denoted as PPh₃-polymer@FDU-12, PPh₃-polymer@SBA-15, and PPh₃-polymer@MCM-41, respectively. For FDU-12 based composite materials, samples with different polymer contents were also prepared. The composite material synthesized with 1.0 g of FDU-12, 576 mg of 4-vinyl-triphenylphosphine, and 81 mg of DVB was denoted as L-PPh₃-polymer@FDU-12, while that synthesized with 1.0 g of FDU-12, 288 mg of 4-vinyl-triphenylphosphine, and 41 mg of DVB was denoted as M-PPh₃-polymer@FDU-12.

2.3. Characterization

XRD patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system using Cu *K_α* radiation. Nitrogen physical adsorption measurement was carried out on Micromeritics ASAP 2020 volumetric adsorption analyzer. Before the measurement, the samples were outgassed at 120 °C for 5 h. The BET surface area was evaluated from the data in the relative pressure range *p/p*₀ of 0.05 to 0.25. The total pore volume was estimated from the amount adsorbed at the *p/p*₀ value of 0.99. The pore diameter was determined from the adsorption branch by the BJH method. Thermogravimetric analysis (TGA) was performed under an air atmosphere with a heating rate of 5 °C/min using a NETZSCH STA-449F3 thermogravimetric analyzer. Transmission electron microscopy (TEM) was performed using an FEI Tecnai G2 Spirit at an acceleration voltage of 120 kV. Scanning electron microscopy (SEM) was undertaken on a JEOL JSM-6360 scanning electron microscope operating at an acceleration voltage of 20–30 kV. FT-IR spectra were collected with a Nicolet Nexus 470 IR spectrometer.

2.4. General procedure for the hydroformylation of 1-octene

The PPh₃-polymer@mesosilica composite materials and rhodium precursor Rh(acac)(CO)₂ (P/Rh = 5) were added to dichloromethane with stirring at room temperature. After 2 h, the solvent was removed under vacuum. The yellow solid material obtained was used directly for the catalytic reaction. Anhydrous toluene (3 mL), 1-octene (280.5 mg, 2.5 mmol), and dodecane were added to a test tube containing a desired amount of PPh₃-polymer@mesosilica composite catalyst (5 μmol Rh) under nitrogen. The test tube was transferred into a stainless steel autoclave and sealed. After purging with CO/H₂ (1/1) several times, the pressure was adjusted to 5 MPa and left with stirring at 80 °C in an oil bath. After reaction, the CO/H₂ pressure was released, and the solid catalyst was separated by centrifugation. The conversion and aldehyde selectivity were analyzed by gas chromatography using an HP-5 capillary column (30 m × 0.32 mm × 0.25 mm). For the catalyst re-

cycling, the solid catalyst obtained after centrifugation was used directly for the next catalytic reaction.

3. Results and discussion

3.1. Synthesis and characterization of PPh_3 -polymer@mesosilica composite materials

High quality host materials of FDU-12, SBA-15, and MCM-41 were employed for the insertion of the polymer in the nanopores. The PPh_3 functionalized composite materials were straightforwardly constructed by *in situ* radical polymerization of DVB and 4-vinyl-triphenylphosphine monomers loaded inside the nanopores of the mesoporous silica. DVB was used as both monomer and cross linker to increase the cross linking degree, which is beneficial for the stability of the polymer in the nanopores. The monomers (DVB and 4-vinyl-triphenylphosphine) and initiator were introduced into the nanopores of the mesoporous silica by a wet impregnation method, followed by equilibration under reduced pressure in order to achieve a uniform distribution. Subsequently, the monomers adsorbed in the nanopores of mesoporous silicas were polymerized by heating to form the polymer layer. Finally, the PPh_3 -polymer@mesosilica composite materials were washed with dichloromethane and ethanol to remove unreacted monomers and polymers loosely adsorbed on the outer surface of the mesoporous silica.

