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Article

Rh catalysts supported on knitting aryl network polymers for the hydroformylation of higher olefins

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ABSTRACT

Rh catalysts supported on knitting aryl network polymers (Rh/KAPs) were prepared for the hydroformylation of higher olefins. Rh catalysts supported on triphenylphosphine-benzene-base polymers (Rh/KAPs-1) showed higher activity for the higher olefins than Rh/SiO₂ catalysts. Fourier transform infrared spectroscopy, thermogravimetry, N₂ adsorption-desorption, X-ray diffraction, transmission electron microscopy, ¹³C NMR, and ³¹P NMR showed that the Rh/KAPs-1 catalysts have high thermal stability, high surface area, hierarchical porosity, highly dispersed Rh nanoparticles, and in situ formed homogeneous active species during the reaction.

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1. Introduction

Hydroformylation is the addition of syngas to olefins to give aldehydes or alcohols [1–3]. It is catalyzed by transition metal complexes and is a successful example of an industrial process in homogeneous catalysis. Although homogeneous catalysts exhibit a higher activity under mild conditions, its industrial application on a large scale is hindered by the separation of the catalyst from the product [4]. The prominent advantage of a heterogeneous catalyst is its easy separation from the product in contrast to a homogeneous catalyst. However, heterogeneous catalysts suffer the problems of low activity and selectivity. As a hot topic, heterogenized homogeneous catalysts for hydroformylation [5–8] have been shown to combine the advantages of homogeneous and heterogeneous catalysts. Solid supports for the heterogenized homogeneous catalysts include inorganic materials (zeolites, activated carbon, silica, etc.) and

porous organic polymers. Porous organic polymers have attracted attention for their outstanding properties such as high surface area, low skeletal density, and chemical functionalities in the porous framework [9–11].

Porous organic polymers have unique properties. Compared to inorganic materials, it is easy to introduce chemical functionalities in the porous framework, which is favorable for the synthesis of functional materials. Compared with metal organic frameworks, they have high thermal stability, which is beneficial for heterogeneous catalysis. So far, the porous organic polymers used have been hyper-crosslinked polymers, polymers of intrinsic microporosity, conjugated microporous polymers, and covalent organic frameworks [12]. These porous materials have wide applications in separation and gas storage [13,14] but rare applications in heterogeneous catalysis [15,16].

Knitting aryl network polymers (KAPs) were synthesized by

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Tan's group [17–20] in 2011. KAPs were synthesized by a one-step Friedel-Crafts reaction using triphenylphosphine as the monomer, aromatic compounds as the co-monomer, and formaldehyde dimethyl acetal as the external cross-linker. KAPs have the advantages of a simple synthesis method, cheap reagents, and different kinds of monomers that give diverse functional polymers. Here we report KAPs supported Rh catalysts (Rh/KAPs) for the hydroformylation of higher olefins.

2. Experimental

2.1. Synthesis of KAPs

Four KAPs samples were synthesized using different co-monomers. Formaldehyde dimethyl acetal (9.12 g, 0.12 mol) and anhydrous FeCl_3 (29.25 g, 0.18 mol) were added to a solution of triphenylphosphine (15.75 g, 0.06 mol) and benzene (4.68 g, 0.06 mol) in 1,2-dichloroethane (100 ml). The mixture was stirred at room temperature and then stirred at 318 K for 5 h to form the original network, which was then heated at 353 K for 67 h. The precipitate was washed with ethanol three times, then washed with ethanol in a Soxhlet apparatus for 24 h, then dried under vacuum at 343 K for 24 h, and finally triphenylphosphine-benzene-base polymers (KAPs-1) were obtained.

Using methylbenzene (5.52 g, 0.06 mol) to replace benzene in the solution above, triphenylphosphine-methylbenzene-base polymers (KAPs-2) were obtained via the same synthesis method.

