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Structure aspects and hydroformylation performance of water-soluble HRh(CO)[P(m-$C_6H_4SO_3Na)_3]_3$ complex supported on SiO_2

Youzhu Yuan*, Hongbin Zhang, Yiquan Yang, Yu Zhang, Khirui Tsai

State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen 361005, PR China

Abstract

The solution NMR (^{31}P and ^{1}H) and FTIR spectroscopies were employed to investigate the structure information of water-soluble complex HRh(CO)[P(m-$C_6H_4SO_3Na)_3]_3$ (**1**) [P(m-$C_6H_4SO_3Na)_3$: trisodium salt of tri-(m-sulfophenyl)-phosphine, TPPTS] supported on SiO_2 (**1**/SiO_2). The $^{31}P(^{1}H)$ NMR spectra showed that a pair of new twin-peak at about 31.5, 32.1 ppm while no typical twin-peak at 44.0, 44.7 ppm for the phosphorus species ascribed to the complex **1** were observed at **1**/SiO_2. However, the typical phosphorus peaks for the complex **1** appeared in the case of using TPPTS or Na_2CO_3-preimpregnated SiO_2 as supports. Moreover, the immobilization caused a considerable oxidation of the liberated TPPTS to OTPPTS (OTPPTS, i.e. OP(m-$C_6H_4SO_3Na)_3$: trisodium salt of tri-(m-sulfophenyl)-phosphine oxide) species as evidenced by $^{31}P(^{1}H)$ NMR spectroscopy. The phosphorus-31 peaks at 31.5, 32.1 ppm at **1**/SiO_2 were found to be unchanged before and after the propene hydroformylation. The FTIR results revealed that the CO band appeared at about 1870 cm^{-1} for the **1**/SiO_2 catalyst, which was lower than that for the precursor complex **1**. It is concluded that there exists a strong interaction between the complex **1** and the acidic support of SiO_2, resulting in the deformation of the Rh–phosphine complex containing less than three TPPTS ligands, which further transformed by dehydrogenation and dimerization under evacuation to form a species likely $[Rh(CO)(TPPTS)_2]_2$ as a main surface complex species at the catalyst **1**/SiO_2. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Water-soluble Rh-complex; NMR; Hydroformylation; FTIR; Supported aqueous-phase catalyst

1. Introduction

Research into heterogenization of HRh(CO) $[P(C_6H_4)_3]_3$ ($P(C_6H_4)_3$: triphenylphosphine) for hydroformylation and selective hydrogenation has received high attention in the past several decades from both academic and industrial interests [1]. Besides the milestone preparation of water-soluble TPPTS and corresponding Rh–phosphine complexes such as $HRh(CO)(TPPTS)_3$ (**1**) [2,3], supported liquid-phase catalysts (SLPC) [4,5] and supported aqueous-phase catalysts (SAPC) [6] are known as attractive alternatives for heterogenized catalysts for olefin hydroformylation. The SAPC where the complex **1** or rhodium complex precursor and water-soluble ligand like TPPTS are immobilized in a thin water layer adhered within the pores of a high surface-area silicates [7] makes the separation of catalyst from reaction mixture to be greatly simplified, thus, facilitating successive operation. Using this system higher alkenes can be converted at a relatively high rate without metal leaching. It still faces the problems, however, how to improve the lower regioselectivity to the product aldehydes (i.e. molar ratio of normal:branched (n:i) aldehydes) and also the catalytic stability due to the

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* Corresponding author. Fax: +86-592-2183047.
E-mail address: yzyuan@xmu.edu.cn (Y. Yuan).

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oxidation of water-soluble phosphine ligands [8,9]. In literature, the results on SAPC for hydroformylation, thus, far were mostly based on rhodium, cobalt and platinum/nickel with TPPTS as the ligand [10,11] or sulfonated diphosphines including those with a large bite angle as ligands [12], limited attention has been paid on the structure information in the SAPC system [13].