As shown in Fig. 1, the XRD patterns of the parent SBA-15 and MCM-41 exhibited three diffraction peaks assigned to the (100), (110), and (200) faces, which are characteristics of mesoporous materials with a 2-D hexagonal mesostructure. The XRD pattern of FDU-12 showed an intense peak corresponding to the (111) reflection along with a shoulder peak assigned to the (311) reflection, showing that FDU-12 has the cubic $\text{Fm}\bar{3}\text{m}$ symmetry. The XRD characterization suggested that mesoporous silicas (SBA-15, FDU-12, and MCM-41) with different porous structure have been successfully synthesized. After incorporation of the polymer in the nanopores, the PPh_3 -polymer@mesosilica composite materials obtained ex-

Fig. 1. Small angle powder XRD patterns of (1) FDU-12, (2) PPh_3 -polymer@FDU-12, (3) SBA-15, (4) PPh_3 -polymer@SBA-15, (5) MCM-41, and (6) PPh_3 -polymer@MCM-41.

hibited similar reflection patterns to their parent silica materials, indicating that the periodic mesopore structure was retained.

The textural properties of the mesoporous silica and the corresponding PPh_3 -polymer@mesosilica composite materials were characterized by N_2 adsorption experiment. The results are summarized in Fig. 2 and Table 1. As can be seen in Fig. 2, all of the samples exhibited a type IV N_2 adsorption isotherm, showing that all the samples possess mesoporous pore structure. The PPh_3 -polymer@mesosilica composite materials showed adsorption curves and hysteresis loops similar to their parent supports, suggesting that the porous structure was not changed after polymer inclusion, which was consistent with the XRD results. As the polymer content increased, the H2 hysteresis loop of the FDU-12 based composite materials became less defined, probably due to the occupation by the polymer in the pores. After the inclusion of polymer in the nanopores of the mesoporous silica, the BET surface area, pore volume, and pore diameter decreased slightly (Table 1). For example, the BET surface area, pore volume, and pore size of PPh_3 -polymer@SBA-15 and PPh_3 -polymer@MCM-41 decreased from 672 m^2/g , 1.24 cm^3/g , and 8.2 nm to 561 m^2/g , 0.84 cm^3/g , and 8.0 nm, and 932 m^2/g , 0.80 cm^3/g , and 2.3 nm to 783 m^2/g , 0.69 cm^3/g , and 2.0 nm, respectively. As the polymer content

Fig. 2. N_2 adsorption isotherms of (1) FDU-12, (2) PPh_3 -polymer@FDU-12, (3) M- PPh_3 -polymer@FDU-12, (4) L- PPh_3 -polymer@FDU-12, (5) SBA-15, (6) PPh_3 -polymer@SBA-15, (7) MCM-41, and (8) PPh_3 -polymer@MCM-41.

Table 1Textural parameters of synthesized mesoporous silica and PPh₃-polymer@mesosilica composite materials.

Sample	Mass loss ^a (%)	BET surface area (m ² /g)	Pore volume ^b (cm ³ /g)	Pore size ^c (nm)
FDU-12	—	719	0.73	16.1
L-PPh ₃ -polymer@FDU-12	33.9	375	0.33	8.2
M-PPh ₃ -polymer@FDU-12	23.0	401	0.39	10.4
PPh ₃ -polymer@FDU-12	14.0	543	0.54	11.6
SBA-15	—	672	1.24	8.2
PPh ₃ -polymer@SBA-15	13.4	561	0.84	8.0
MCM-41	—	932	0.80	2.3
PPh ₃ -polymer@MCM-41	13.3	783	0.69	2.1

^a Mass loss between 200 and 800 °C.^b Single point pore volume calculated at relative pressure p/p_0 of 0.99.^c BJH method from adsorption branch.

increased from 14.0% to 33.9%, the BET surface area, pore volume, and pore size of the FDU-12 based composite materials decreased from 543 m²/g, 0.54 cm³/g, and 11.6 nm to 375 m²/g, 0.33 cm³/g, and 8.2 nm, respectively. The reduction in the textural parameters was probably due to the introduction of polymer into the pores. The N₂ adsorption experiment results demonstrated that the PPh₃-polymer@silica composite materials obtained possess high surface area and large pore volume and pore size, which would be beneficial for the exposure of active site and diffusion of the substrates.

