

Heterogenized HRh(CO)(PPh₃)₃ on zeolite Y using phosphotungstic acid as tethering agent: a novel hydroformylation catalyst

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Abstract

Heterogenization of HRh(CO)(PPh₃)₃ tethered through phosphotungstic acid to zeolite Y support, gives a novel hydroformylation catalyst with excellent stability, reusability and even improved activity. The activity, selectivity and stability of this catalyst for hydroformylation of a variety of linear and branched olefinic substrates have been demonstrated. The heterogenized HRh(CO)(PPh₃)₃ catalyst was recycled several times without loss of any activity. The catalyst was characterized by powder XRD, SEM, XPS, and ³¹P CP MAS NMR to establish true heterogeneity and morphological characteristics.

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Keywords: Catalyst; Heterogeneous; Hydroformylation; Olefin; Phosphotungstic acid; Recycle; Rhodium; Tungsten; Zeolite; NMR

1. Introduction

The past three decades in catalysis saw various efforts to support metal complexes on inert, insoluble, inorganic matrices for “heterogenization” of soluble metal complexes to solid catalysts for a variety of industrially important reactions [1]. Numerous methods of heterogenization have been investigated [2–5] for applications to various reactions. However, lower activity–selectivity, leaching of metals, limitations of the support-pore sizes, and deactivation of the catalysts have limited the actual use of “heterogenized” catalysts in industry, leaving the challenge of looking into newer versions or modifications of the heterogenized catalysts [6]. Recently, a novel approach to immobilizing homogeneous catalysts on solid supports (e.g., clay, carbon, La₂O₃, Al₂O₃, SiO₂) in which the organometallic complex was tethered to the inorganic matrices has been reported [7–9] for asymmetric hydrogenation of various alkenes, alkynes, and aldehydes with enhanced catalytic activity and reusability. Herein, we demonstrate a novel approach to heterogenizing Wilkinson’s hydroformylation catalyst, HRh(CO)(PPh₃)₃, by tethering it to zeolite Na–Y through phosphotungstic acid as a tethering agent to obtain a highly stable and reusable catalyst for hydroformylation of olefins as it is one of the largest scale

applications of homogeneous catalysis in industry [10,11]; see Scheme 1.

Zeolite Y was our obvious choice as the support, owing to its large cavity (12-Å supercage) accessible through four 7.4-Å windows, high surface area (~700 m² g⁻¹), channel structures, and thermochemical stability [12]. Earlier, in order to overcome the separation problems, several immobilized catalysts for hydroformylation have been proposed [13–20]. In these reports, interesting concepts emerged but unfortunately, they suffered either due to lower activity–selectivity, lower rates limited by the solubility of olefins in water, stability during recycle or reuse, or use of expensive ligands and hence, were not considered suitable for practical applications. In this article, we demonstrate that a heterogeneous catalyst composed of HRh(CO)(PPh₃)₃ tethered to zeolite Y provides a catalyst with high stability and reusability, besides better activity than the previously known heterogeneous catalysts.

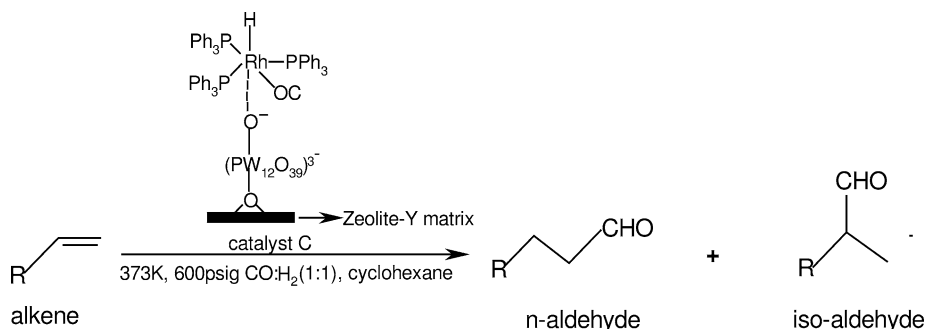
2. Experimental methods

2.1. Synthesis of tethered HRh(CO)(PPh₃)₃ on phosphotungstic acid (PTA) anchored to zeolite Y

The tethered catalyst was prepared following the procedure reported by Augustine and co-workers [7,8]. To a