It is well documented in the relationship of structure-performance in homogeneous and biphasic catalytic systems due to the easy characterization and well-defined structure as compared to the corresponding SAPC system [14]. Use of high resolution MAS NMR technique is one of the efficient ways to clarify the coordination chemistry in the SAPC system [8,13,15]. However, the measurements of MAS NMR spectra are time-consuming and usually MAS spectra with lower resolution are far from satisfactory for catalyst characterization. Alternatively, when the dried supported catalyst of SAPC is exposed to water it is possible to record a ^{31}P NMR spectrum using conventional solution NMR techniques [15]. The objective of this work is to investigate the structural information at SiO_2-supported water-soluble TPPTS–Rh-complex catalysts in connection to the hydroformylation performance by means of solution NMR with the combination of pyridine–TPD and FTIR spectra.

2. Experimental

A commercial available SiO_2 was washed by distilled water and sieved to 80–100 mesh which has pore diameter of 6–12 nm, pore volume of $1.03\,cm^3\,g^{-1}$ and BET surface-area of $380\,m^2\,g^{-1}$. For comparison, SiO_2 was preimpregnated with 2% Na_2CO_3 followed by drying in an oven at 393 K for over night. TPPTS was synthesized by the known method [2,16–18]. $^{31}P(^1H)$ NMR spectroscopy showed it consisted of 15% OTPPTS (trisodium salt of tri-(*m*-sulfophenyl)-phosphine oxide). Thermogravometric analysis (TGA) on the TPPTS showed a 10% weight loss attributed to the residual water. The TPPTS had a solubility of $0.63\,g\,ml^{-1}$ at room temperature and the same IR bands as reported in [16–18]. The complex **1** was synthesized according to the literature method [15]. $^{31}P(^1H)$ NMR: 44.7, 44.0 ppm; IR (cm^{-1}): 2010s, 1928s.

A water solution of **1** ($0.01\,mmol\,ml^{-1}$) was poured into a Schlenk flask containing 0.1 g degassed SiO_2. After further degassing the mixture by vacuum boiling, argon was introduced and the slurry was kept at room temperature for 1 h while vibration. The water was removed under vacuum at room temperature. The final product was a dry, free-flowing yellow powder and denoted as **1**/SiO_2, which was stored under Ar at room temperature. The water content was analyzed by TGA to be 8–10%.

Solution $^{31}P(^1H)$ NMR spectra were recorded on a Varian FT Unity$^+$ 500 spectrometer at 200 MHz at room temperature. Phosphorous-31 NMR chemical shifts are reported relative to 85% H_3PO_4. Samples of SAPC in the NMR tube were introduced about 40% D_2O before measurements. FTIR spectra were measured on a Nicolet-740 spectrometer with a resolution of $4\,cm^{-1}$. The surface-areas of the samples were measured by a conventional BET nitrogen adsorption method at 77 K using a SORPTOMATIC-1900 machine.

The propene hydroformylation reaction was performed in a high-pressure fixed-bed flow reactor connecting an on-line gas chromatgraph (102-GD, Shanghai Analysis Factory, China) equipped with FID detector and a column of Porapak Q (2 m). The propene:CO:H_2 ratio used here was always 1:1:1. The results showed the total hydrogenation products were lower than 1% under present experiment condition.

3. Results

3.1. Pyridine–TPD

It is known that the hydrophilic SiO_2 support possesses acidity at the surface. Pyridine–TPD spectra for SiO_2 and Na_2CO_3/SiO_2 are shown in Fig. 1. The pyridine–TPD for the SiO_2 showed a peak at about 420 K, whereas that for Na_2CO_3/SiO_2 showed no peak in the same temperature range. In fact the pyridine adsorption on Na_2CO_3/SiO_2 sample was negligible.

3.2. Solution $^{31}P(^1H)$ NMR spectra of SiO_2-supported **1**

The solution $^{31}P(^1H)$ NMR spectra for TPPTS, **1**, and a SiO_2-supported TPPTS and a SAPC sample

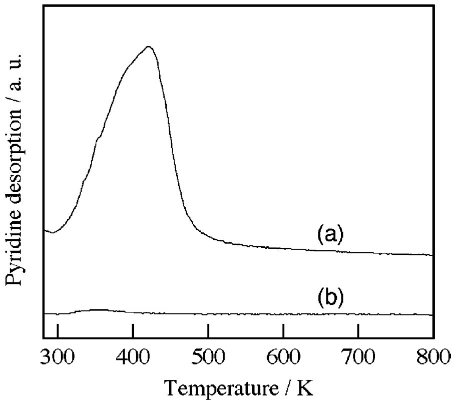


Fig. 1. TPD spectra of pyridine adsorbed on SiO_2 (a) and Na_2CO_3/SiO_2 (b).