Using biphenyl (3.08 g, 0.02 mol) to replace methylbenzene in the solution above and changing the amounts of anhydrous FeCl_3 and triphenylphosphine to 19.5 and 5.25 g, respectively, triphenylphosphine-biphenyl-base polymers (KAPs-3) were obtained via the same synthesis method.

Using 1,3,5-triphenylbenzene (6.12 g, 0.02 mol) instead of biphenyl in the solution above, triphenylphosphine-1,3,5-triphenylbenzene-base polymers (KAPs-4) were obtained via the same synthesis method.

2.2. Preparation of Rh/KAPs and Rh/ SiO_2 catalysts

The KAPs and SiO_2 supports were impregnated with an ethanol solution of RhCl_3 . The samples were dried at room temperature for 24 h, then dried at 393 K for 12 h, then reduced by H_2 at 453 K for 4 h, and finally stored under N_2 . The Rh loading of each catalyst was 1 wt%.

2.3. Characterization of the catalysts

Fourier transform infrared (FT-IR) spectra were measured on a Bruker Tensor 27 FT-IR spectrometer. All spectra were recorded with a resolution of 4 cm^{-1} , 32 scans, and in the range 4000–400 cm^{-1} . Thermogravimetric analysis (TG) was performed on a thermal analyzer (Netzsch STA 449F3). The samples were heated at the rate of 10 K/min from 293 K up to 923 K under N_2 . The specific surface area was measured using a Quantachrome Instruments Autosorb-1 system. The samples

were outgassed at 373 K for 20 h before measurement. The pore size distribution curves were obtained from the adsorption branch using the non-local density functional theory (NLDFT) method with the carbon slit pore model. Powder X-ray diffraction (XRD) patterns were recorded with a PANalytical X'pert PRO powder X-ray diffractometer with $\text{Cu K}\alpha$ radiation. The apparatus was operated at 40 kV and 40 mA using the rate of $10^\circ/\text{min}$ and the range of 10° – 70° . Transmission electron microscope (TEM) images were taken on a JEOL JEM-2000EX electronic microscope. Solid-state ^{13}C MAS NMR experiments were carried out on a VARIAN Infinity plus spectrometer equipped with a 2.5 mm probe. The spectra were recorded using a delay of 3.0 s and a magic angle spinning rate of 12 kHz. Solid-state ^{31}P MAS NMR were performed on a VARIAN Infinity Plus spectrometer equipped with a 2.5 mm probe at a frequency of 161.8 MHz. The spectra were recorded using a delay of 3.0 s and a magic angle spinning rate of 10 kHz. Solid-state ^{31}P NMR chemical shifts were referenced to 85% H_3PO_4 . In situ FT-IR spectra of adsorbed CO were measured on a Bruker Tensor 27 FT-IR spectrometer. All spectra were recorded with a resolution of 4 cm^{-1} , 32 scans, and in the range 4000–400 cm^{-1} . The samples were reduced by H_2 (40 ml/min) at 393 K for 1 h, then purified in a flow of N_2 (40 ml/min) for 0.5 h, and then used for FT-IR measurement (spectrum A). Then, CO (40 ml/min) was introduced for 0.5 h under atmospheric pressure. Spectrum B was recorded after purging the chamber with N_2 for 0.5 h. Subtracting spectrum A from spectrum B gave the FT-IR spectra of adsorbed CO.

2.4. Hydroformylation reaction

The hydroformylation of higher olefins was carried out in a 30 ml autoclave. In a typical run, 11.1 mg of catalyst, the desired amount of higher olefins, and 6 g of toluene were added into the autoclave under N_2 . The reactor was purged three times with the premixed gas ($\text{CO}:\text{H}_2 = 1:1$) and heated from room temperature to the reaction temperature of 373 K. During the reaction, the pressure in the reactor was held constant (2.0 MPa) by the injection of more premixed gas ($\text{CO}:\text{H}_2 = 1:1$) with a pressure regulator. The catalyst was separated by centrifugation. The products were analyzed by an Agilent 7890A gas chromatograph with an HP-5 column using an FID detector and propanol as an internal standard.

