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Article

Quaternary phosphonium polymer-supported dual-ionically bound $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ catalyst for heterogeneous ethanol carbonylation

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ARTICLE INFO

Article history:

Received 11 June 2020

Accepted 8 July 2020

Available online 5 September 2020

Keywords:

Heterogeneous ethanol carbonylation

Single-site catalyst

Carbonylation active center

 $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$

Ultrastable dual-ionically bound

immobilization

Porous ionic polymer

ABSTRACT

A single-Rh-site catalyst (Rh-TPISP) that was ionically-embedded on a P(V) quaternary phosphonium porous polymer was evaluated for heterogeneous ethanol carbonylation. The $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ unit was proposed to be the active center of Rh-TPISP for the carbonylation reaction based on detailed Rh L_3 -edge X-ray absorption near edge structure (XANES), X-ray photoelectron spectroscopy (XPS), and Rh extended X-ray absorption fine structure (EXAFS) analyses. As the highlight of this study, Rh-TPISP displayed distinctly higher activity for heterogeneous ethanol carbonylation than the reported catalytic systems in which $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ is the traditional active center. A TOF of 350 h^{-1} was obtained for the reaction over $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$, with >95% propionyl selectivity at 3.5 MPa and 468 K. No deactivation was detected during a near 1000 h running test. The more electron-rich Rh center was thought to be crucial for explaining the superior activity and selectivity of Rh-TPISP, and the formation of two ionic bonds between $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ and the cationic P(V) framework ($[\text{P}]^+$) of the polymer was suggested to play a key role in firmly immobilizing the active species to prevent Rh leaching.

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1. Introduction

Noble metal species (especially Rh or Ir complexes) dissolved in liquid reaction media are widely used as catalysts for homogeneous carbonylation [1]/hydroformylation [2] and are generally active and selective, but are difficult to separate from the reaction mixture. Heterogenizing the traditional homoge-

neous processes while retaining satisfactory activity, selectivity, and stability, to easily recover the noble metal catalysts, has remained a remarkable challenge for decades [3].

Supported heterogeneous catalysts prepared by traditional methods such as precipitation or impregnation are usually less efficient and non-selective because the supported metal is generally loaded on the support as nanoparticles or clusters [4–8]

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This work was supported by the National Key R&D Program of China (2017YFB0602203), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA21020300) and the National Natural Science Foundation of China (XDB17020400).

DOI: 10.1016/S1872-2067(20)63676-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 42, No. 4, April 2021

that are in various dispersive states with different microcosmic structures. Single-site catalysts [9–16] are promising as heterogeneous catalysts for achieving catalytic efficiency and selectivity comparable to that of homogeneous systems. For example, Wang et al. reported achieving good performance for heterogeneous methanol carbonylation using an Ir-La/C catalyst. The addition of La promotes the dispersion of Ir over the support, and the Ir-La molecular active sites formed during the reaction are structurally similar to those of the homogeneous Ir-Ru catalyst used in the carbonylation reaction [17,18]. Moreover, studies reveal that the metal centers can be anchored in the singly dispersed state by coordinative bonding with the ligand sites in the structure of modified porous organic polymers [1,19] to form metal-ligand bonds. In our previous work, porous organic polymers (or ligands) [20,21] containing ligand groups were synthesized and used to coordinate metal atoms. The so-made heterogeneous catalysts showed excellent performance, comparable to that of the corresponding homogeneous catalysts [22–24].

For heterogenization of typical Rh homogeneous methanol carbonylation catalysts, the metal-ligand bond that immobilizes the catalyst is susceptible and prone to cleavage due to the existence of co-catalyst iodide species, leading to metal leaching and deactivation [25,26]. However, ion-pair interaction [27–29] may be more feasible and robust for minimizing leaching as the active $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ center and the intermediates are all negatively charged during the homogeneous methanol carbonylation process [25]. Moreover, in comparison with metal-ligand bond immobilization, ion-pair interaction may offer the additional advantage of non-occupation of the coordination sites of the metal center, which may lead to less sacrifice of its activity. Haynes et al. [27,28] reported that the Rh single anion complex $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ can be ionically-embedded by formation of a single ionic bond between the anion complex and the positively charged framework of methylated polyvinylpyridines (denoted as $[\text{Rh}(\text{CO})_2\text{I}_2]^- \cdots [\text{N}^+]$), and the performance of the so-obtained catalyst was comparable to that of the homogeneous congener.

The studies mentioned above reported effective methods of immobilizing metal centers on supports. The structures of the active centers are generally similar to the traditional structure of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, and the catalytic performance is also comparable to that of homogeneous catalysts for carbonylation. Thus, the aim to obtain activity superior to that of homogeneous catalysts with higher stability is the driving force for the present development of a negatively multi-charged active center that is structurally different from the homogeneous catalysts, which

would permit the formation of more than one ionic bond with the positively charged framework of porous organic polymers.