containing about 40 wt.% D_2O are shown in Fig. 2a–c, respectively. When TPPTS was supported on SiO_2, the $^{31}P(^1H)$ NMR showed two peaks at 5.1 and 35.2 ppm straightforwardly assignable to the free TPPTS and OTPPTS, respectively. However, no typical twin phosphorus-31 peaks at 44.7, 44.0 ppm for the complex **1** but another pair of twin-peaks with broadness at about ∼32.1 and 31.5 ppm for newly formed phosphorus species and an increased peak at 35.2 ppm for the phosphorus in the OTPPTS were observed in the SAPC sample. The intensity for the peak at 35.2 ppm significantly increased from 10 mol% in the precursor **1** to about 30 mol% in the SAPC sample, probably due to an oxidation of the phosphorous ligands liberated from the complex during the impregnation. The new peaks at 32.1 and 31.5 ppm contained 60 mol% amount of phosphorous species. Taking the weak or no coordination ability of OTPPTS to rhodium atom into account, we estimated the ratio of the phosphorous in the new peak to rhodium atom to be closely to 2:1 (mol). Further NMR experimental results revealed that the newly formed Rh–TPPTS species at SiO_2 surface strongly interacted with SiO_2 so that it was impossible to be simply removed from the SiO_2 surface by washing with D_2O.

To investigate the property of the interaction between the Rh-complex **1** and SiO_2 support and clarify the reason why the interaction generated, we chose several supports, such as GDX-102 (a copolymer of ethylene benzen and xylene), Na_2CO_3-preimpregnated SiO_2 (Na_2CO_3/SiO_2), TPPTS-impregnated SiO_2 (TPPTS/SiO_2) to immobilize the Rh-complex **1** and characterize the structure information by the solution NMR. All the samples for the NMR measurements contained about 40% D_2O. The results are shown in Fig. 3. Clearly, the $^{31}P(^1H)$ NMR peaks at 44.7 and 43.9 ppm for **1** appeared when it was supported on GDX-102, though there was an increase in the peak intensity for OTTPTS at

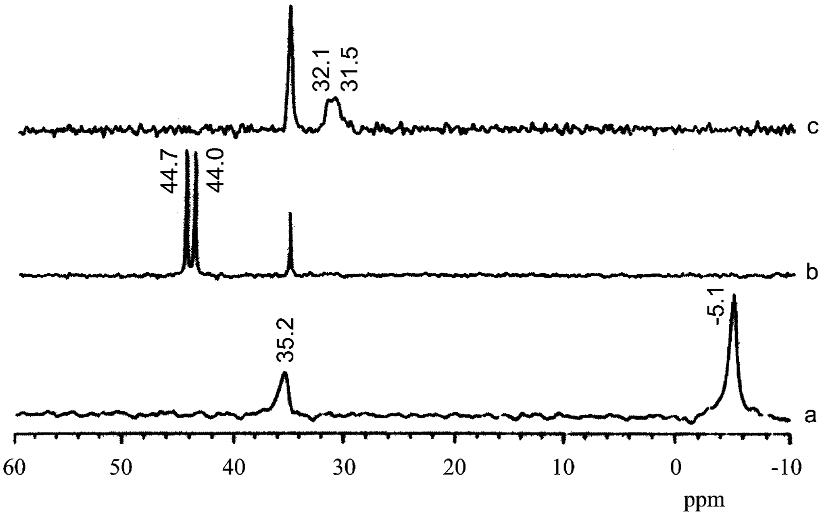


Fig. 2. $^{31}P(^1H)$ NMR spectra for: (a) TPPTS/SiO_2 containing 40% D_2O; (b) **1** in D_2O, pH = 6.9; (c) **1**/SiO_2 containing 40% D_2O.