3. Results and discussion

3.1. Characterization results

3.1.1. FT-IR

Figure 1 shows FT-IR spectra of KAPs obtained using different co-monomers (benzene, methylbenzene, biphenyl, and 1,3,5-triphenylbenzene). The series of peaks around 1600–1450 cm^{-1} were attributed to the benzene skeleton stretch. The peaks around 1250–950 and 900–650 cm^{-1} resulted from C–H in-plane bending and out-of-plane bending vibrations of the benzene ring. A peak at 1435 cm^{-1} was due to the vibration of the P– CH_2 bond [21], which showed that tri-

Fig. 1. FT-IR spectra of KAPs prepared from different co-monomers and the Rh/KAPs-1 catalyst. (1) KAPs-1 (from benzene); (2) KAPs-2 (from methylbenzene); (3) KAPs-3 (from biphenyl); (4) KAPs-4 (from 1,3,5-triphenylbenzene); (5) Rh/KAPs-1 catalyst.

phenylphosphine was the monomer in the framework of the KAPs. As shown in Fig. 1, no significant difference was observed in the FT-IR spectra of the KAPs-1 and Rh/KAPs-1 catalyst. The peak at 1435 cm^{-1} also existed, which revealed that the KAPs-1 supports were unchanged in the preparation of the catalysts.

3.1.2. TG analysis

Thermal stability is a necessary property of the porous polymers for use as supports. The TG analysis (Fig. 2) shows that the Rh/KAPs-1 catalyst has a superior thermal stability with the decomposition temperature of 600 K. The thermal stability of Rh/KAPs-1 was comparable to Nafion NR50, one of the most stable polymers. As is well known, many polymers as the support are limited by their poor thermal stability. However, KAPs as the support can be widely applied in heterogeneous catalysis because of their superior thermal stability.

3.1.3. Textural properties

The Rh/KAPs-1 catalyst possessed the highest surface area of the Rh/KAPs catalysts (Table 1). The BET surface area was

Fig. 2. TG curve of the Rh/KAPs-1 catalyst.

Table 1

Textural properties of the Rh/KAPs and Rh/SiO₂ catalysts.

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)
Rh/KAPs-1	723	0.92
Rh/KAPs-2	524	0.66
Rh/KAPs-3	672	0.70
Rh/KAPs-4	549	0.58
Rh/SiO ₂	187	0.84

as high as 723 m^2/g . For comparison, the BET surface area of the Rh/SiO₂ catalyst was 187 m^2/g . The N₂ adsorption-desorption isotherms of the Rh/KAPs-1 catalyst are shown in Fig. 3(a). A steep N₂ uptake at $p/p_0 < 0.001$ was due to the filling of micropores, while the hysteresis loop was from the contribution of mesopores. A sharp rise at $p/p_0 = 0.6$ –1.0 indicated the presence of a macroporous structure. These results demonstrated the hierarchical porosity of the Rh/KAPs-1 catalyst, which was further confirmed by the pore size distribution curves of the Rh/KAPs-1 catalyst (Fig. 3(b)). Actually, hierarchical porosity is beneficial for a heterogeneous catalysis process. A high surface area and abundant micropores are favorable for the dispersion of catalytically active sites, and the macropores accelerate mass transfer in heterogeneous catalysis.

3.1.4. XRD and TEM analysis

Figure 4 reveals the XRD patterns of the KAPs-1 and Rh/KAPs-1 catalyst. There was only a broad peak, suggesting

Fig. 3. N₂ adsorption-desorption isotherms (a) and pore size distribution (b) of the Rh/KAPs-1 catalyst.

Fig. 4. XRD patterns of the KAPs-1 (1) and Rh/KAPs-1 catalyst (2).

the amorphous structure of KAPs-1. This result may be due to the high dispersion of the Rh species or the low Rh loading of the Rh/KAPs-1 catalyst. TEM images of Rh/KAPs-1 and Rh/SiO₂ catalysts are shown in Fig. 5. The Rh species of the Rh/KAPs-1 catalyst were better dispersed than those in the Rh/SiO₂ catalyst.