The previously tentatively proposed Rh dianion $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ [30], immobilized by two cationic P sites, displayed much higher heterogeneous methanol carbonylation activity (TOF = 3500 h⁻¹, 3.5 MPa, 468 K) than that of the reported “Acetica™” system containing the $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ species (TOF = 1700 h⁻¹, 4.0 MPa, 463 K), which might indicate that the quaternary phosphonium polymer favors the generation of $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ [27,28]. Thus, herein, by using the quaternary phosphonium polymer as a support, a newly-synthesized analogous quaternary phosphonium polymer supported catalyst, Rh-TPISP, is studied in-depth. The structure of the Rh active center and the dual-ionically immobilized interaction are rigorously characterized. The catalyst is employed for heterogeneous ethanol carbonylation to ethyl propionate (EP) and propionic acid (PA). Compared with benzoic acid and sorbic acid, PA [31,32] is used as a healthier preservative that does not physically harm the human body. EP from the esterification of PA is widely employed as a fragrance agent for commodity and foodstuff. The huge market demand for non-toxic and eco-friendly PA derivatives has motivated studies of the PA production process, as shown in Table 1. The hydroformylation of ethylene [23,33] followed by the oxidation of propionaldehyde [34] is the main process for generating PA. The process is active and selective to propionate, but is a two-step procedure and the oxidation of propionaldehyde is performed in a batch unit, which is usually inefficient with complicated separation. Reppe carbonylation of ethylene [35–37], as another commercialized method for producing PA, is a one-step procedure but is performed in a non-selective batch unit at high pressure. Homogeneous ethanol carbonylation is a single-step selective process for generating PA [38–41], but the homogeneous catalysis of ethanol carbonylation is much less effective than that of methanol carbonylation [42–48], and the development of heterogeneous ethanol carbonylation processes remains challenging because of the low stability of the catalysts. Nefedov et al. [49] and Notesteina et al. [50,51] reported valuable studies on heterogeneous ethanol carbonylation. The Rh species were supported on a zeolite, with a highest TOF of approximately 70 h⁻¹ at 1 atm and 473 K, and the Rh species were supported on Cs heteropolyacid with a maximal propionate selectivity of 96% under 1 atm at 473 K with the addition of water. Herein, we demonstrate that the dual-ionically bound Rh-TPISP catalyst is highly active and selective for heterogeneous ethanol carbonylation and maintains excellent stability during a 1000 h running test, attributed to the $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ center and the for-

Table 1

The comparison of three methods for the propanoic acid production.

Method	Catalyst	Property	T/K	P/MPa	Conversion/ %	Selectivity/ %
Oxidation of propionaldehyde (from hydroformylation of ethylene) [34]	Co/Mn	Two-step; Complicated separation; Autoclave	353–373	0.6–2.0	97	95
Reppe carbonylation [37]	Ni (and Ru)	One-step; High pressure; Low propionate selectivity; Autoclave	473	10	80	70
Homogeneous/Heterogeneous ethanol carbonylation [38,50,51]	Rh	One-Step; Autoclave/Fixed-bed	443–473	0.1–4.5	5–100	5–96.6

mation of two ionic bonds.

2. Experimental

2.1. Catalyst preparation

All the reagents were of analytical grade and were used as purchased without further purification unless otherwise stated. Triphenylphosphine, ethyl triphenylphosphonium iodide, azo-diisobutyronitrile (AIBN), and super-dry *N,N*-dimethylformamide (DMF) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Ethanol, acetone, and ethyl ether were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. CH_2Cl_2 and ethyl ether were dried with molecular sieves and distilled before use. Ethyl iodide was bought from Shangdong Xiya Chemical Industry Co., Ltd. $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ was purchased from J&K Chemical Ltd. All operations were carried out under Ar. The tris(4-vinphenyl)phosphine ligand (denoted as $\text{P}(\text{4vPh})_3$) was synthesized according to the literature [22].

2.1.1. Synthesis of quaternary phosphonium salt monomer of ethyl tris(4-vinphenyl)phosphonium iodide ($\text{P}(\text{4vPh})_3\text{EtI}$ monomer).

The quaternary phosphonium salt monomer of ethyl tris(4-vinphenyl)phosphonium iodide ($\text{P}(\text{4vPh})_3\text{EtI}$) was synthesized by quaternization of $\text{P}(\text{4vPh})_3$ with ethyl iodide via a hydrothermal reaction. A typical run was performed as follows: under Ar atmosphere, 3 g $\text{P}(\text{4vPh})_3$ (8.82 mmol), 2.0 g ethyl iodide (12.82 mmol), and 20 mL acetone were combined in a solvothermal reactor and stirred at 298 K for 3 h until absolute dissolution. The solution was stirred and heated at 333 K under Ar atmosphere for 48 h. After cooling to room temperature, the obtained solid was washed thrice with 20 mL diethyl ether,

then filtered and dried under vacuum. The final product was a slight yellow solid (yield $\geq 95\%$). The synthesis process is shown in Scheme 1. ^1H NMR (see Fig. S1(A)) (400 MHz, CDCl_3): δ 1.32–1.41 (3H), 3.70–3.75 (2H), 5.51 (3H), 5.94 (3H), 6.73–6.77 (3H), 7.67–7.80 (12H); ^{13}C NMR (see Fig. S1(B)) (100 MHz, CDCl_3): δ 6.81, 6.87, 17.54, 18.00, 116.06, 116.94, 119.39, 127.93, 128.06, 133.94, 134.05, 134.88, 134.89, 144.10, 144.13; ^{31}P NMR (see Fig. S1(C)) (161.8 MHz, CDCl_3): δ 25.07.

2.1.2. Synthesis of ethyl tris(4-vinphenyl)phosphonium iodide self-polymer (denoted as TPISP).

In the typical method [52], 2 g $\text{P}(\text{4vPh})_3\text{EtI}$, 0.05 g AIBN, and 20 mL DMF were combined in a solvothermal reactor and stirred at 298 K for 3 h until absolute dissolution. The solution was then stirred and heated at 373 K under Ar atmosphere for 24 h. After cooling to room temperature, the white solid was filtered and washed with 60 mL DMF, and then dried under vacuum at 373 K for 6 h. The obtained polymer is denoted as TPISP.

2.1.3. Synthesis of Rh-TPISP catalyst.

In the typical synthesis, the following procedure was performed under Ar atmosphere. $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ (5.5 mg) was dissolved in 30 mL CH_2Cl_2 , followed by the addition of 1.0 g TPISP. After stirring for 24 h under Ar atmosphere at 298 K, the sample was filtered, washed with 60 mL CH_2Cl_2 , and dried at 333 K under vacuum to remove CH_2Cl_2 . The obtained product is designated as Rh-TPISP.