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Scheme 1. Tethering of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ complex to zeolite Y by PTA for hydroformylation.

solution of phosphotungstic acid (100 μmol) in 15 ml of ethanol, a slurry of zeolite Y (1.5 g of Na–Y, Si/Al = 2.37) in 45 ml ethanol was added and stirred vigorously for 6 h. The white solid (PTA–Y) obtained was filtered, washed thoroughly with ethanol to ensure complete removal of phosphotungstate anion from the solid, and dried at 373 K for 6 h. Part of this solid (0.5 g) was suspended in 20 ml ethanol, and 30 μmol of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ was added and refluxed under stirring for 18 h. The $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ complex was prepared according to a procedure reported earlier [21]. The light gray solid product (Wk–PTA–Y) was then washed with ethanol repeatedly (Soxhlet extraction for 18 h) to remove unanchored Rh-complex to PTA–Y, dried at 353 K, and used as such for hydroformylation reactions. The specifications of the Wk–PTA–Y catalyst were: Rh content, 0.49% w/w; W content, 1.59% w/w; average particle size, $0.5 \times 0.7 \mu\text{m}$; surface area, $720 \text{ m}^2 \text{ g}^{-1}$ for Na–Y and $372 \text{ m}^2 \text{ g}^{-1}$ for Wk–PTA–Y.

2.2. Instrumentation

^{31}P CP–MAS NMR spectra of PTA–Y and Wk–PTA–Y were obtained on a Bruker DRX 500 FT-NMR spectrometer at 202.64 MHz and 11.7 T using a 3-mm CP-MAS probe. The chemical shifts were referred to H_3PO_4 at 0 ppm and the spectra were collected at a spectral width of 20 kHz, with a flip angle of 45° , 6000 real data points, and 5 s relaxation delay. X-ray photoelectron spectroscopy (XPS) measurements of Wk–PTA–Y were recorded in a VG Microtech ESCA 3000 instrument at 10^{-10} Torr pressure, a pass energy of 50 eV, and using unmonochromatized $\text{Mg-K}\alpha$ (photon energy –1253.6 eV) as the radiation. Powder X-ray diffraction (XRD) of zeolite Na–Y, PTA–Y, and Wk–PTA–Y was obtained at room temperature on a Rigaku D MAX III VC diffractometer using Ni-filtered $\text{Cu-K}\alpha$ radiation, $\lambda = 1.5404 \text{ \AA}$, where 2θ ranges were from 5° to 50° at a scan rate of $8^\circ/\text{min}$. For scanning electron microscopy (SEM), the crystalline supports were suspended in isopropanol, cast on gold-plated discs, followed by drying under vacuum and then were imaged on a Philips XL 30 instrument. The specific surface area of the catalyst was determined by the BET method using N_2 adsorption measured on an Omnisorb CX-100 Coulter instrument. Prior

to adsorption, the catalyst was activated at 423 K for 6 h at pressure 10^{-4} Torr. Inductively coupled plasma with atomic emission spectra (ICP–AES) analyses of Wk–PTA–Y as well as reaction mixtures after the hydroformylation reaction were performed in a Perkin–Elmer 1200 instrument to determine metal content. Gas chromatography (GC) of the reactants and products was performed in on HP 5890 instrument fitted with a FFAP capillary column.