TEM measurement was also performed. As shown in Fig. 3, all the samples have a uniform, well defined mesoporous structure. Bulk polymer formation was not found on the external surface of the silica particles, demonstrating that most of the monomers were polymerized inside the silica mesopores [31]. The SEM images showed that both MCM-41 and PPh₃-

Fig. 3. TEM images of (a) FDU-12, (b) PPh₃-polymer@FDU-12, (c) SBA-15, (d) PPh₃-polymer@SBA-15, (e) MCM-41, and (f) PPh₃-polymer@MCM-41, and SEM images of (g) MCM-41 and (h) PPh₃-polymer@MCM-41.

Fig. 4. FT-IR spectra of (1) FDU-12, (2) L-PPh₃-polymer@FDU-12, (3) M-PPh₃-polymer@FDU-12, (4) PPh₃-polymer@FDU-12, (5) PPh₃-polymer@SBA-15, (6) PPh₃-polymer@MCM-41, and (7) PPh₃-polymer.

polymer@MCM-41 have a spherical morphology with a particle size of 100–200 nm. No bulk polymers were found in the SEM of PPh₃-polymer@MCM-41, which further demonstrated that most of the monomers were polymerized inside the silica mesopores.

Fig. 4 shows FT-IR spectra of silica FDU-12 and the PPh₃-polymer@mesosilica composite materials. All the materials displayed the general characteristic bands of pure silica at 3456 and 1085 cm⁻¹ for $\nu(\text{O-H})$ and $\omega(\text{Si-O})$, respectively. The weak bands at 2850–3000 cm⁻¹ in the composite materials were assigned to the C-H stretching vibration of phenyl group. The bands at 1400–1500 cm⁻¹ were attributed to the C=C vibration of the phenyl group. The bands at 650–770 cm⁻¹ were assigned to the vibration of the phenyl ring. All these observations demonstrated the successful incorporation of the polymer within the mesoporous silica.

The quantitative determination of the incorporated polymer was made by TGA (Fig. 5 and Table 1). The mass loss below 200 °C corresponded to adsorbed water. There was a little increase

Fig. 5. TGA curves of (1) L-PPh₃-polymer@FDU-12, (2) M-PPh₃-polymer@FDU-12, (3) PPh₃-polymer@FDU-12, (4) PPh₃-polymer@SBA-15, and (5) PPh₃-polymer@MCM-41.

of mass at 230–300 °C, which was attributed to the oxidation of the element P. The mass loss between 200 and 800 °C demonstrated that more than 95% of the monomers were converted to a stable polymer.

3.2. Catalytic performance of Rh-PPh₃-polymer@mesosilica composite catalysts for the hydroformylation of 1-octene

After coordination of the metal precursor Rh(acac)(CO)₂, the composite catalyst was obtained. The catalytic performance of the solid Rh-PPh₃-polymer@mesosilica composite catalyst was tested by the hydroformylation of 1-octene. The results are summarized in Table 2. The homogeneous metal precursor Rh(acac)(CO)₂ catalyzed the reaction very fast, but the aldehyde selectivity for the aldehyde products was poor (80%, entry 1). After adding some PPh₃ ligands into the reaction solution, the selectivity was increased to 99% (n/b = 73/27, entry 2). By tethering the metal precursor to the PPh₃ functionalized polymer, 54% conversion and 98% aldehyde selectivity (entry 3) were obtained within 9 h. The activity was enhanced by tethering the metal precursor to the PPh₃-polymer@mesosilica composite materials, which catalyze the reaction to the desired aldehyde products smoothly with high selectivity (92%–96%). For example, with Rh-PPh₃-polymer@FDU-12 as the catalyst, the substrate was fully converted within 9 h with 94% aldehyde selectivity (entry 6). The increased activity was related to the large surface area and pore volume of the catalyst, which are beneficial for the exposure of active sites and mass transport of substrates.

The influence of polymer content on the catalytic performance of the Rh-PPh₃-polymer@FDU-12 composite catalysts was investigated (entries 4–6). On increasing the polymer con-

tent from 14.0% to 33.9%, the activity of composite catalyst decreased significantly. Within 9 h, the conversion decreased from 98% to 69%, while the selectivity was maintained almost the same (94%–96%). The lower activity at high polymer content was due to the decreased surface area and pore volume, which would cause a decreased diffusion rate of reactants and products during the catalytic process.

