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Synthesis, Characterization and Catalytic Properties of Coordination Complexes Based on $[Mo(CO)_3(CH_3CN)_3]$ and Poly(4-vinylpyridine)

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Abstract The synthesis, characterization, and catalytic properties of the zero-valent, group six metal complex formed by the reaction of $[Mo(CO)_3(CH_3CN)_3]$ and poly(4-vinylpyridine) (P(4-VP)) is described in this work. The pyridyl groups of the organic polymer are covalently bonded to the Mo centers as suggested by X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), and Fourier transform infrared (FT-IR) techniques. The polymer-immobilized metal catalyst was also characterized by DTA–TGA, differential scanning calorimetry (DSC) analysis and its morphology and elemental analyses were studied by scanning electron microscopy/energy dispersive X-ray (SEM/EDX) techniques. In the presence of 2-ethoxyethanol the solid is an active catalyst for the heterogeneous hydrogenation of styrene to ethyl benzene.

Keywords Molybdenum · Poly(4-vinylpyridine) · Spectroscopic characterization · Catalysis · Hydrogenation

1 Introduction

The practice of immobilizing catalytically active transition metal complexes on polymers has spawned a class of materials that incorporate the major advantages of both heterogeneous and homogeneous systems into a single system: e.g. the high activity, specificity and reproducibility typical of homogeneous catalysts can be paired with the ease of product separation and catalyst recovery characteristic of heterogeneous catalysts [1–3].

Work in our laboratories have long been concerned with the use of transition metal compounds immobilized on poly(4-vinylpyridine) (P(4-VP)) as catalysts for the hydroesterification and hydroformylation of 1-hexene under CO/H_2O [4], for the water-gas shift reaction [5], for the reduction of nitrobenzene [6] and nitrofurans under CO/H_2O [7] and for the hydrodechlorination of chlorobenzene under CO/H_2O [8]. Due to their facile preparation, good stability, and moderate to high catalytic activities we have been able to demonstrate the versatility of these metal containing organic polymers as active catalysts for the aforementioned systems.

The $[Mo(CO)_3(CH_3CN)_3]$ compound is an attractive candidate to form coordination complexes with the pyridyl moieties of poly(4-vinylpyridine) with the precedence for

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this type of complex already being set. For example, soluble Mo-amine complexes of the type [$Mo(CO)_3(amine)_3$] (amine = pyridine or 4-methylpyridine) are known [9, 10].

In the present study we extend the use of the poly (4-vinylpyridine)/divinylbenzene(2%) polymeric matrix as a macromolecular ligand with which to displace the coordinated solvent molecules of [$Mo(CO)_3(CH_3CN)_3$]. Herein we report the preparation, characterization by XPS, EPR, DSC, FT-IR, DTA–TGA, and SEM/EDX techniques and the catalytic activity of (P(4-VP)-immobilized [$Mo(CO)_3L_3$] (where L is the polymeric 4-VP arms) on the hydrogenation of styrene to ethylbenzene.

2 Experimental

2.1 Materials and Instrumentation

Acetonitrile (Aldrich) was treated with P_2O_5 and distilled under nitrogen atmosphere before use. 2-Ethoxyethanol (Aldrich) was distilled from anhydrous stannous chloride. Styrene (Resimon-Venezuela) was treated with NaH and distilled under nitrogen atmosphere before use. Triphenylphosphine from Strem Chemical was used as received. Poly(4-vinylpyridine)/divinylbenzene(2%), was used as provided by Reilly Industries. All gases and gas mixtures were purchased from BOC gases and used as received. [$Mo(CO)_3(CH_3CN)_3$] was synthesized and characterized as reported in [11] (ν_{CO}, KBr disk, 1,975(m), 1,913(f), 1,887(h), 1,840(m), and 1,795(f) cm^{-1}) (lit. [12] nujol, 1,975(s), 1,915(s), 1,900(s), 1,832(s), and 1,783(s) cm^{-1}).