3.1.5. ¹³C MAS NMR and ³¹P MAS NMR

The ¹³C MAS NMR spectra of the Rh/KAPs-1 catalyst (Fig. 6(a)) displayed a resonance peak at $\delta = 42.1$ due to the carbon in the methylene linker formed from the Friedel-Crafts reaction. The resonance peaks at $\delta = 137.5$ and 129.5 were attributed to substituted aromatic carbon and non-substituted aromatic carbon, respectively [18]. In comparison to KAPs-1 (Fig. 6(b)), the ³¹P MAS NMR resonance peak of the Rh/KAPs-1 catalyst was shifted from 26.1 to 27.3, which indicated the coordination of the Rh species with the P atom in KAPs-1 [22,23]. Thus, KAPs-1 possessed not only a high surface area and hierarchical porosity but also the ability to successfully coordinate Rh species with the phosphorous atom.

3.1.6. In situ FT-IR characterization of adsorbed CO

Figure 7 exhibits the in situ FT-IR spectra of adsorbed CO on the Rh/KAPs-1 and Rh/SiO₂ catalysts. The peaks of the Rh/KAPs-1 catalyst at 2081 and 2004 cm⁻¹ resulted from homogeneous active HRh(CO)(PPh₃)₃ species [24,25]. In the FT-IR

Fig. 6. ¹³C MAS NMR (a) and ³¹P MAS NMR (b) spectra of the KAPs-1 (1) and Rh/KAPs-1 catalyst (2).

Fig. 7. In situ FT-IR spectra of adsorbed CO on Rh/KAPs-1 (1) and Rh/SiO₂ (2) catalysts.

Fig. 5. TEM images of Rh/KAPs-1 (a,b) and Rh/SiO₂ (c) catalysts.

Table 2Hydroformylation of higher olefins over Rh/KAPs-1 and Rh/SiO₂ catalysts.

Catalyst	Substrate	Conversion (%)	Selectivity (%)			Yield (%)	l/b ratio
			Aldehydes	Paraffins	Iso-olefins		
Rh/KAPs-1		>99	57	5	38	57	0.83
Rh/SiO ₂		99	26	10	64	26	1.01
Rh/KAPs-1		99	42	24	34	42	0.51
Rh/SiO ₂		79	34	28	39	27	0.76
Rh/KAPs-1		78	51	23	26	40	0.58
Rh/SiO ₂		51	47	25	28	24	0.78
Rh/KAPs-1		62	63	18	19	39	0.73
Rh/SiO ₂		38	47	23	30	18	0.94

Reaction conditions: autoclave reactor, pressure held at 2.0 MPa by injection of premixed gas (CO:H₂ = 1:1) via a pressure regulator, $T = 373\text{ K}$, $t = 4\text{ h}$, substrate/catalyst (S/C) molar ratio = 3000.

spectra of the Rh/SiO₂ catalysts, the peak at 2056 cm⁻¹ was assigned to linearly adsorbed CO, and the peaks at 2096 and 2027 cm⁻¹ were due to the anti-symmetrical and symmetrical vibrations of geminal Rh(CO)₂ [26–28]. Based on these results, it was concluded that the Rh/KAPs-1 catalyst could form homogeneous active species for the reaction, while linear adsorbed CO and geminal Rh(CO)₂ were observed on the Rh/SiO₂ catalyst. The formation of homogeneous active species was due to the high dispersion of the Rh species coordinated to the phosphorous atom in KAPs-1.