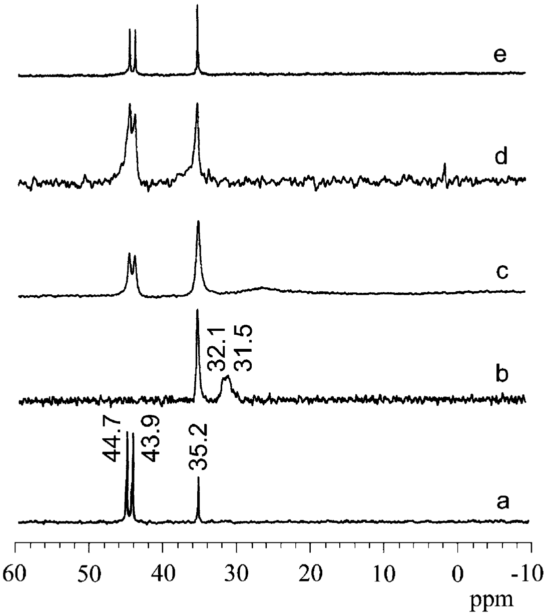


Fig. 3. ^{31}P(^{1}H) NMR spectra for: (a) **1** in D_2O; (b) **1**/SiO_2 containing 40% D_2O; (c) **1**/TPPTS/SiO_2 containing 40% D_2O; (d) **1**/Na_2CO_3/SiO_2 containing 40% D_2O; (e) **1**/GDX-102 containing 40% D_2O.

35.2 ppm (Fig. 3e). The typical ^{31}P(^{1}H) NMR peaks for the phosphorus-31 species in the precursor **1** were appeared when using TPPTS/SiO_2 or Na_2CO_3/SiO_2 as supports, though the peak intensity for the OTPPTS was increased considerably.

Before and after propene hydroformylation at 373 K, the ^{31}P(^{1}H) NMR spectra for the catalyst **1**/SiO_2 were no significant difference each other as shown in Fig. 4, indicating that the SiO_2 surface could stabilize the deformed structure of Rh-complex at **1**/SiO_2.

Fig. 5 shows that ^{31}P(^{1}H) NMR spectra of **1**/SiO_2 with different Rh loading weights. In the case of loading weigh less than 0.1 mmol Rh/γ-SiO_2, we found that the spectroscopy only showed a signal at $\delta = 35.2$ ppm for OTPPTS and a signal at about $\delta = 30$ ppm for the species which strongly interacted with SiO_2. The signals at 44.7 and 43.9 ppm for the complex **1** were appeared in the case of loading weight of 0.2 mmol Rh/γ-SiO_2, in which there were about 30 mol% of phosphorus species in the state of original complex **1**.

3.3. FTIR spectra for $\mathbf{1}/SiO_2$

The FTIR spectra for the complex **1** and **1**/SiO_2 are shown in Fig. 6. The complex **1** presented an IR band at 2010 cm^{-1} for the stretch vibration of Rh–H and a peak at 1928 cm^{-1} for the carbonyl species, which are coincided with the results in [13]. The peak at 1630 cm^{-1} was assignable to the water existed in the sample. After immobilization on SiO_2, the IR peaks for the surface complex were differed from those for the precursor **1** as shown in Fig. 6b. The peaks at 2010 and 1928 cm^{-1} for the complex **1** were replaced

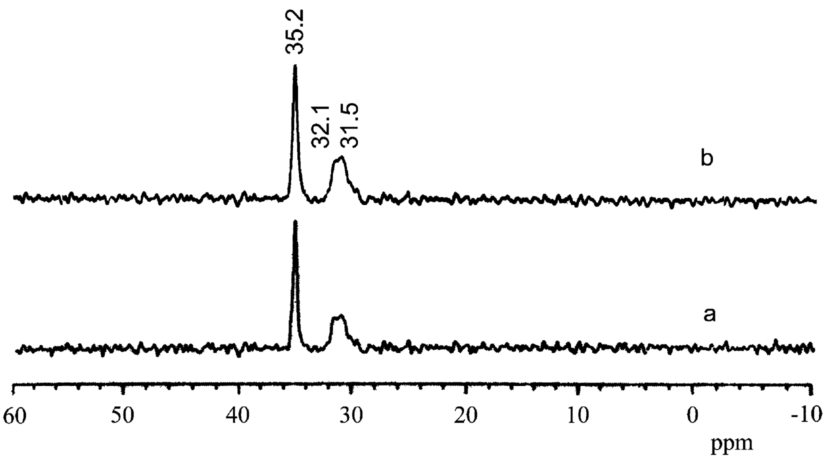


Fig. 4. ^{31}P(^{1}H) NMR spectra for **1**/SiO_2 containing 40% D_2O: (a) before propene hydroformylation; (b) after propene hydroformylation for 4 h.