2.1.4. Synthesis of standard sample $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$.

The starting material $\text{Rh}_2(\text{CO})_4\text{I}_2$ was prepared according to the method of Maitlis and coworkers [53]. A 5 mL methanol solution of $\text{Rh}_2(\text{CO})_4\text{I}_2$ (0.24 g, containing 0.84 mmol Rh) and a

Scheme 1. Model of the process to prepare Rh-TPISP as catalyst for heterogeneous ethanol carbonylation.

5 mL methanol solution of ethyl triphenylphosphonium iodide $[\text{PPh}_3\text{Et}]^+\text{I}^-$ (0.406 g, 0.97 mmol) were mixed and stirred at 293 K under CO atmosphere (0.1 MPa). The mixture was filtered, and the filtrate was evacuated and cooled to 273 K for crystallization. The so-obtained orange crystals were filtered and collected. The remaining filtrate was cooled to 243 K for recrystallization. All crystals were dried under vacuum to furnish $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}]^-$. Yield 0.364 g, 62%.

2.2. Characterization

The $\text{P}(\text{4vPh})_3\text{EtI}$ monomer, TPISP, and Rh-TPISP (Rh content = 0.27 wt% or 0.026 mmol/g_{cat}) were characterized by liquid ^1H , ^{13}C , and ^{31}P NMR; solid ^{13}C CP/MAS, ^{31}P MAS NMR, P K-edge X-ray absorption near edge structure (XANES); X-ray photo-electron spectroscopy (XPS); thermogravimetric (TG); nitrogen physical absorption; scanning electron microscope (SEM); energy dispersive X-ray spectroscopy (EDS-mapping); transmission electron microscopy (TEM); Fourier-transform infrared (FT-IR); inductively coupled plasma (ICP); high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM); Rh L_3 -edge X-ray absorption near edge structure (XANES); and Rh K-edge X-ray absorption fine structure (EXAFS) analyses. The liquid ^1H , ^{13}C , and ^{31}P NMR data were collected on a Bruker NMR spectrometer at 400, 100, and 161.8 MHz, respectively. The solid ^{13}C CP/MAS NMR data were collected on a VARIAN Infinity plus spectrometer at 6 kHz. Using 85% H_3PO_4 as a reference, the solid ^{31}P MAS NMR data were acquired on a VARIAN Infinity plus spectrometer equipped with a 2.5 mm probe at the frequency of 161.8 MHz. P K-edge and Rh L_3 -edge XANES spectra were collected in the total electron yield (TEY) mode or fluorescence mode at pressures below 5×10^{-8} Pa at the 4B7A beamline of the Beijing Synchrotron Radiation Facility (BSRF), China. XPS spectra were acquired on a Thermo Fisher ESCALAB 250Xi instrument and were calibrated against the C 1s peak (284.6 eV) as an internal reference. Thermogravimetric analysis was performed on a STA 449F3 TG-DSC instrument under nitrogen flow (20 mL min⁻¹) at a rate of 10 K min⁻¹ in the range of 303 to 1173 K. Nitrogen sorption isotherms at the temperature of liquid N_2 (77 K) were collected on a Quantachrome Autosorb iQ2 instrument. The measurement was initiated after outgassing the instrument for 10 h at 393 K. SEM and EDS mapping were performed with a JSM-7800F scanning electron microscope. TEM analysis was conducted on a JEM-2100 transmission electron microscope. The FT-IR spectra were collected on a NICOLET iS50 Fourier-transform infrared spectrometer in the range of 4000–400 cm⁻¹ with 32 scans and a resolution of 4 cm⁻¹. Inductively coupled plasma optical emission spectrometry (ICP-OES) measurement was carried out on a PerkinElmer Optima 7300DV apparatus. Complete digestion of the powder samples on an Anton Paar Multiwave 300 system was necessary before the ICP test. As a common run, 0.05 g of sample was completely digested by microwave digestion for 30 min at 800 W in the presence of 5 mL of aquaregia and 2 mL of H_2O_2 , followed by addition of water to 50 or 150 mL. Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed

with a PerkinElmer apparatus (NexION 300D). Before the ICP-MS test, 5 g of the collected liquid sample was concentrated by heating and then diluted with 50 mL of deionized water. HAADF-STEM measurements were performed on a JEM-ARM200F instrument. The Rh K-edge X-ray absorption fine structure (EXAFS) spectra of the catalyst and standard sample were collected by using a monochromator with a Si (311) crystal, at the BL14W1 beamline of SSRF, SINAP (Shanghai, China). The storage ring was operated with an injection current of 200 mA at 3.5 GeV. Ru foil was employed as the reference sample.

2.3. Heterogeneous ethanol carbonylation on Rh-TPISP

Heterogeneous ethanol carbonylation on Rh-TPISP was conducted in a continuous flow fixed-bed zirconium reactor with an inner diameter of 6 mm. The catalyst dosage was 0.1000 g (containing 0.0026 mmol Rh). The reactor was heated from 303 to 468 K at a rate of 5 K min⁻¹ under a pressure of 3.5 MPa with a CO flow of 1.34 mmol min⁻¹. A premixed liquid solution of ethanol and ethyl iodide ($n_{\text{EtOH}}/n_{\text{EtI}} = 3.39:1$) was introduced into the zirconium vaporizer upstream from the reactor by a pump at a rate of 0.05 mL min⁻¹. The overall molar ratio of EtOH/EtI/CO was 1/0.29/2.2. The liquid product was collected in a condenser at 276 K. The tail gas was analyzed on-line with a Porapak-QS column and thermal conductivity detector (TCD) using an Agilent 7890A gas chromatograph. The liquid product with methanol as an internal standard was analyzed off-line by using an Agilent 7890A gas chromatograph equipped with a FID and a FFAP column.