2.3. Hydroformylation reaction setup

All the hydroformylation reactions were carried out in a 50-ml microclave reactor (Parr Instrument Company, USA) with a known quantity of olefin and the tethered catalyst at 373 K and 4.08 MPa of 1 : 1 $\text{CO} + \text{H}_2$ using cyclohexane as a solvent. The details have been reported elsewhere [22]. As the reaction progressed, $\text{CO} + \text{H}_2$ in 1 : 1 ratio was supplied from a reservoir vessel (maintained at higher pressure than the reactor) using a constant pressure regulating device. Since most of our experiments showed a material balance between $(\text{CO} + \text{H}_2)$ consumed and olefin conversions with the aldehyde products formed, to the extent of $> 98\%$ (see Table 2 and Fig. 2), by this procedure, constant pressure as well as composition of CO and H_2 was maintained during an experiment. It was also confirmed by analysis of the CO and H_2 content in the gas phase by GC after the reaction in a few cases. *The hydroformylation reaction should be carried out with utmost precaution and under the supervision of an experienced guide, as hazardous CO gas and high-pressure reaction conditions are involved.*

2.4. Leaching and recycle experiments with the tethered catalyst, Wk–PTA–Y

Catalyst leaching experiments have been performed by hot filtration of the reaction mixture at 373 K and subsequent testing of the catalytic activity of the filtrate for hydroformylation without addition of catalyst. This solution and the catalyst thus recovered (dissolved in conc. HNO_3) were also analyzed to determine of rhodium and tungsten content by ICP–AES analyses. For catalyst recycling experiments, the tethered catalyst was allowed to settle down and the clear supernatant liquid was decanted slowly. The residual solid

catalyst was reused with a fresh charge of solvent and reactants for further recycle runs, maintaining the same reaction conditions. In the recycling studies, the rhodium content of the catalyst and subsequent hydroformylation reaction mixtures were analyzed for metal content.

3. Results and discussion

3.1. Characterization of the Wk-PTA-Y catalyst

The “heterogenized” Wk-PTA-Y catalyst was characterized by powder XRD, SEM, ^{31}P CP MAS NMR, and XPS for possible elucidation of the structure, bonding, and oxidation state of the complex tethered to zeolite Y. The microporous phases of zeolite Y, PTA-Y, and Wk-PTA-Y catalyst were characterized by powder XRD. The distinct reflections and crystallinity remained unaltered from one another, as observed by the powder XRD patterns in Fig. 1.

This shows that (a) there is no change in crystallinity or morphology (determined by peak positions) of zeolite Y embedded with PTA compared to that of the neat zeolite Y sample and (b) the porous framework of the Wk-PTA-Y catalyst was not affected or damaged during the complex formation when the $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ complex was tethered to the PTA-Y support. To further consolidate this fact, we also scanned the Wk-PTA-Y catalyst by SEM before and after hydroformylation reactions. The crystalline patterns of the catalyst remained unaffected even after the 6th recycle. This conclusion further supports the integrity of the Rh-complex tethered by PTA to the zeolite matrix and retaining the texture of the porous structure of zeolite Y even after reuse.

In order to understand interactions of the species and to seek conclusive evidence of the true heterogeneity of

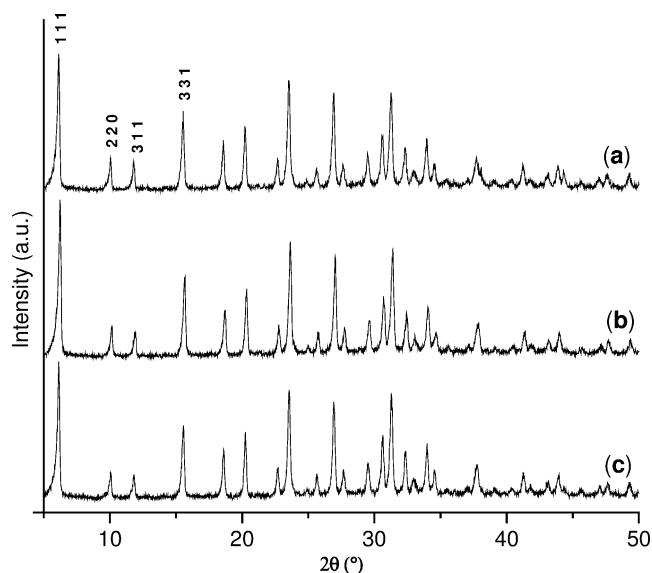


Fig. 1. Powder XRD patterns of (a) zeolite Y, (b) PTA-Y, and (c) Wk-PTA-Y.