The combination of high surface area with a control of the pore size and pore connectivity of the silica support has a significant influence on the activity of the Rh-PPh₃-polymer@mesosilica composite catalysts. All the solid catalysts with different silica supports can efficiently convert 1-octene with almost full conversion and excellent selectivity to the desired aldehyde products (Table 2, entries 6–8). To investigate the catalytic difference between the various supports, the reaction kinetic plots were also recorded. As shown in Fig. 6, as the reaction time increased, the conversion of 1-octene increased. All the Rh-PPh₃-polymer@mesosilica composite catalysts show better catalytic activity than the pure polymer catalyst. The TOF of the solid catalysts decreased in the order of Rh-PPh₃-polymer@MCM-41 > Rh-PPh₃-polymer@SBA-15 > Rh-PPh₃-polymer@FDU-12 > Rh-PPh₃-polymer, which was the same as the order of their BET surface area. Their aldehyde selectivity was slightly different, and the Rh-PPh₃-polymer@FDU-12 composite catalyst showed a little higher selectivity than the others (range from 92% to 94%). The above results indicated that Rh-PPh₃-polymer@mesosilica composite catalysts with high surface area and pore volume benefit the catalytic performance while the pore size and pore connectivity may influence their activity and selectivity. After the reaction, the rhodium leached amount from the solid catalyst was measured, and very little metal loss was found. The leached amount

Table 2

Catalytic performance of solid Rh-PPh₃-polymer@mesosilica composite catalysts.

Entry	Sample	Rh loading (mmol/g)	Conversion ^a (%)	Aldehyde selectivity ^a (%)	n/b ^b	Metal leaching ^c (%)	TOF ⁱ (h ⁻¹)
1	Rh(CO) ₂ (acac)	—	>99	80	57/43	—	—
2	Rh(CO) ₂ (acac)+PPh ₃	—	>99	99	73/27	—	—
3	Rh-polymer	0.54	54	98	79/21	0.56	92
4	Rh-L-PPh ₃ -polymer@FDU-12	0.20	69	95	75/25	0.08	—
5	Rh-M-PPh ₃ -polymer@FDU-12	0.14	92	96	74/26	0.08	—
6	Rh-PPh ₃ -polymer@FDU-12	0.08	98	94	71/29	0.07	105
7	Rh-PPh ₃ -polymer@SBA-15	0.08	99	92	69/31	0.24	151
8	Rh-PPh ₃ -polymer@MCM-41	0.08	99	92	71/29	0.04	191
9 ^d	Rh-PPh ₃ -polymer@FDU-12	0.08	99	78	56/44	3.10	—
10 ^e	Rh-PPh ₃ -polymer@FDU-12	0.08	74	85	74/26	0.15	—
11 ^f	Rh-PPh ₃ -polymer@FDU-12	0.08	98	95	72/28	0.05	—
12 ^g	Rh-PPh ₃ -polymer@FDU-12	0.08	22	89	74/26	0.27	—
13 ^h	Rh-PPh ₃ -polymer@FDU-12	0.08	99	90	69/31	0.36	—
14 ⁱ	Rh-PPh ₃ -polymer@FDU-12	0.08	99	84	68/32	0.11	—

Reaction conditions: 5 μmol Rh, 280 mg 1-octene, S/C 500, P/Rh = 5, 80 °C, 5 MPa H₂/CO, 3 ml toluene, 9 h, dodecane as internal standard.

^a Analysis by GC. ^b Normal/branched. ^c Detected by ICP. ^d 1,4-Dioxane as solvent. ^e Water as solvent, for 12 h. ^f Reaction at 100 °C for 6 h.

^g Reaction at 50 °C for 12 h. ^h Reaction at 6 MPa for 6 h. ⁱ Reaction at 3 MPa for 12 h. ^j Turn over frequency.

Fig. 6. Kinetic plots of the hydroformylation of 1-octene on the solid Rh-PPh₃-polymer@mesosilica composite catalysts.

of Rh-PPh₃-polymer@mesosilica composite catalysts (range from 0.04% to 0.24%) was lower than the pure polymer catalyst (0.56%), which demonstrated that silica around the polymer catalyst is beneficial for decreasing metal leaching.