$$\begin{aligned}\text{Conversion} &= (n_{\text{PA}} + 2n_{\text{EP}} + n_{\text{C}_2\text{H}_4})/n_{\text{EtOH}} \\ \text{Selectivity}_{\text{C}_2\text{H}_4} &= n_{\text{C}_2\text{H}_4}/(n_{\text{PA}} + 2n_{\text{EP}} + n_{\text{C}_2\text{H}_4}) \\ \text{Selectivity}_{\text{PA}} &= n_{\text{PA}}/(n_{\text{PA}} + 2n_{\text{EP}} + n_{\text{C}_2\text{H}_4}) \\ \text{Selectivity}_{\text{EP}} &= n_{\text{EP}}/(n_{\text{PA}} + 2n_{\text{EP}} + n_{\text{C}_2\text{H}_4}) \\ \text{TOF}_{\text{propionyl}} &= (n_{\text{PA}} + n_{\text{EP}})/(n_{\text{Rh}} \times t)\end{aligned}$$

The abbreviations are defined as follows— $n_{\text{C}_2\text{H}_4}$: moles of produced ethylene (C_2H_4); n_{PA} : moles of produced propionic acid ($\text{CH}_3\text{CH}_2\text{COOH}$); n_{EP} : moles of produced ethyl propionate ($\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$); n_{EtOH} : total moles of ethanol (EtOH) in feedstock; and t (h): time on stream.

2.4. Homogeneous ethanol carbonylation

Homogeneous ethanol carbonylation was performed in a 150 mL batch reactor made of Hastelloy NS334 material to which 5 g of an ethyl iodide solution of $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}]^-$ (containing 0.0010 g $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}]^-$, 0.00146 mmol Rh), 4 g ethyl iodide, and 9 g ethanol were added. The autoclave was sealed, pressure tested, and purged three times with carbon monoxide. The reaction was then carried out at 468 K with 3.8 MPa of pressure while stirring at 500 rpm for 180 min, followed by cooling the reactor to room temperature in an ice-water bath. The liquid product was analyzed off-line by using an Agilent 7890A gas chromatograph equipped with a FFAP column and a FID detector, with methanol as the internal standard. $\text{TOF}_{\text{propionyl}}$ was calculated as mentioned above in Section 2.3.

Fig. 1. P K-edge XANES of standard $[PPh_3Et]^+I^-$ sample for P(V) species (A), TPISP (B), fresh Rh-TPISP (C), spent Rh-TPISP (D) and standard PPh_3 sample for P(III) species (E).

3. Results and discussion

3.1. Synthesis of TPISP and Rh-TPISP

TPISP was synthesized by free-radical polymerization of the vinyl-functionalized $P(4vPh)_3EtI$ monomer at 373 K for 24 h, as confirmed by solid-state ^{13}C NMR (Fig. S2(A)). In contrast with the liquid-state ^{31}C NMR spectrum of the $P(4vPh)_3EtI$ monomer (Fig. S1(B)), the two peaks at $\delta = 8.08$ and 18.00 ppm in Fig. S2(A) are ascribed to the ethyl group of the monomer. The new peaks appearing at $\delta = 32.19$ and 37.63 ppm in the solid-state ^{13}C NMR spectrum of the TPISP polymer are assigned to saturated alkyl [54] originating from polymerization of the vinyl monomer. Solid ^{31}P NMR and XANES analyses were used to confirm the existence of P(V) species in the polymer framework. Figure S2(B) indicates that only the peak of TPISP at $\delta = 24.8$ ppm is consistent with that of the monomer (see Fig. S1(C)), indicating no changes in the P species during the polymerization process. The P(V) species were further charac-

terized by P K-edge XANES, as shown in Fig. 1. Almost no XANES spectrum corresponding to organic P species has been reported in the open literature; thus, we used triphenyl phosphine PPh_3 (E) and the quaternary phosphonium salt of ethyl triphenylphosphonium iodide $[PPh_3Et]^+I^-$ (A) as standard samples of P(III) and P(V), respectively. Comparison of the XANES spectra of TPISP (B), fresh Rh-TPISP (C), and spent Rh-TPISP (D) with those of the standard samples demonstrates that P is present in the pentavalent oxidation state in the structure of TPISP, fresh Rh-TPISP, and spent Rh-TPISP, similar to $[PPh_3Et]^+I^-$. TG was used to evaluate the thermal stability of the polymer. The TG spectrum presented in Fig. S3 shows that the polymer is stable enough at the reaction temperature. After the initial loss of a tiny amount of residual DMF, there was no further rapid mass loss until 643 K. The porosity of the polymer was investigated from the nitrogen adsorption isotherms shown in Fig. 2. The steep increase in the N_2 uptake at low P/P_0 and the obvious hysteresis loop at higher P/P_0 suggest that the porous polymer is rich in micro- and mesopores, which is in agreement with SEM and TEM images in Fig. S4. The pore volume and BET surface area were calculated as 0.61 cm^3/g and 619 m^2/g , respectively. Moreover, the pore size distribution determined by the DFT method (see Fig. 2(B)) indicates that the pore width is centered at 1–6 nm. Thus, the porosity as well as the thermal stability of the polymer might make it favorable as a catalyst support for a variety of catalytic processes, and the cationic P(V) sites in the framework can serve as target points for anion metal complexes.

The Rh-TPISP catalyst was synthesized by the reaction of TPISP with $Rh_2(CO)_4Cl_2$ dissolved in CH_2Cl_2 (depicted in Scheme 1). As shown in Fig. S5, the yellow dichloromethane solution of $Rh_2(CO)_4Cl_2$ became colorless rapidly upon the addition of TPISP to the liquid phase. The Rh mass loading was 0.27 wt% based on the ICP-OES data in Table S1, which is close to the theoretical value. Figure 2(A) shows that the BET surface area of Rh-TPISP is 527 m^2/g , which is slightly smaller than that of the TPISP support. Some of the mesopores were lost based on the pore size distribution of TPISP and Rh-TPISP determined by the DFT method (Fig. 2(B)), demonstrating partial filling of the mesopores by the Rh species. No characteristic

Fig. 2. N_2 sorption isotherms (A) and pore size distributions (B) of TPISP and Rh-TPISP analyzed by DFT method.