complexes PTA and $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ tethered to zeolite Y, ^{31}P CP-MAS NMR spectra of PTA, $\text{HRh}(\text{CO})(\text{PPh}_3)_3$, and Wk-PTA-Y were recorded before and after the reactions. There was only one major ^{31}P signal ($\delta_{\text{iso}} -19.8$ ppm) of the PTA complex, as envisaged from the structure, while that of the $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ complex had two major ^{31}P signals ($\delta_{\text{iso}} 34.4, 45.4$ ppm), each split by J -coupling to other ^{31}P and ^{103}Rh ($n = 100\%$) nuclei. The spectral pattern observed in $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ thus elucidated the trigonal bipyramidal geometry of the complex. In comparison to ^{31}P spectra of the PTA and Rh-complex, Wk-PTA-Y catalyst showed a totally different spectrum with two distinct peaks ($\delta_{\text{iso}} -12.1, 32.0$ ppm). The shifts in NMR of the Wk-PTA-Y catalyst may be due to interaction of PTA and Rh-complex tethered to the zeolite Y matrix, where a Rh-O-W-O-Si type bond formation may have taken place (see Scheme 1). Interaction of this type is feasible, as bonding of types Rh-O-W in the solution phase [23] and $\text{O}_{\text{PTA}}\text{-Si}$ [24] has been reported earlier.

Wk-PTA-Y catalyst was also characterized by XPS for tungsten, silicon, aluminium, phosphorus, carbon, and rhodium atoms for their respective binding energies (BE) and oxidation states. The BE values of the elements present in Wk-PTA-Y (see Table 1) complied well with values obtained from the Rh-complex supported on zeolite, as reported earlier [25]. This illustrated that all rhodium was present as Rh (I) without suffering from any beam damage by the catalyst and showed the integrity of the complex $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ tethered to PTA-Y on zeolite Y. A slight change from the usual BE values of tungsten was observed for Wk-PTA-Y, which could be due to the rich electron density on the tungsten atom arising from the Rh-O-W linkage in the catalyst.

Crystal structures of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ [26] and $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 21\text{H}_2\text{O}$ [27] showed that the dimensions of the complexes are close to $10.8 \times 10.7 \times 10.8 \text{ \AA}^3$ and $7.1 \times 6.8 \times 7 \text{ \AA}^3$, respectively. This reflects a possible entrapment of the PTA through the zeolite Y windows (7.4 \AA) inside its supercage (12 \AA), but inclusion of the Rh-complex through the windows is not feasible. Since the exact chemistry of the tethered moiety is not yet well understood, we hypothesize a weak coordinate-covalent interaction (similar to that observed by Burk et al. [9]) between oxygen atoms of PTA and

Table 1
XPS values for different elements present in Wk-PTA-Y

Values	Elements						
	W	Al	Si	P	C	Rh	
						$3d_{5/2}$	$3d_{3/2}$
Observed (eV)	29.5	77.6	106.1	133.0	288	313.2	317.8
Corrected (eV) ^a	26.5	74.6	103.1	130.0	285	310.2	314.8
Literature (eV) ^b	31.0	74.7	103.4	130.1	285	309.1	313.9

^a Corrected to C 1s with binding energy of 285 eV using adventitious carbon.

^b Handbook of X-Ray Photoelectron Spectroscopy, Physical Electronics, Perkin-Elmer, 1979.

the Rh-atom of the $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ complex. This sort of ionic interaction fastens the Rh-complex tightly to the oxygen atoms of PTA tethered to the zeolite Y matrix, thus restricting the complex from leaching out in the liquid phase during reaction (see Scheme 1).

3.2. Hydroformylation of olefins using the Wk-PTA-Y catalyst

Wk-PTA-Y catalyst was evaluated for its activity and selectivity in hydroformylation of terminal and branched alkenes, the results of which are presented in Table 2.