3.2. Catalytic activity

For comparison, the Rh/KAPs-1 and Rh/SiO₂ catalysts were tested for the hydroformylation of higher olefins. As listed in Table 2, the Rh/KAPs-1 catalyst exhibited better activity and selectivity to aldehydes in hydroformylation: 1-hexene (>99% conversion, 57% selectivity to aldehydes); 1-octene (99% conversion, 42% selectivity to aldehydes); 1-decene (78% conversion, 51% selectivity to aldehydes); 1-dodecene (62% conversion, 63% selectivity to aldehydes). The difference in the sup-

port led to the different activity between the Rh/KAPs-1 and Rh/SiO₂ catalysts. As illustrated above, a high surface area and hierarchical porosity were beneficial for heterogeneous catalysis, while the in situ formation of homogeneous active species [29,30] improved the catalytic activity for hydroformylation. The recyclability of the Rh/KAPs-1 catalyst was tested for the hydroformylation of 1-hexene (Fig. 8). The Rh/KAPs-1 catalyst can be reused with negligible loss of activity, and the Rh species in the filtrate was 0.3% in the first recycle.

4. Conclusions

The Rh/KAPs-1 catalyst displayed high activity for the hydroformylation of higher olefins. Compared to the Rh/SiO₂ catalyst, Rh/KAPs-1 possessed highly dispersed Rh nanoparticles on the surface of KAPs-1 and formed homogeneous active species during the reaction. KAPs have a simple synthesis method and cheap reagents, and different kinds of monomers can be used to obtain different functional polymers. Further studies are needed on how to use KAPs efficiently.

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Fig. 8. Recycle of the Rh/KAPs-1 catalyst for the hydroformylation of 1-hexene.

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摘要: 考察了编织芳基网络聚合物(KAPs)负载的Rh催化剂(Rh/KAPs)在高碳烯烃氢甲酰化反应中的催化性能。结果表明,三苯基膦-苯基底KAPs负载Rh催化剂(Rh/KAPs-1)具有优异的高碳烯烃氢甲酰化反应活性,产物醛收率显著高于Rh/SiO₂催化剂。傅里叶变换红外光谱、热重、氮气吸附-脱附、X射线衍射、透射电子显微镜、¹³C核磁共振和³¹P核磁共振结果显示,Rh/KAPs-1催化剂具有优异的热稳定性及大的比表面积和多级孔道结构,Rh颗粒处于高度分散状态,并可在反应过程中形成均相催化活性物种。

关键词: 三苯基膦; 编织芳基网络聚合物; 铈; 多相催化剂; 高碳烯烃氢甲酰化

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1. 前言

氢甲酰化反应是由过渡金属羰基化合物催化的烯烃与合成气生成比原料烯烃高一个碳的醛或醇的反应^[1–3],它是迄今为止均相催化工业应用的最成功典范之一。均相催化体系虽然具有较高的催化活性和温和的反应条件,但催化剂同反应物料分离困难,阻碍了其大规模工业化应用^[4]。比较而言,多相催化剂与反应物料容易分离,但催化活性和选择性较低。均相催化剂固载化一直是氢甲酰化的研究热点^[5–8],固载化催化剂既具有均相催化剂优良的反应活性又具有多相催化剂易于分离的优点。研究的固载化载体主要包括无机载体(分子筛、活性炭和SiO₂等)和有机聚合物载体,其中有机聚合物载体因具有高比表面积、低骨架密度以及易于引入有机官能团等优点而备受关注^[9–11]。

相比于无机多孔材料,有机聚合物易于在碳链中引入各种官能团,从而有利于合成有目的性的功能化材料;且有机聚合物比金属有机骨架材料(MOFs)的热稳定性高,为在多相催化领域的应用提供了保障。目前,有机聚合物主要包括超交联聚合物(HCPs)、固有微孔聚合物(PIMs)、共轭微孔聚合物(CMPs)和共价有机骨架材料(COFs)^[12]。近年来,这些有机聚合物材料广泛应用于物质分离和气体吸附等领域^[13,14],而在多相催化领域的应用仍处于起步阶段^[15,16]。