Fig. 3. HAADF-STEM images of fresh Rh-TPISP (A) and spent Rh-TPISP (B).

peak of the Rh-P coordination was observed around 507 cm^{-1} in the IR spectrum (Fig. S6) of Rh-TPISP [23,55], suggesting that the anionic Rh species generated from cleavage of the Rh-Cl-Rh bond in the $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ precursor are embedded in the TPISP framework via electrostatic interaction with the cationic P(V) sites, as discussed further below based on XANES and EXAFS analyses.

3.2. Discussion of the dual-ionically bound mode

EDS-mapping of the SEM data (Fig. S7) revealed uniform dispersion of the Rh species in fresh and spent Rh-TPISP, and no visible Rh particles were observed in the TEM images shown in Fig. S8. The HAADF-STEM images in Fig. 3 indicate that almost all of the Rh species were monodisperse. Additionally, the XPS Rh 3d profile and XANES data for the Rh L_3 -edge were used to certify the chemical state of Rh in Rh-TPISP. The Rh3d XPS profiles of the standard samples, i.e., Rh(0), Rh(PPh_3)₃I (Rh(I)), $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ (Rh(I)), and RhI_3 (Rh(III)) showed peaks at 307.0, 307.9, 308.5, and 308.4 eV, respectively, as taken from the literature [56,57]. The Rh binding energy peaks of fresh and spent Rh-TPISP were observed at 307.4 eV (Fig. 4), confirming that the Rh oxidation states in fresh and spent Rh-TPISP are between 0 and +1. The XANES data for $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ and Rh powder in Fig. 5 were collected for standard samples of Rh(I) and Rh(0). The normalized peak intensity of the Rh L_3 -edge is positively correlated with the Rh oxidation state. The intensities of the Rh L_3 -edge of fresh and spent Rh-TPISP are 3.48 and

Fig. 5. Rh L_3 -edge normalized XANES of fresh Rh-TPISP (A), spent Rh-TPISP (B) catalyst, $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ (C), and Rh powder (D).

Table 2

Fitting results of Rh K-edge EXAFS traces of fresh Rh-TPISP, spent Rh-TPISP and $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$ from Fig. 6.

Samples	Shell	N	R (Å)	σ (10^{-3} Å^2)	R factor
Rh foil	Rh-Rh	12.0	2.68	—	—
Fresh Rh-TPISP	Rh-C	0.9 ± 0.4	2.04 ± 0.04	3.2 ± 0.0	0.014
	Rh-I	3.1 ± 0.4	2.69 ± 0.01	2.9 ± 1.0	
Spent Rh-TPISP	Rh-C	1.0 ± 0.0	2.04 ± 0.06	3.0 ± 0.0	0.015
	Rh-I	3.1 ± 0.5	2.69 ± 0.01	2.4 ± 1.1	
standard sample of $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$	Rh-C	2.3 ± 0.4	1.84 ± 0.01	2.5 ± 1.0	0.019
	Rh-I	2.0 ± 0.1	2.70 ± 0.01	2.8 ± 0.1	

The value of S_0^2 was 0.87 and obtained from Rh foil, and it was fixed in the subsequent fitting of Rh K-edge data.

3.51, respectively, which are close to that of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$, illustrating that the oxidation states of the Rh species are 0 to +1, which is consistent with the XPS results. The EXAFS spectra of Rh were also used to study the coordination environment of the Rh species. After the fitting analysis of the Rh K-edge k^2 -weighted Fourier-transform data of both fresh and spent Rh-TPISP in Table 2 and Fig. 6, an accurate structure of $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ (one Rh-CO bond and three Rh-I bonds) was deduced as the active Rh species of Rh-TPISP, which is absolutely different from the typical active center of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ in the

Fig. 4. Rh 3d XPS spectra of fresh Rh-TPISP (A) and spent Rh-TPISP (B).

Fig. 6. Raw spectra and fitting analysis of Rh K-edge k^2 -weighted Fourier transform spectra from EXAFS of fresh Rh-TPISP (A,B), spent Rh-TPISP (C,D) and $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$ (E,F), and the deduced molecular structures of (A), (C) and (E).

homogeneous or AceticaTM processes. However, it should be noted that the bond length of Rh-Rh is similar to the Rh-I bond length, and thus it is difficult to exclude the possibility of Rh-Rh bonds based on Fig. 6. WT is in fact the most efficient method for distinguishing different coordination shells with the same or similar bond distances. As shown in Fig. 7, although the R values of Rh foil and the fresh and spent catalysts are almost the same (2.3 Å), the k value of Rh foil is different from that of the other two catalysts (fresh and spent Rh-TPISP). The k value of Rh-Rh is 9.1 Å⁻¹ and that of Rh-I in the fresh and spent catalysts is approximately 10.8 Å⁻¹ [58]. It is clear that no Rh-Rh bond can be observed in the fresh and spent catalysts, demonstrating that Rh in the fresh and spent Rh-TPISP is dispersed in

the monodisperse state. For further study of the structure of the active Rh species in Rh-TPISP, the EXAFS spectrum of the standard $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$ sample was also collected, as shown in Fig. 6. The peak at 2.69–2.70 Å, ascribed to the Rh-I coordination bond in $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$, is obviously weaker than that in Rh-TPISP, suggesting that the coordination number of Rh-I in Rh-TPISP is more than two. Further, the peak at 1.84 Å, ascribed to the Rh-CO bond in $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$, is obviously stronger than that of Rh-TPISP at 2.04 Å [59], indicating that the coordination number of Rh-CO in Rh-TPISP is less than two. The IR spectrum in Fig. 8 shows two peaks at 2051 and 1986 cm⁻¹, assigned to the symmetric and asymmetric stretching vibration of the carbonyls as a decisive verification of the two Rh-CO bonds in $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$. However,

Fig. 7. Wavelet Transform of Rh foil (A), fresh Rh-TPISP (B) and spent Rh-TPISP (C).