Infrared spectra were recorded on a Perkin-Elmer 1760X-FT spectrophotometer using KBr pellets for solid samples. Electron paramagnetic spectroscopy experiments were carried out in a conventional Varian E-line X-band spectrometer, using a rectangular cavity operating in the TE 102 mode. The scanning electron micrographs were recorded on a Hitachi S-500 microscope with an energy dispersive X-ray detector. The thermal behavior studies were carried out using a TA Instruments SDT 2960 Simultaneous DTA–TGA analyzer. Glass transition temperatures were measured on a Perkin-Elmer DSC 7 at a rate of 20 °C min^{-1} under a nitrogen purge.

Photoelectron spectra of the solid were recorded with a VG-220i-XL ESCALAB spectrometer using monochromatised X-ray Mg Kα radiation (1,235.6 eV). The solid was mounted on a standard sample stud. Nominal resolution was measured as full width at half maximum of 1.0 (core-level spectrum) to 1.5 eV (survey spectrum). The analyzed core-level lines were calibrated against the C_{1s} binding energy set at 285 eV of CH_x neutral carbon. The signals were deconvoluted using mixed Gaussian–Lorentzian curves where the Gaussian character was set at 80%.

2.2 Catalyst Preparation

A mixture of 0.5 g of P(4-VP) and a given amount of [$Mo(CO)_3(CH_3CN)_3$] dissolved in 10 mL of acetonitrile was stirred for 72 h under a nitrogen atmosphere until approximately 90% of the molybdenum was extracted from the solution by the polymer. Reaction progress was followed by Mo atomic absorption spectroscopy of the solution using a GBC Avanta atomic absorption spectrophotometer operated in the flame mode. The amount of the absorbed molybdenum on P(4-VP) was determined by subtracting the initial amount of [$Mo(CO)_3(CH_3CN)_3$] in solution from that present at subsequent time points. The resulting yellow polymer was filtered, washed with 5 mL of acetonitrile and dried in vacuo at room temperature. This material will be referred to hereafter as Mo/P(4-VP).

2.3 Catalyst Testing

Catalytic runs were performed in a 30 mL mechanically stirred and electrically heated stainless steel Parr reactor. In a typical run, 0.5 g of the catalyst ([Mo] = 2 wt% (1×10^{-4} mol)), 0.54 g (5.2×10^{-3} mol) of styrene, 0.1 g of toluene (internal standard), triphenylphosphine (typically 0.09 g, 3.3×10^{-4} mol)) and 10 mL of 2-ethoxyethanol were added to the reaction vessel. The system was then flushed with nitrogen to remove the air and subsequently flushed with hydrogen to remove all the nitrogen from the system. The reaction vessel was then charged with H_2 at the desired pressure (30 atm), and electrically heated to 90–110 °C for 24 h. The pressure and temperatures used were chosen based upon previously reported systems [13]. After 24 h, the reaction was stopped, the reactor cooled to room temperature, excess pressure was vented and the products were analyzed by GC and GC–MS techniques. The GC–MS of the ethylbenzene (molecular ion peak at *m*/*e* = 91 and base peak at *m*/*e* = 106) product is similar to a pure sample of ethylbenzene.

3 Results and Discussion

3.1 General Aspects

Dissolution of a solid sample of [$Mo(CO)_3(CH_3CN)_3$] (0.0379 g, 1.25×10^{-4} mol) in 10 mL acetonitrile at room temperature leads to the formation of a yellow solution. When this solution is put in contact with 0.5 g of P(4-VP) under nitrogen for 72 h at room temperature with continuous stirring a pale-yellow solid material and a colorless solution eventually results.

After charging the pale-yellow suspension of Mo/P (4-VP) ([Mo] = 2 wt%) in 10 mL 2-ethoxyethanol with H_2 (30 atm) and heating the reaction vessel to 90 °C, the color of the solid darkens, characteristic of the formation of the mature catalyst system. The solution above this solid remains uncolored.