编织芳基网络聚合物(KAPs)是华中科技大学谭必恩课题组^[17–20]于2011年合成的新型微孔有机聚合物。KAPs是以三苯基膦作为单体,引入芳香族化合物(如苯、甲苯、联苯和1,3,5-三苯基苯等)作为共单体,外加交联剂二甲氧基甲烷,利用FeCl₃催化的傅-克反应一步形成的微孔聚合物。该材料合成方法简单,原料价格低廉,最重要的是通过调变单体和共单体的种类,可以获得各种功能化的聚合物材料。本文将KAPs用于负载金属Rh形成多相催化剂(Rh/KAPs),系统考察了该催化剂在氢甲酰化反应中的催化性能。

2. 实验部分

2.1. 载体KAPs的合成

合成4种共单体不同的KAPs样品。将三苯基膦(15.75 g, 0.06 mol)和苯(4.68 g, 0.06 mol)加入到1,2-二氯乙烷(100 ml)溶液中,再分别加入二甲氧基甲烷(9.12 g, 0.12 mol)和无水FeCl₃(29.25 g, 0.18 mol)。室温下搅拌至完全溶解,升温至318 K搅拌5 h形成基本的交联网络,

再升温至353 K反应67 h。得到的沉淀用乙醇洗涤3次并索氏提取24 h,最后在343 K真空干燥24 h,即得三苯基膦-苯编织芳基网络聚合物KAPs-1。将上述溶液中的苯换成甲苯(5.52 g, 0.06 mol),同法制得三苯基膦-甲苯编织芳基网络聚合物KAPs-2。将上述溶液中三苯基膦用量改为5.25 g (0.02 mol),无水FeCl₃用量改为19.5 g (0.12 mol),甲苯改为联苯(3.08 g, 0.02 mol),同法制得三苯基膦-联苯编织芳基网络聚合物KAPs-3。将上述溶液中联苯改为1,3,5-三苯基苯(6.12 g, 0.02 mol),同法制得三苯基膦-1,3,5-三苯基苯编织芳基网络聚合物KAPs-4。

2.2. 催化剂制备

用定量的RhCl₃乙醇溶液分别浸渍KAPs和SiO₂载体,室温下阴干24 h,393 K干燥12 h,再在453 K用H₂还原4 h,最后在N₂下保存备用,所得催化剂Rh/KAPs和Rh/SiO₂的Rh负载量均为1 wt%。

2.3. 催化剂表征

样品的傅里叶变换红外光谱(FT-IR)测定在Bruker公司的Tensor 27型红外光谱仪上进行,分辨率为4.0 cm⁻¹,32次扫描累加,扫描范围4000–400 cm⁻¹。样品的热重(TG)实验在Netzsch STA 449F3型热重分析仪上进行,催化剂装填量为9.0 mg,在N₂氛围下从293 K升温至923 K,升温速率10 K/min。样品的比表面积和孔径分布测定在Quantachrome Instruments公司的Autosorb-1型吸附分析仪上进行,样品预先在373 K处理20 h,孔径分布分析采用NLDFT方法,选用carbon (slit pore)模型。样品的X射线衍射(XRD)测定在PANalytical公司的X'pert PRO型X射线衍射仪上进行,Cu K α 辐射源,管压40 kV,管流40 mA,扫描速度10°/min,扫描范围2 θ = 10°–70°。样品的透射电镜(TEM)测定在日本JEOL公司JEM-2000EX型透射电子显微镜上进行。样品的¹³C固体核磁实验(¹³C MAS NMR)在VARIAN公司Infinityplus型核磁共振波谱仪上进行,2.5 mm ZrO₂转子,弛豫延迟时间3.0 s,转动频率12 kHz。样品的³¹P固体核磁实验(³¹P MAS NMR)仪器同上,2.5 mm ZrO₂转子,振动频率161.8 MHz,弛豫延迟时间3.0 s,转动频率10 kHz,以85% H₃PO₄为化学位移的参考外标。样品的CO吸附原位FT-IR测定在Bruker公司的Tensor 27型红外光谱仪上进行,分辨率4.0 cm⁻¹,32次扫描累加,扫描范围4000–400 cm⁻¹。首先,样品在393 K用H₂ (40 ml/min)还原1 h,随后切换成N₂ (40 ml/min)吹扫0.5 h,扫描谱图记为谱图A。然后,将N₂切换成CO (40 ml/min)吹扫0.5 h,随后再切换成N₂吹扫0.5 h,扫描谱图记为谱图B。谱图B与谱图A的差谱即为样品吸附CO的