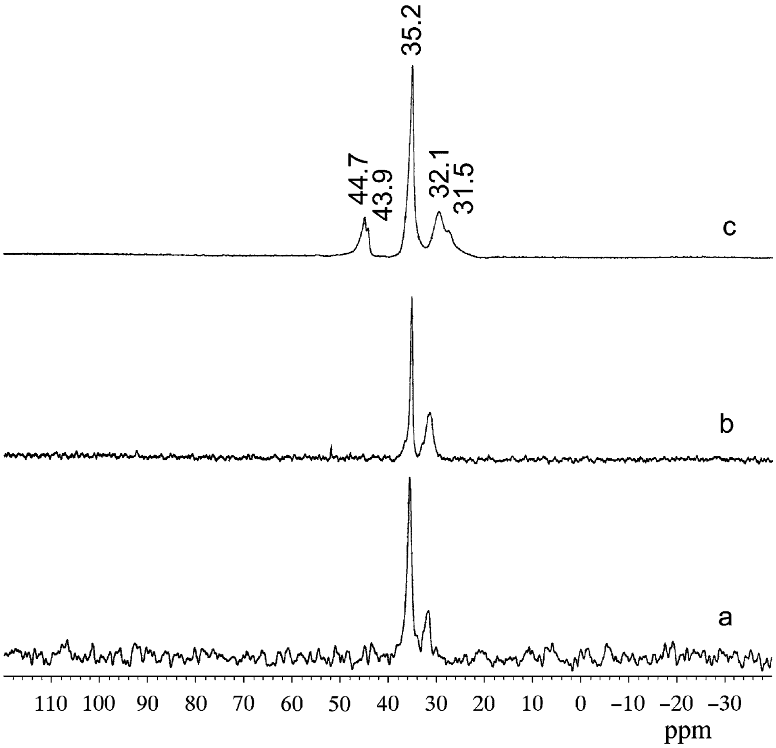


Fig. 5. $^{31}P(^1H)$ NMR spectra for **1**/SiO_2 containing 40% D_2O: (a) 0.0025 mmol **1**/γ-SiO_2; (b) 0.0125 mmol **1**/γ-SiO_2; (c) 0.2 mmol **1**/γ-SiO_2.

by those at 1992 and 1870 cm^{-1} for the **1**/SiO_2, respectively. After evacuation at 373 K for 2 h, the peak at 1992 cm^{-1} became of broadness while that at 1870 cm^{-1} increased in intensity as shown in Fig. 6c.

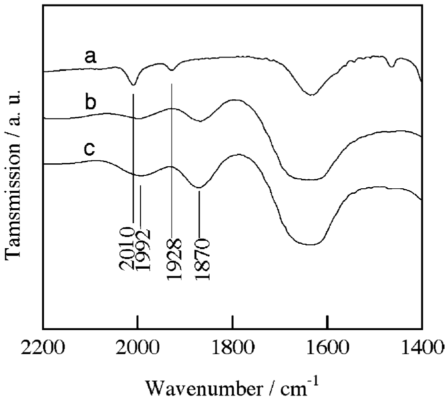


Fig. 6. FTIR spectra for: (a) **1**/KBr; (b) **1**/SiO_2; (c) **1**/SiO_2 after evacuation at 373 K for 2 h.

3.4. $^{31}P(^1H)$ NMR spectra of **1** *in the presence of solution base and acid*

Fig. 7A and B shows the spectra of $^{31}P(^1H)$ NMR and ^1H NMR for the complex **1** in D_2O solution in the presence of NaOH. It was observed that the intensity of chemical shift at $\delta = 35.1$ ppm for the OTPPTS increased slightly with the addition of NaOH, but no other new peaks produced. The corresponding ^1H NMR spectra revealed the peaks at $\delta = -9.56$ ppm keeping quartet splitting with the NaOH amount as shown in Fig. 6b, indicating that the bonding of Rh–H remained intact by adding NaOH up to high concentration. The broadness of the peaks at aryl-H range (7.1–7.7 ppm) may be due to the fast spin-spin interaction in the presence of NaOH. The results suggested that there were no change in structure of **1** in the presence of NaOH.