3.2 Characterization Studies

The SEM with energy dispersive X-ray (EDX) technique was used for studying the morphology of the solid samples. We previously reported a SEM micrograph of a P(4-VP) sample, from which it is observed that the P(4-VP) is formed by agglomerates of grains with a smooth surface [6]. In Fig. 1 is displayed the micrograph of the solid product of the reaction of P(4-VP) with the $[Mo(CO)_3(CH_3CN)_3]$ in acetonitrile. Elemental analysis revealed that the presence of Mo was confined to the etched areas with Mo being absent from the smooth regions. The observed surface modifications in some areas of the polymeric ligand can be attributed to the anchoring of Mo to the P(4-VP).

EPR experiments show no signals for the $[Mo(CO)_3(CH_3CN)_3]$ complex as expected (Mo(0) d^6, low spin complex).

Fig. 1 Scanning electron micrograph of the Mo/P(4-VP) fresh catalyst sample. Magnification 5,000×

The FT-IR spectrum (KBr pellet) of the fresh $[Mo(CO)_3(CH_3CN)_3]$ sample shows five CO stretching bands (ν_{CO}) at 1,975(m), 1,913(s), 1,887(sh), 1,840(m), and 1,795(s) cm^{-1} corresponding to the isomers (*fac* y *mer*) [12]. The FT-IR spectrum (KBr pellet) of a $[Mo(CO)_3(CH_3CN)_3]$/P(4-VP) sample shows also five (ν_{CO}) bands at 2,010(m), 1,898(s), 1,864(sh), 1,821(m), and 1,772(s) cm^{-1} indicating the presence of the *fac* and *mer* immobilized isomers. The observed shift of the ν_{CO} bands between 11 and 35 cm^{-1} is indicative of the coordination of three pyridyl groups of the P(4-VP) to the Mo isomers. The substitution of the three molecules of CH_3CN from precursor $[Mo(CO)_3(CH_3CN)_3]$ by pyridyls causes the observed red shift in four of the five ν_{CO} bands due to the greater electron donating ability of pyridine.

Furthermore, the FT-IR spectrum (KBr pellet) of a P(4-VP) sample shows one C–N ring stretching band (ν_{CN}) at 1,598(s) and side group absorption bands (C–C ring stretching vibrations) at 1,557(m), 1,493(m), 1,451(m), and 1,417(s) cm^{-1}. The FT-IR spectrum of fresh prepared KBr pellets of $[Mo(CO)_3(CH_3CN)_3]$/P(4-VP) ([Mo] = 2 wt%) also shows the same bands negligibly shifted (+1 cm^{-1}). The slight blue shift observed in the $\nu_{C\text{–}N}$ in the Mo/P (4-VP) could indicate the N-coordination of the P(4-VP) polymer to the metal [14–16]. Unfortunately, a comprehensive molecular explanation is not available. It is likely that the presence of the coordinated-CO decreased the blue shift due to the back-bonding donation of $d\pi$ atomic orbital of the Mo to the π^*-antibonding molecular orbital of the CO which, leads to a competition for electronic density with the π-bonding molecular orbitals of the pyridine ring [17].

After converting the Mo/(P4-VP) to a dark-yellow solid by heating under H_2, its FT-IR spectrum (KBr pellets) shows the same five bands in the ν_{CO} region observed in the fresh catalyst, suggesting the presence of a similar carbonyl species anchored to the nitrogen-functionalized polymer. The addition of 0.09 g (3.3×10^{-4} mol) PPh_3 (PPh_3/Mo = 3) to the above described catalytic system causes the disappearance of the ν_{CO} bands at 2,010 and 1,821 cm^{-1}, likely due to the displacement of coordinated CO's by PPh_3 ligands.

Table 1 shows the XPS data for the fresh (pale-yellow solid) catalyst. The N_{1s} spectrum for the free P(4-VP) features a symmetric peak at 401.2 eV. However, the N_{1s} peaks of either catalysts form are broader and asymmetric and each peak can be deconvoluted into two peaks; one at 400.4 eV and another at 402.1 eV. The peak at 400.4 eV indicates that a fraction of the pyridine nitrogen of the P(4-VP) interacts with the molybdenum center.