Fig. 8. IR spectra of TPISP (A), fresh Rh-TPISP (B), spent Rh-TPISP (C), and $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$ (D).

Table 3

The influence of reaction temperature on heterogeneous ethanol carbonylation over Rh-TPISP catalyst

Temperature (K)	Selectivity (%)			Conversion (%)	TOF (h ⁻¹)
	Ethylene	Propionic acid	Ethyl propionate		
433	0	17.1	82.9	1.1	77
453	11.2	10.2	78.6	2.5	178
468	14.7	7.2	78.1	5.1	348
483	26.6	2.9	70.5	9.3	602

Reaction conditions: 0.10 g Rh-TPISP catalyst, $n_{\text{EtOH}}/n_{\text{EtI}} = 3.39:1$, $F_{\text{CO}} = 30$ mL/min, WHSV = 33.7 h⁻¹, 2.5 MPa, time on stream = 41 h.

only one peak was observed at 2044 cm⁻¹ in the IR spectra of Rh-TPISP, suggesting that the structure of the active Rh center contains only one Rh–CO bond [60–63], which is consistent with the proposed active site model of [Rh(CO)I₃]²⁻. As is commonly recognized, the carbonyl group acts as not only a σ -donor, but also as a strong π -acceptor, whereas the iodide anion (I⁻) can only act as a σ -donor, which suggests higher electron-donating ability of I⁻ than carbonyl. The Rh center with three iodide ligands should be more electron-rich than the single ionic bond of [Rh(CO)₂I₂]²⁻ in the AceticaTM process, as well as that of the homogeneous process. Laasonen [64] reported that [Rh(CO)₂I₃]²⁻ is more electron-rich than [Rh(CO)₂I₂]²⁻ because the extra I ligand acts as a σ -donor, which is similar to the case of [Rh(CO)I₃]²⁻ in the present study. [Rh(CO)I₃]²⁻, as the Rh site in Rh-TPISP, is expected to be formed by the departure of one coordinated chlorine and one coordinated carbonyl in Rh₂(CO)₄Cl₂, followed by coordination with three iodide atoms from the excessive iodide species in TPISP. [Rh(CO)I₃]²⁻ is the active Rh center of Rh-TPISP, and is thought to be firmly immobilized on the polymer by formation of two ionic bonds with two P(V) sites that are labeled as [P]⁺ on the framework of TPISP. As shown in Fig. 6(A) and (C), [Rh(CO)I₃]²⁻ interacts with the polymer via two ionic bonds that are herein denoted as [P]⁺–[Rh(CO)I₃]²⁻–[P]⁺ in order to show the structural differences compared with the single ionic bond [Rh(CO)₂I₂]²⁻–[N]⁺ in the AceticaTM process and the traditional coordination bonds in the homogeneous process. It was reported that the strong interaction of the ion-pair makes the catalyst used in the AceticaTM process more stable than the

Table 4

The influence of pressure on heterogeneous ethanol carbonylation over Rh-TPISP catalyst

Pressure (MPa)	Selectivity (%)			Conversion (%)	TOF (h ⁻¹)
	Ethylene	Propanoic acid	Ethyl propionate		
0.5	25.5	3.7	70.8	3.5	208
1	18.9	3.7	77.4	4.8	314
2.5	14.7	7.2	78.1	5.1	348
3.5	4.4	9.3	86.3	6.9	436

Reaction conditions: 0.10 g Rh-TPISP catalyst, $n_{\text{EtOH}}/n_{\text{EtI}} = 3.39:1$, $F_{\text{CO}} = 30$ mL/min, WHSV = 33.7 h⁻¹, 468 K, time on stream = 41 h.

heterogenized catalyst containing coordination bonds [27]. It is reasonable to deduce that the two ionic bonds should be stronger than a single ionic bond owing to the almost doubled interaction of the ion-pairs in the structure of the Rh-TPISP catalyst, which is thought to play a key role in stabilizing the Rh species and preventing leaching into the liquid phase during the ethanol carbonylation reaction.

3.3. Application of Rh-TPISP for heterogeneous ethanol carbonylation

The Rh-TPISP catalyst with two ionic bonds was applied in heterogeneous ethanol carbonylation. The test results in Table 3 show that the reaction temperature distinctly influenced the catalyst performance. Rh-TPISP displayed low activity (TOF = 77 h⁻¹) at 2.5 MPa and 433 K, but with 100% selectivity for propionyl. Increasing the temperature to 483 K increased the TOF to 602 h⁻¹, with a decline in the propionyl selectivity to 73.4%, indicating that higher temperature enhances the TOF, but is detrimental to the propionyl selectivity. Table 4 shows the influence of pressure on ethanol carbonylation. When the pressure was increased from 0.5 to 3.5 MPa, the TOF increased from 208 to 436 h⁻¹, accompanied by an increase in the propionyl selectivity from 74.5% to 95.6%. Thus, higher pressure favors the formation of propionyl products and enhances the carbonylation activity. Notably, the activity of 436 h⁻¹ achieved in the reaction over Rh-TPISP was much higher than that previously reported for corresponding homogeneous and heterogeneous systems [38,49–51], accompanied by a satisfactory

Table 5

The comparison of the heterogeneous Rh-TPISP system with the homogeneous system for ethanol carbonylation.

Catalysts	Process	Active	T/K	P/MPa	T ^b /h	Conversion ^c /%	S ^d /%	TOF _{propionyl} ^e /h ⁻¹
Rh-TPISP ^a	Heterogeneous	[Rh(CO)I ₃] ²⁻	468	3.5	17	7.6	88.8:0.7:0.5	491
Rhaq ^a	Homogeneous	[Rh(CO) ₂ I ₂] ⁻	468	3.8	3	1	81.0:19.0:0	281

^a Reaction result was obtained from our experiment and the mass fraction of additives is 50%EtOH:50%EtI.

^b Time on stream or reaction time.