原位FT-IR谱.

2.4. 催化剂评价

高碳烯烃氢甲酰化评价反应在30 ml哈氏合金高压釜中进行. 将11.1 mg催化剂、一定量的高碳烯烃和6 g 甲苯溶剂在惰性气氛下加入到高压釜中. 用合成气($\text{CO}:\text{H}_2 = 1:1$)置换釜内气体3次, 充入合成气, 升温至373 K进行反应. 反应进程中, 打开进气阀, 关闭出气阀, 通过调压阀不断补充气体, 使釜内压力始终保持在2.0 MPa. 反应物在磁力搅拌下反应4 h, 采用离心方法分离产物与催化剂. 分离后的产物以正丙醇为内标物, 在Agilent 7890A型气相色谱仪上, 使用配有HP-5毛细柱的氢火焰检测器(FID)分析.

3. 结果与讨论

3.1. 催化剂的表征结果

3.1.1. FT-IR结果

图1示出了分别以苯、甲苯、联苯和1,3,5-三苯基苯作为共单体合成的KAPs样品以及KAPs-1负载Rh的多相催化剂Rh/KAPs-1的FT-IR谱. 其中, 在1600–1450 cm^{-1} 附近的峰与苯环的骨架伸缩振动有关; 在1250–950和900–650 cm^{-1} 附近的峰由苯环C–H面内弯曲振动和苯环C–H面外弯曲振动所形成. 同时, 在1435 cm^{-1} 的振动峰归属为P–CH₂键的伸缩振动^[21], 表明三苯基膦作为单体存在于微孔聚合物骨架中. 从图1还可以看出, KAPs-1和Rh/KAPs-1的谱图基本一致, P–CH₂键的伸缩振动峰(1435 cm^{-1})显著地得以保留, 说明在催化剂制备过程中没有破坏KAPs-1的基本结构.

3.1.2. TG结果

良好的热稳定性是聚合物材料用作多相催化剂载体的重要条件. 图2为Rh/KAPs-1催化剂的TG曲线. 可以看出, 在600 K, Rh/KAPs-1催化剂未出现明显的热分解现象, 表明其具有高的热稳定性, 同目前聚合物材料中热稳定性优异的Nafion NR50 (600 K)相当. 因此, KAPs-1可用于多相催化反应中.

3.1.3. 比表面积和孔结构

如表1所示, 苯作为共单体形成的KAPs-1负载的Rh催化剂具有最大的比表面积 723 m^2/g , 而Rh/SiO₂催化剂为187 m^2/g . 图3为Rh/KAPs-1催化剂的吸附-脱附等温线和孔径分布图. 可以看出, 在相对低压区域($p/p_0 < 0.001$), N₂吸附量显著增加, 表明存在大量微孔; 有滞后环暗示有介孔存在; 同时在中高压区域($p/p_0 = 0.6\text{--}1.0$) N₂吸附量明显上升, 表明有大孔存在, 正如图3(b)所示.

实际上, 这种多级孔道结构和大比表面积十分有利于多相催化反应的进行: 大比表面积和丰富的微孔结构可以使活性组分高度分散于载体材料上, 同时介孔和大孔的存在有利于传质的进行.