Three C_{1s} peaks are present in the fresh catalyst. The first (main) peak at 284.6 eV, is attributed to the aliphatic carbons of adsorbed contaminants, the second at 284.8 is

Table 1 XPS data for the fresh (pale-yellow solid) catalyst

XPS peak	Binding energy (fresh catalyst)
C_{1s}	284.6, 284.8, and 287.9
N_{1s}	400.4 and 402.1
O_{1s}	533.5
$Mo_{3d5/2}$	228.8

attributed to carbon linked to the nitrogen atom of the pyridine heterocycle [18]. The third peak at 287.9 eV is attributed to the carbon of the carbonyl ligand bond to the Mo center. A $Mo_{3d5/2}$ doublet is also present in the XPS spectrum of the fresh Mo/P(4-VP) catalyst at 228.8 eV; corresponding to Mo(0) [19]. An O_{1s} line is also seen at 533.5 eV, which could be assigned to Mo(0)–CO species.

The atomic ratios $I_N/I_{Mo} = 3.1$, for the fresh catalyst were calculated from the XPS-peaks intensity ratios using the Scofield cross-section relative to each core level [20]. In such calculations, it is assumed that the transmission factor T of the spectrometer and the mean free electron path λ are both function of the kinetic energy (KE) of the considered photoelectron [21]. The value of 3.1 for the N/Mo ratio is indicative of three N atoms bonded to Mo.

Further, the DTA–TGA data (Fig. 2) show that the Mo/P(4-VP) complex is stable at 290 °C, however a weight loss observed around 100 °C is due to the moisture content leaving the sample. Differential scanning calorimetry (DSC) was used to determine the glass transition temperatures. The poly(4-vinylpiridine)/2% cross-linked polymer, which exhibits a glass transition temperature (T_g) at 127.1 °C, sees a T_g increase of 15 °C after the immobilization of 2 wt% of $[Mo(CO)_3(CH_3CN)_3]$. The resulting polymeric coordination complex exhibits a synergistic thermal property and it is related to the coordination of the pyridine moieties of the P(4-VP) on the coordination sphere of the Mo center. It is possible that the Mo centers form bridges between two or more separate polymer chains via pyridyl coordination, forming coordination cross-links as suggested by the XPS results. These cross-links hinder mobility of the polymers and provide an explanation for the change in T_g. It should be noted that the phenomena of enhancing the glass transition temperature of poly(4-vinylpyridine) after coordination to ruthenium [14], osmium [22] and copper complexes [23] has been reported.

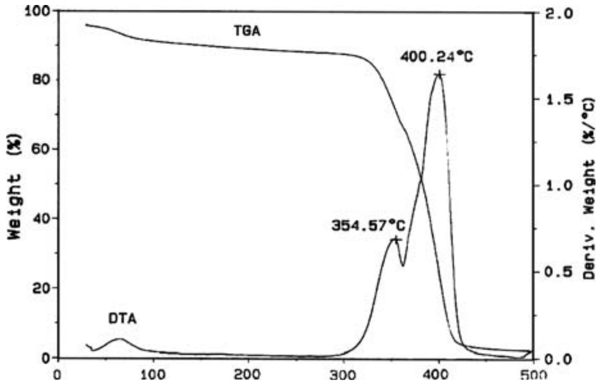


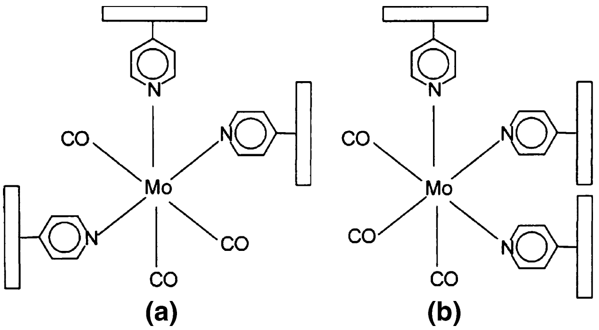
Fig. 2 DTA–TGA curves for the Mo/P(4-VP) fresh catalyst sample