^c Conversion = $(n_{\text{PA}} + 2n_{\text{EP}} + n_{\text{C}_2\text{H}_4})/n_{\text{EtOH}}$

^d Selectivity_{C₂H₄} = $n_{\text{C}_2\text{H}_4}/(n_{\text{PA}} + 2n_{\text{EP}} + n_{\text{C}_2\text{H}_4})$

^d Selectivity_{PA} = $n_{\text{PA}}/(n_{\text{PA}} + 2n_{\text{EP}} + n_{\text{C}_2\text{H}_4})$

^d Selectivity_{EP} = $n_{\text{EP}}/(n_{\text{PA}} + 2n_{\text{EP}} + n_{\text{C}_2\text{H}_4})$

^e TOF_{propionyl} = $(n_{\text{PA}} + n_{\text{EP}})/(n_{\text{Rh}} \cdot t)$

n_{EtOH} : the total mole of added EtOH.

$n_{\text{C}_2\text{H}_4}$: the mole of produced ethylene (C₂H₄) after reaction.

n_{PA} : the mole of propionic acid after reaction.

n_{EP} : the mole of ethyl propionate after reaction.

t (h): time on stream.

Fig. 9. Stability test of Rh-TPISP for heterogeneous ethanol carbonylation.

propionyl selectivity of 95% at 3.5 MPa and 468 K. For further comparison under similar reaction conditions, the catalytic performance of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ ($[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$ standard sample) in the batch reaction system was evaluated. As shown in Table 5, the homogeneous system yielded a TOF of 281 h^{-1} , which is much lower than that of Rh-TPISP (491 h^{-1} at TOS of 17 h), indicating the higher carbonylation activity of $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ compared to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$.

There is little research on the stability of catalysts for ethanol carbonylation [50,51]; thus, we studied the stability of Rh-TPISP for carbonylation, as depicted in Fig. 9. A stable TOF of 350 h^{-1} was maintained for approximately 1000 h in the reaction at 3.5 MPa and 468 K.

The Rh-TPISP catalyzed heterogeneous ethanol carbonylation is hypothesized to proceed via a mechanism analogous to the reported homogeneous and heterogeneous ethanol carbonylation mechanism [50,65], except for the difference in the structure of the active Rh center, which is depicted in Scheme 2

Scheme 2. Proposed mechanism for heterogeneous ethanol carbonylation on Rh-TPISP according to typical homogeneous ethanol carbonylation [50] and heterogeneous ethanol carbonylation [65].

to provide better understanding of the excellent catalytic performance of Rh-TPISP. It has been demonstrated that the mechanisms of methanol carbonylation and ethanol carbonylation are similar. The oxidative addition of EtI to $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$, to form Rh(III) species, is thought to be the rate-determining step, and has been verified as a $\text{S}_{\text{N}}2$ displacement process [66]. Subsequent migratory insertion of CO forms Rh-propionyl species of $[(\text{EtCO})\text{RhI}_4]^{2-}$. After CO coordination, reductive elimination of EtCOI and subsequent attack by ethanol or water releases EP or PA, thus completing the reaction cycle. Meanwhile, the original $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ active center is recovered. The overall charge of the anion complex is -2 throughout the cycle. As mentioned above, the higher electron density of the Rh center in $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ than that in $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ may reasonably favor oxidative addition as the rate-determining step, which is proposed to be the key factor for accelerating the reaction [1,67,68]. Furthermore, the obviously greater ionic bond length of $[\text{P}]^+ \cdots [\text{Rh}(\text{CO})\text{I}_3]^{2-} \cdots [\text{P}]^+$ relative to the coordination bond in common catalysts [27] may reduce the steric hindrance of the Rh center of Rh-TPISP, which promotes the oxidative addition step. Table S1 shows that the Rh loading remained at 0.22% after TOS for approximately 1000 h with little Rh leaching. The results of the ICP-MS measurement in Table S2 shows a trace amount of Rh in the liquid phase from the reactor system, which is negligible compared with that of the fresh catalyst. The difference in the Rh percentage of the fresh catalyst versus the spent catalyst (Table S1) is attributed to the increase in the weight of the spent catalyst caused by adsorbed propionyl in the pores of the carrier. It is proposed that the more robust $[\text{P}]^+ \cdots [\text{Rh}(\text{CO})\text{I}_3]^{2-} \cdots [\text{P}]^+$ interaction stabilizes the Rh species and contributes to the excellent stability of the catalyst. Apart from the main carbonylation cycle, ethylene is generated through β -hydride elimination from $[\text{EtRh}(\text{CO})\text{I}_4]^{2-}$, as shown in Scheme 2. A higher partial pressure of CO can accelerate CO insertion into $[\text{EtRh}(\text{CO})\text{I}_4]^{2-}$ to generate $[(\text{EtCO})\text{RhI}_4]^{2-}$ and thereby suppress the formation of ethylene. On the other hand, ethylene can also be formed from ethanol dehydration under highly concentrated HI at elevated temperature. Thus, the ethylene selectivity can be restrained feasibly under high pressure and appropriate temperature conditions.