The turnover frequency (TOF), conversion of olefins, and selectivity values were evaluated from the concentration–time profiles, a typical example of which for hydroformylation of styrene is shown in Fig. 2. We have observed concentration–time as well as $(\text{CO} + \text{H}_2)$ consumed versus time data in most of the experiments. The material balance of $\text{CO} + \text{H}_2$ conversion, olefin concentration, and aldehyde products formed was found to be consistent in all the cases. The data presented in Table 2 are for olefin conversion > 98% using the tethered catalyst.

Reaction products were analyzed by GC, GC-MS, and ^1H NMR (where required). Hydroformylation with Wk-PTA-Y catalyst showed excellent conversions (> 98%) of terminal and branched alkenes to respective aldehydes, high TOF (TOF ranging from 275 to 775 h^{-1} for various olefinic substrates), stability (after six recycles, the catalyst was still very active with the same TOF), and high aldehyde selectivity (> 99%) even in the absence of free PPh_3 , often used in the homogenous or immobilized systems [11,20,30]. We observed lower hydroformylation activity (TOF values) for the tethered catalyst in comparison to the $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ catalyst, which might possibly be due

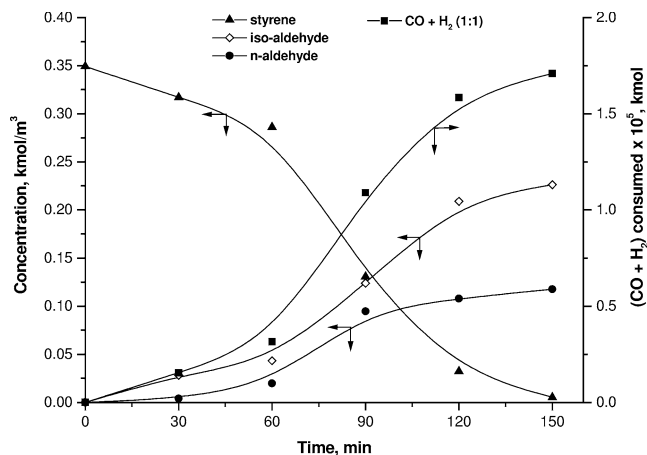


Fig. 2. Concentration–time profile for styrene hydroformylation with Wk-PTA-Y.

to the spatial restriction of the substrate molecules to the catalytic site of Wk-PTA-Y. To prove the catalyst stability and true heterogeneity, we performed leaching experiments, where hot reaction-mixture filtrates at 373 K were tested for hydroformylation activity without addition of fresh catalyst and adding the substrates. Since no activity was observed for 10 h, we could conclude that metal leaching from the catalyst does not occur in the reaction medium. The hot filtrates were also subjected to ICP-AES analyses of Rh and W content (< 0.01% Rh and W loss), which exhibited almost no leaching of Rh or W metals from the tethered catalyst during reactions. The catalyst was found to be very stable, restoring high activity and selectivity even after six recycles for hydroformylation of styrene with the same batch of the catalyst (see Fig. 3).

Table 2

Hydroformylation of olefins with Wk-PTA-Y and $\text{HRh}(\text{CO})(\text{PPh}_3)_3$