The influence of the reaction conditions, such as temperature, H₂/CO pressure, and solvent, was also investigated (Table 2, entries 9–14). On increasing the reaction temperature to 100 °C, the substrate was fully converted within 6 h. In contrast, on decreasing the temperature to 50 °C, the conversion only reached 22% after 12 h. On varying the CO/H₂ pressure, the catalyst showed the similar tendency that a higher pressure resulted in higher activity. With 1,4-dioxane as the reaction medium, the reaction activity was comparable to toluene, but the product selectivity decreased (Table 2, entry 9). Notably, the composite solid catalyst also catalyzed the reaction in water medium under similar reaction conditions. After reaction for 12 h, 74% conversion and 85% selectivity were obtained (Table 2, entry 10).

The recyclability of the solid catalyst was tested by using Rh-PPh₃-polymer@FDU-12 as a model catalyst for the hydroformylation of 1-octene in toluene (Fig. 7). The solid catalyst can be reused more than 15 times without loss of activity. The solid catalyst after recycling was characterized by N₂ adsorp-

Fig. 7. Recyclability of Rh-PPh₃-polymer@FDU-12 in the hydroformylation of 1-octene. The reaction conditions are the same as in Table 2.

Fig. 8. TEM image of Rh-PPh₃-polymer@FDU-12 after recycling test.

tion and TG to investigate its stability. The BET surface area and pore volume decreased to 358 m²/g and 0.36 cm³/g, respectively. The polymer content was almost the same as with the catalyst before reaction, which demonstrated that the composite catalyst was stable. However, the aldehyde selectivity decreased to 58% after 15 recycle, which was much lower than with the fresh catalyst. The TEM image of the solid catalyst after recycling 15 times showed the existence of rhodium nanoparticles on the support (Fig. 8). This may be the main reason for the decreased selectivity.

4. Conclusions

We demonstrated the successful immobilization of rhodium complexes in PPh₃-polymer@mesosilica composite materials for the hydroformylation of 1-octene. Under optimized conditions, the solid materials exhibited high surface area, large pore size, and large pore volume, which are beneficial for the exposure of active sites and diffusion of substrate. The solid catalysts efficiently catalyzed the hydroformylation of 1-octene with good yield (99%) and aldehyde selectivity (95%). Efficient solid catalysts can be prepared by the polymerization of the ligands in the nanopores of a mesoporous silica.

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Graphical Abstract

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Rh-PPh₃-polymer@mesosilica composite catalyst for the hydroformylation of 1-octene

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Rh-PPh₃-polymer@mesosilica composite catalysts were prepared and shown to catalyze the hydroformylation of 1-octene with high activity and aldehyde selectivity.

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铑-三苯基膦配合物功能化的聚合物@介孔氧化硅复合材料在1-辛烯氢甲酰化反应中的应用

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摘要: 通过在介孔氧化硅材料中原位聚合的方法制备了三苯基膦功能化的有机聚合物@介孔氧化硅复合材料PPh₃-polymer@FDU-12。采用X射线衍射、氮气吸附脱附、透射电镜和热重等手段对其结构和组成进行了表征。该复合材料与金属前驱体Rh(acac)(CO)₂配位后得到的固体催化剂, 在长链烯烃1-辛烯的氢甲酰化反应中, 醛选择性可达92%–96%, 并表现出高于聚合物的活性(>99%转化率)。这主要归因于介孔氧化硅材料的高比表面积和有序的孔结构更有利于反应物和催化活性中心的接触。研究发现, 调变复合材料中聚合物的含量或使用不同孔道结构的氧化硅载体(SBA-15, MCM-41和FDU-12)都会影响固体催化剂的反应活性和选择性。该方法得到的多相催化剂具有较好的循环使用性能, 在循环使用15次后仍能保持较好的反应活性, 但醛选择性有所降低。

关键词: 铑-三苯基膦配合物功能化聚合物@氧化硅复合材料; 多相催化; 氢甲酰化反应

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