3.3 Proposed Structures for Mo/P(4-VP) Complexes

The FT-IR, XPS, and DSC results constitute experimental evidence for the formation of a coordination complex between the pyridyl donors on the P(4-VP) and the molybdenum center of the $[Mo(CO)_3(CH_3CN)_3]$ complex. Based on these spectroscopic results we propose the solid catalysts contain two Mo(0) species as shown in Scheme 1. The structures (**a**) and (**b**) correspond to *mer* and *fac* immobilized isomers. Based on the DSC results it is likely that the Mo(0) species in (**a**) and (**b**) are coordinated in a cross-link fashion throughout the polymeric matrix.

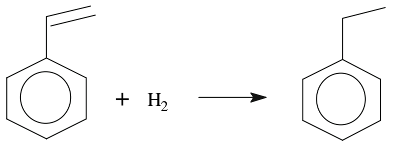
3.4 Hydrogenation Catalysis

The Mo/P(4-VP) catalyst in contact with 2-ethoxyethanol effectively catalyzes the hydrogenation of styrene to ethylbenzene under hydrogen atmosphere (Eq. 1) in presence of triphenylphosphine (PPh_3). The turnover frequencies for ethylbenzene production were calculated as mol of ethylbenzene produced per mol of Mo in 24 h (TF(ethylbenzene) = [(mol of ethylbenzene)/((mol of Mo) × (rt))] × 24 h, where (rt) = reaction time in hours). The calculated catalytic activity defined as TF(ethylbenzene) was reproducible to ca. 10% for a series of experimental runs. Furthermore, control experiments show that no reaction was detected in the absence of the polymer-immobilized Mo complex. The reaction conditions were: [Mo] = 2 wt% (1×10^{-4} mol), 0.5 g of P(4-VP), [styrene] = 0.54 g (5.2×10^{-3} mol), styrene/Mo = 50, 10 mL of 2-ethoxyethanol under $P(H_2) = 30$ atm at



Scheme 1 Proposed Mo(0) structures for the fresh catalysts

90–110 °C in 24 h. The data obtained from these studies are reported in Table 2.



(1)

From the data reported in Table 2 we can deduce that:

1. In the absence of triphenylphosphine (entry 1) the catalytic activity is negligible. The presence of triphenylphosphine is necessary in order to observe significant conversions (entries 2–7).
2. The most active PPh_3/Mo molar ratio is 3 (entries 2–5). The FT-IR spectrum of the catalytic sample of Mo/P(4-VP) in the presence of PPh_3 shows the disappearance of ν_{CO} bands at 2,010 and 1,821 cm^{-1}. This displacement of CO's by PPh_3 ligands leads the formation of mixed carbonyl/phosphine Mo species, which are more catalytic active.
3. A change of the temperature from 90 (TF = 1.6/24 h) to 110 °C (TF = 7.3/14 h) at the same PPh_3/Mo molar ratio = 3 causes an increase in catalytic activity of about of 4.6-fold (entries 4, 6, and 7).

3.4.1 *Effect of the Temperature*

To determine the activation parameters for the hydrogenation of styrene to ethylbenzene under hydrogen atmosphere, TF(ethylbenzene)/24 h values for the Mo/P(4-VP) system were measured at various temperatures in the 90–130 °C range (Table 2, entries 4 and 6–9). Figure 3 displays the ln TF(ethylbenzene)/24 h values versus 1/*T* plot for [Mo] = 2 wt%, 0.5 g of P(4-VP), [styrene] = 0.54 g (5.2×10^{-3} mol), styrene/Mo = 50, 10 mL of 2-ethoxyethanol under $P(H_2)$ = 30 atm at 24 h. The Arrhenius-type plot of ln TF(ethylbenzene)/(24 h) values versus 1/*T* was nonlinear in the 90–130 °C range, giving instead a segmented curve. The apparent activation energies obtained from the slopes of the two segments are −47.2 J/mol·K at temperatures >110 °C and 88.1 kJ/mol·K at temperatures <110 °C. Segmented plots of this type indicate a change in the rate-limiting step between competitive reactions [24]. In fact, at temperature >110 °C, polymerization of the styrene to polystyrene was observed.