4. Conclusions

TPISP, as a thermally stable porous organic polymer with a positively charged framework, was prepared through free-radical polymerization of the vinyl-P(V) quaternary phosphonium monomer and used as a support to prepare a dual-ionically supported Rh-based material, Rh-TPISP, as a new heterogeneous ethanol carbonylation catalyst. This catalyst not only exhibits excellent stability during 1000 h of reaction but also affords a TOF of 436 h^{-1} with a satisfactory propionyl selectivity of 95% at 3.5 MPa and 468 K, which is much higher than that of reported corresponding homogeneous and heterogeneous systems. For a deep study of the catalyst structure, Rh L₃-edge XANES, XPS, EXAFS, and other analyses were used to characterize $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ as the structure of the Rh active center for the carbonylation reaction; this anion is thought to

be firmly immobilized by the cationic sites ($[P]^+$) of the quaternary phosphonium skeleton via the formation of two ionic bonds ($[P]^+ \cdots [Rh(CO)_3I_3]^{2-} \cdots [P]^+$), playing a key role in the catalyst stability. Rh in $[Rh(CO)_3I_3]^{2-}$ with three iodide ligands in Rh-TPISP is thought to be more electron-rich than Rh with a single ionic bond or with the traditional coordination bonds in the homogeneous process, which is thought to be the key factor for accelerating the oxidative addition of EtI as the rate-determining step of ethanol carbonylation. Thus, the carbonylation activity of the developed catalyst surpassed that of other reported ethanol carbonylation catalysts. The Rh-TPISP catalyst is of great academic importance for studying ionic immobilization technology for the preparation of stable and active heterogeneous single-site carbonylation catalysts. This catalyst offers a new promising avenue for the potential development of heterogeneous ethanol carbonylation.

Acknowledgments

The K-edge X-ray absorption fine structure (EXAFS) of Rh K-edge was supported by BL14W1 beamline of SSRF, SINAP (Shanghai, China), and the XANES of P K-edge and Rh L_3 edge were supported by the 4B7A beamline at the Beijing Synchrotron Radiation Facility (BSRF, China).

The authors declare no competing financial interests.

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Graphical Abstract

Chin. J. Catal., 2021, 42: 606–617 doi: 10.1016/S1872-2067(20)63676-2

Quaternary phosphonium polymer-supported dual-ionically bound $[Rh(CO)_3I_3]^{2-}$ catalyst for heterogeneous ethanol carbonylation

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The higher electron density of the Rh center in $[Rh(CO)_3I_3]^{2-}$ and the ultrastable dual-ionically bound mode of $[P]^+ \cdots [Rh(CO)_3I_3]^{2-} \cdots [P]^+$ result in excellent activity and stability of Rh-TPISP for heterogeneous ethanol carbonylation.

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通过“双离子键”固载于季磷盐聚合物的 $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ 物种在多相乙醇羰基化中的应用

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摘要: 贵金属物种(Rh或Ir络合物)在均相羰基化和氢甲酰化催化过程得到了广泛的应用, 但始终存在分离繁琐等问题, 其均相多相化可很大程度上简化分离操作, 故一直广受重视. 单位点催化剂因其具有可与均相相比拟的较高金属利用率和

选择性而成为均相多相化的重要研究方向之一。研究发现,在碘物种存在的情况下用于固载金属物种的配位键容易断裂,进而导致金属物种的流失,而通过离子键固载的 $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ 物种更加稳定,比如著名的甲醇羰基化“AceticaTM”工艺中, $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ 负一价阴离子物种是以离子键的方式固定在带有阳离子骨架的甲基化聚乙烯吡啶树脂上。与甲醇羰基化过程类似的乙醇羰基化过程是生产重要化工中间体丙酸的主要途径之一,但该过程的均相多相化始终存在着稳定性差这一关键问题。为了解决这一问题,基于之前将固载于季磷盐聚合物的 $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ 应用于甲醇羰基化的工作,我们将类似的季磷盐聚合物固载Rh基催化剂Rh-TPISP用于多相乙醇羰基化过程,通过多种表征进一步证明了Rh物种和P物种结构,并提出了“双离子键”模型。

P的K边XANES证明了聚合物TPISP的季磷化阳离子骨架特征。HAADF-STEM测试表明Rh-TPISP中的Rh呈现单位点分散的状态。Rh的XPS和XANES结果证明了Rh-TPISP中Rh物种的价态介于0~+1。通过EXAFS的拟合解析给出了 $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ 活性中心结构。由于 $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ 为经典的羰基化活性中心,为了进一步证明该结构的正确性,我们将Rh-TPISP的EXAFS和IR谱图与标样 $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$ 对比发现:在EXAFS谱图中,Rh-TPISP中的Rh-C峰高低于 $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$ 的Rh-C峰高,而Rh-TPISP中的Rh-I峰高高高于 $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$ 的Rh-I峰高,这就说明Rh-TPISP中Rh物种的Rh-C配位数小于2,而Rh-I配位数大于2;在IR谱图中,标样 $[\text{PPh}_3\text{Et}]^+[\text{Rh}(\text{CO})_2\text{I}_2]^-$ 中有两个羰基振动峰,与该物种的两个Rh-C配位键相符,而Rh-TPISP中的只有一个羰基振动峰,说明Rh-C配位数为1。因此,Rh-TPISP催化剂的季磷盐骨架中的每个P物种带有一个正电荷,每个带有两个负电荷的 $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ 通过与两个 $[\text{P}]^+$ 的静电作用进行固载,形成“双离子键”结构。

该催化剂在固定床乙醇羰基化过程中表现出优异的羰基化活性、选择性和稳定性。在3.5 MPa、195 °C反应近1000 h后,Rh-TPISP催化剂TOF保持在约 350 h^{-1} ,丙酰基选择性为95%以上,高出所有文献报道的均相和多相乙醇羰基化活性。其较高的活性主要是因为 $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$ 比传统Rh活性相 $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ 具有更强的富电子性,而较高的稳定性主要是由于“双离子键”这种强静电作用比“AceticaTM”工艺中“单离子键”更有利于Rh物种的固载。故Rh-TPISP催化剂中的“双离子键”对其优异的催化性能具有极其重要的作用,对后续多相乙醇羰基化的发展具有重要意义。

关键词: 多相乙醇羰基化; 单位点催化剂; 羰基化活性中心 $[\text{Rh}(\text{CO})\text{I}_3]^{2-}$; 超稳定双离子键固载; 多孔离子聚合物

收稿日期: 2020-06-11. 接受日期: 2020-07-08. 上网日期: 2020-09-05.

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基金来源: 国家重点研发计划(2017YFB0602203); 中国科学院战略性先导科技专项(XDA21020300); 国家自然科学基金(XDB17020400).

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