Catalysts	Substrate	Conv. (%)	Selectivity		TOF (h^{-1})	TON	Time (h)
			Ald%	n/iso			
$\text{HRh}(\text{CO})(\text{PPh}_3)_3$	Styrene (S)	98.0	98.9	0.39	2898	2666	0.92
Wk-PTA-Y	Styrene (S)	98.1	99.8	0.51	771	1797	2.33
$\text{HRh}(\text{CO})(\text{PPh}_3)_3$	<i>p</i> -Me-S	97.9	97.8	0.47	2073	2239	1.08
Wk-PTA-Y	<i>p</i> -Me-S	99.2	99.7	0.51	677	1578	2.33
$\text{HRh}(\text{CO})(\text{PPh}_3)_3$	<i>p</i> -Acetoxy-S	97.9	98.3	0.43	1575	1890	1.20
Wk-PTA-Y	<i>p</i> -Acetoxy-S	99.2	99.9	0.47	680	1360	2.00
$\text{HRh}(\text{CO})(\text{PPh}_3)_3$	<i>p</i> - <i>t</i> Bu-S	97.6	94.3	0.52	1035	1585	1.53
Wk-PTA-Y	<i>p</i> - <i>t</i> Bu-S	99.1	99.2	0.54	350	1135	3.25
$\text{HRh}(\text{CO})(\text{PPh}_3)_3$	1-Hexene	98.8	98.8	2.57	2455	2455	1.00
Wk-PTA-Y	1-Hexene	99.3	99.1	2.48	670	1675	2.50
$\text{HRh}(\text{CO})(\text{PPh}_3)_3$	1-Octene	98.8	98.2	2.44	1380	1835	1.33
Wk-PTA-Y	1-Octene	99.1	99.2	2.33	437	1312	3.00
$\text{HRh}(\text{CO})(\text{PPh}_3)_3$	1-Decene	98.1	92.2	1.38	984	1506	1.53
Wk-PTA-Y	1-Decene	98.6	99.3	1.50	328	1065	3.25
$\text{HRh}(\text{CO})(\text{PPh}_3)_3$	1-Dodecene	97.2	89.1	0.80	638	1220	1.91
Wk-PTA-Y	1-Dodecene	98.2	98.9	1.22	277	900	3.25

Reaction conditions: Wk-PTA-Y: 4 kg m^{-3} ; Rh-content in Wk-PTA-Y: 0.49% w/w; $\text{HRh}(\text{CO})(\text{PPh}_3)_3$: 0.96 kg m^{-3} substrate, 0.349 kmol m^{-3} ; P_{CO} : 2.04 MPa; P_{H_2} : 2.04 MPa; agitation speed: 16.67 Hz; temperature: 373 K; solvent: cyclohexane; volume: 2.5×10^{-5} m^3 ; TON = kmol of aldehydes formed/kmol of Rh; TOF = kmol of aldehydes formed/kmol of Rh/h.

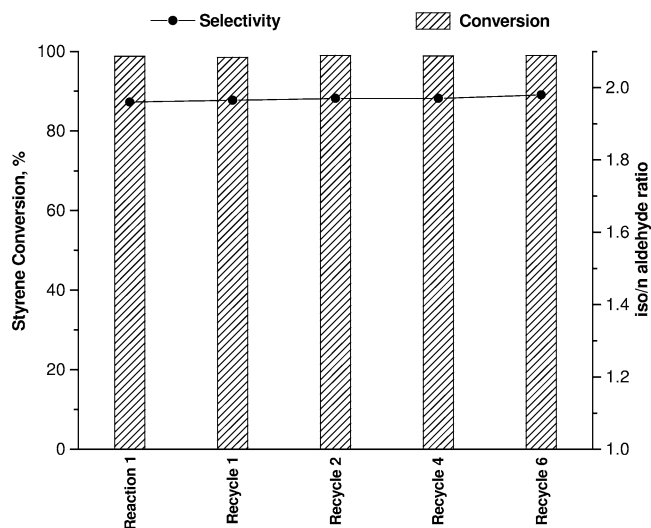


Fig. 3. Recycle studies using Wk-PTA-Y catalyst for hydroformylation of styrene.

Thus, the heterogeneous catalyst reported here is superior to the catalysts reported previously [19,28–33] in terms of hydroformylation rates, TOF, stability, and heterogeneity in particular. Recent reports using immobilized rhodium complexes anchored to MCM-41 matrix [19], polyelectrolyte [32], and delamellated matrix [33] for hydroformylation of olefins showed lower TOF (165 h^{-1} for 1-hexene, as reported by Schwab and Mecking [32]) and significant Rh leaching during recycles as compared to our system.

4. Conclusions

A novel catalyst system, for hydroformylation of olefins to aldehydes, consisting of a tethered $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ catalyst bound through phosphotungstic acid to zeolite Y, has been reported. The tethered catalyst was found to be highly stable and recyclable for hydroformylation of a variety of olefins. By this approach, one can bind suitable homogeneous metal complex catalysts to other microporous supports to obtain stable and recyclable catalyst systems, as demonstrated by the example of hydroformylation of olefins.

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