3.1.4. XRD和TEM结果

图4为KAPs-1和Rh/KAPs-1的XRD谱. 除了KAPs-1的空白峰之外, 未检测到新的衍射峰. 这可能是由于Rh/KAPs-1样品中Rh颗粒高度分散或Rh负载量太低, 低于XRD检测限. 图5是Rh/KAPs-1和Rh/SiO₂的TEM照片. 由图可见, 相对于Rh/SiO₂样品, Rh/KAPs-1样品中Rh颗粒更加分散.

3.1.5. ¹³C MAS NMR和³¹P MAS NMR结果

由Rh/KAPs-1催化剂的¹³C MAS NMR谱(图6(a))可见, 在 $\delta = 42.1$ 附近的峰归属为傅-克反应形成的亚甲基的碳, 在 $\delta = 137.5$ 和129.5附近的峰分别归属为苯环取代碳和未取代碳^[18]. 比较KAPs-1和Rh/KAPs-1的³¹P MAS NMR谱(图6(b)), 振动峰从26.1移到27.3, 这可能是因为KAPs-1中三苯基膦上的P原子同负载的金属Rh发生了相互作用^[22,23]. 此种聚合物不但具有高的比表面积和多级孔道结构, 而且聚合物骨架中包含有机配体三苯基膦, 它可以同高分散于载体表面的金属Rh发生相互作用.

3.1.6. CO吸附原位FT-IR结果

图7为Rh/KAPs-1和Rh/SiO₂的CO吸附原位FT-IR谱. Rh/KAPs-1催化剂上的2081和2004 cm^{-1} 吸附峰归属为均相氢甲酰化活性物种HRh(CO)(PPh₃)₃^[24,25]; Rh/SiO₂催化剂上的2056 cm^{-1} 吸收峰对应于线式吸附CO, 而2096和2027 cm^{-1} 附近的双吸收峰归属为孪式吸附CO的反对称和对称振动^[26–28]. 结果表明, 在接近反应条件的环境中, Rh/KAPs-1催化剂上可捕捉到均相催化的活性物种, 而Rh/SiO₂催化剂上只能观测到CO在金属Rh上的线式吸附和孪式吸附. Rh/KAPs-1上的均相催化活性物种是由负载的金属Rh同存在于微孔聚合物骨架中三苯基膦上的P原子在反应过程中原位生成的.

3.2. 氢甲酰化反应活性

为了比较Rh/KAPs-1和Rh/SiO₂的催化性能, 将它们用于高碳烯烃的氢甲酰化反应中. 由表2可见, Rh/KAPs-1催化剂在1-己烯(转化率 > 99%, 庚醛选择性57%)、1-辛烯(转化率99%, 壬醛选择性42%)、1-癸烯(转化率78%, 十一醛选择性51%)和1-十二烯(转化率62%, 十三醛选择性63%)氢甲酰化反应中具有优异的烯烃转化率和产物醛选择性, 明显优于Rh/SiO₂催化剂. 其原因主要在于两种催化剂载体的不同. 如前所述, KAPs-1具

有高比表面积和多级孔道结构,因而适合用作载体应用于多相催化反应;另外,存在于微孔骨架中的三苯基膦配体同高分散的金属Rh原位生成均相催化反应的活性物种^[29,30],从而提高了氢甲酰化反应活性.循环实验表明,在1-己烯氢甲酰化中,Rh/KAPs-1催化剂循环使用3次(图8),其催化活性未见明显变化,第一次循环实验后母液中金属Rh流失量为0.3%.

4. 结论

Rh/KAPs-1催化剂在高碳烯烃氢甲酰化反应中具有优异的催化活性,明显优于Rh/SiO₂催化剂.这是由于金

属活性组分高度分散于具有大比表面积KAPs-1上;同时,KAPs-1可以同金属Rh在反应过程中形成与均相催化剂相同的活性物种. KAPs-1作为一种新兴的微孔聚合物,其合成方法简单,原料价格低廉,易于引入对反应有利的化学官能团,因此近一年多来引起了人们高度关注.如何将其有效地应用于多相催化反应还有待进一步深入研究.

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