Table 2 Hydrogenation of styrene catalyzed by Mo/P(4-VP)[a]

Entry	*T* (°C)	PPh_3/Mo (molar ratio)	Conversion (%)	TF(ethylbenzene)[b]
1	90	0	<1	<1
2	90	1	1.8	1.0
3	90	2	1.6	0.8
4	90	3	3.2	1.6
5	90	4	1.9	0.9
6	100	3	10.0	5.2
7	110	3	14.7	7.3
8	120	3	9.6	4.7
9	130	3	7.1	3.5

[a] [Mo] = 2 wt% (1×10^{-4} mol), 0.5 g of P(4-VP), [styrene] = 0.54 g (5.2×10^{-3} mol), styrene/Mo = 50, 10 mL of 2-ethoxyethanol under $P(H_2)$ = 30 atm for 24 h

[b] TF(ethylbenzene) = [(mol of ethylbenzene)/((mol of Mo) × (rt))] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty <10%

3.4.2 *Effect of the Pressure of Hydrogen*

The plot of TF(ethylbenzene) values versus $P(H_2)$ for [Mo] = 5×10^{-4} mol at 110 °C shown in Fig. 4 is almost linear, indicating that the reaction is first-order in $[H_2]$ at this temperature in the 5–30 atm range. Based on this first-order dependence we suggest a possible mechanism in that

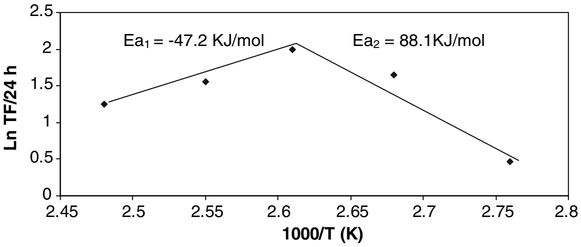


Fig. 3 The Arrhenius plot for the catalytic hydrogenation of styrene. [Mo] = 2 wt% (1×10^{-4} mol), 0.5 g of P(4-VP), [styrene] = 0.54 g (5.2×10^{-3} mol), styrene/Mo = 50, 10 mL of 2-ethoxyethanol under $P(H_2)$ = 30 atm for 24 h

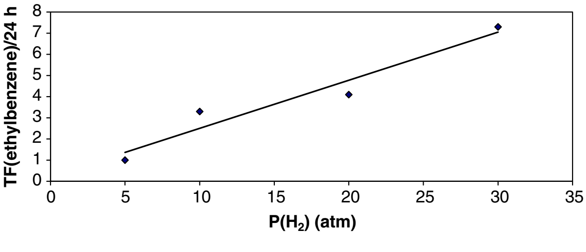


Fig. 4 Plot of TF(ethylbenzene)/24 h versus $P(H_2)$: [Mo] = 2 wt% (1×10^{-4} mol), 0.5 g of P(4-VP), [styrene] = 0.54 g (5.2×10^{-3} mol), styrene/Mo = 50, 10 mL of 2-ethoxyethanol under $P(H_2)$ at 110 °C for 24 h. Lines drawn for illustrative purpose only

the rate-limiting step (k_2) is preceded by coordination of H_2, e.g.

$$[\mathrm{Mo}] + \mathrm{H}_2 \xrightarrow{k_1} [\mathrm{Mo}-\mathrm{H}_2] \xrightarrow{k_2,\ \mathrm{styrene}} \mathrm{ethylbenzene} \qquad (2)$$

The ethylbenzene rate law for such behavior would be:

$$\mathrm{Rate} = k_1k_2\mathrm{P}(\mathrm{H}_2)[\mathrm{Mo}]_{\mathrm{tot}} \qquad (3)$$

where $[\mathrm{Mo}]_{\mathrm{tot}} = [\mathrm{Mo}] + [\mathrm{Mo{-}H_2}]$, k_1 includes the solubility of H_2 in the medium and k_2 the [solvent] and [styrene]. The above expression, Eq. 3 can be reduced to:

$$\mathrm{TF(ethylbenzene)} = k_1k_2\mathrm{P}(\mathrm{H}_2) \qquad (4)$$

For this kinetics model plots of TF(ethylbenzene) versus P(H_2) are expected to be linear with slopes of k_1k_2 and zero intercept. Experimental data support this with the TF(ethylbenzene) plot versus P(H_2) being linear with nearly a zero intercept value, as predicted by Eq. 4. Furthermore, by plotting ln TF(ethylbenzene) versus ln P(H_2) a slope with a value ca. 1 is observed (Table 3).

3.4.3 *Recycling Efficiency of the Immobilized Hydroxycarbonylation Catalyst*

In order to check the resistance to leaching and the recycling efficiency of the polymer anchored catalyst, two types of experiments were carried out: first, the solution remaining after a catalytic run was analyzed for [Mo] by atomic absorption spectroscopy with less than 0.1% of Mo being detected in solution. Also, activity toward the hydrogenation of styrene was not observed when a mixture of 10 mL 2-ethoxyethanol and 0.54 g of styrene under 30 atm of H_2 at 199 °C for 24 h was tested under similar experimental conditions to the above described, but in the absence of the immobilized Mo/P(4-VP) system. Second, the recycling efficiency of the anchored catalyst was carried out by reusing a sample of the polymer-anchored catalyst numerous times. No significant changes of the hydrogenation catalytic activity after repetitive use were observed (TF(ethylbenzene) = 7.3, 6.8, 6.6, and 6.5 $(24\ \mathrm{h})^{-1}$, for the first, second, third, and fourth use, respectively) under the same catalytic conditions. The polymer-anchored catalyst was thus deemed highly stable.

Table 3 Effect of the hydrogen pressure on the hydrogenation of styrene catalyzed by Mo/P(4-VP)[a]

Entry	P(H_2) atm	Conversion (%)	TF(ethylbenzene)[b]
10	5	17.6	1.0
11	10	7.1	3.3
12	20	8.3	4.1

[a] [Mo] = 2 wt% (1×10^{-4} mol), 0.5 g of P(4-VP), [styrene] = 0.54 g (5.2×10^{-3} mol), styrene/Mo = 50, 10 mL of 2-ethoxyethanol, PPh_3/Mo = 3 under P(H_2) at 110 °C for 24 h

[b] TF(ethylbenzene) = [(mol of ethylbenzene)/((mol of Mo) × (rt))] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty <10%

4 Conclusions

The following conclusions can be drawn from the characterization and catalytic studies of the hydrogenation of styrene by $[\mathrm{Mo(CO)_3(CH_3CN)_3}]$ immobilized on the aminated polymer P(4-VP) in contact with 2-ethoxyethanol under H_2.

The characterization of the Mo/P(4-VP) by SEM, FT-IR and XPS techniques shows the variation of the molybdenum environment during the immobilization process. This study suggests that the molybdenum metal center is being coordinated by the pyridyl groups of the solid P(4-VP). Coordination cross-links are also proposed and is consistent with the DSC data. The FT-IR studies of the fresh catalyst show that both the *fac* and *mer* isomers of the immobilized carbonyl Mo(0) polymer-complexes are present.

It was shown that after $[\mathrm{Mo(CO)_3(CH_3CN)_3}]$ was immobilized on P(4-VP) it was an effective catalyst system for the hydrogenation of styrene to ethylbenzene by H_2 in 2-ethoxyethanol in the presence of triphenylphosphine. The presence of PPh_3 is believed to cause the formation of mixed carbonyl/phosphine Mo immobilized species which are, in fact, the catalytically active species.

Furthermore, the catalyst was also found to be highly resistant to degradation without significant loss of metal from the system over several runs.

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