However, the $^{31}P(^1H)$ NMR spectra for the **1** changed remarkably in the presence of inorganic acids as shown in Fig. 7. When introducing HCl,

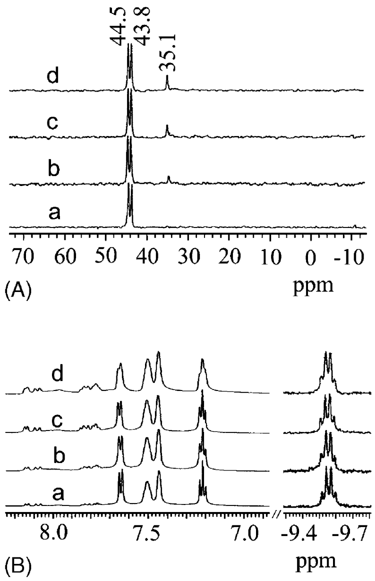


Fig. 7. (A and B) ^{31}P(^{1}H) NMR spectra for **1** in the presence of solution NaOH.

H_2SO_4, HNO_3 or H_3PO_4 different concentration, the peak intensities for the phosphorus of the complex **1** decreased drastically while the intensity for the OTPPTS increased with the acid amount. In the case of high concentration of acid, the phosphorus-31 peak due to the complex **1** became negligible, while the phosphorus-31 due to OTPPTS at 35.0 ppm and the new species at 27–30 ppm increased significantly. The results suggested that the structure of the complex **1** was unstable in the presence of acid media.

3.5. *Hydroformylation performance on SAPC*

Table 1 shows that propene hydroformylation performance on the catalysts of **1**/SiO_2, **1**/TPPTS/SiO_2 and **1**/Na_2CO_3/SiO_2 at 373 K, respectively. Lower activity but slightly higher regioselectivity to butylaldehyde on **1**/TPPTS/SiO_2 and **1**/Na_2CO_3/SiO_2 were obtained as compared to that on **1**/SiO_2. When a catalyst with a loading weight of complex **1** on SiO_2 higher than monolayer, it presented much lower catalytic activity for the propene hydroformylation. From the ^{31}P(^{1}H) NMR results and the catalysis in Table 1, we considered that active species on **1**/SiO_2 likely to be $[Rh(CO)(TPPTS)_2]_n$ (n = 1, 2) (phosphorus-31 showed a peak at about 32.1, 31.5 ppm) rather than intact **1** on SiO_2 (phosphorus-31 showed the twin-peaks at 44.7, 43.9 ppm). The coordination unsaturated species $[Rh(CO)(TPPTS)_2]$ which could be readily generated from $[Rh(CO)(TPPTS)_2]_n$ (n = 1, 2) at SiO_2 surface provided a possible coordinating position for activation of propene, leading to an increase in the reaction activity.

4. Discussion

We previously [8] reported that by the results of ^{31}P(^{1}H) MAS NMR characterization a large part of phosphine ligands TPPTS were not in the states of coordination in the SAPC prepared freshly from Rh(*acac*)$(CO)_2$ complex and TPPTS, and that a considerable quantity of the complexes containing two phosphine ligands with the chemical shift of 32.4 ppm (assigned to $[Rh(CO)TPPTS_2]$ species)

Table 1
Propene hydroformylation on **1**/SiO_2 catalyst[a]

Support	Rh loading (mmol $g_{SiO_2}^{-1}$)	L/Rh	Conversion (%)	n:i	STY (mmol h^{-1} g_{Rh}^{-1})	TOF (s^{-1})
SiO_2	0.3	3	31.4	1.6	1362	0.039
	0.03	3	18.7	1.7	8113	0.232
TPPTS/SiO_2[b]	0.03	30	3.3	2.3	1432	0.041
Na_2CO_3/SiO_2	0.03	3	4.8	2.0	2082	0.059

[a] Reaction conditions: $T = 373$ K, C_3H_6:CO:H_2 = 1:1:1 (v/v), total pressure = 1.0 MPa, GHSV (STP) = 9000 ml h^{-1} g_{cat}^{-1}. The data were achieved after 120 min when static state was reached.

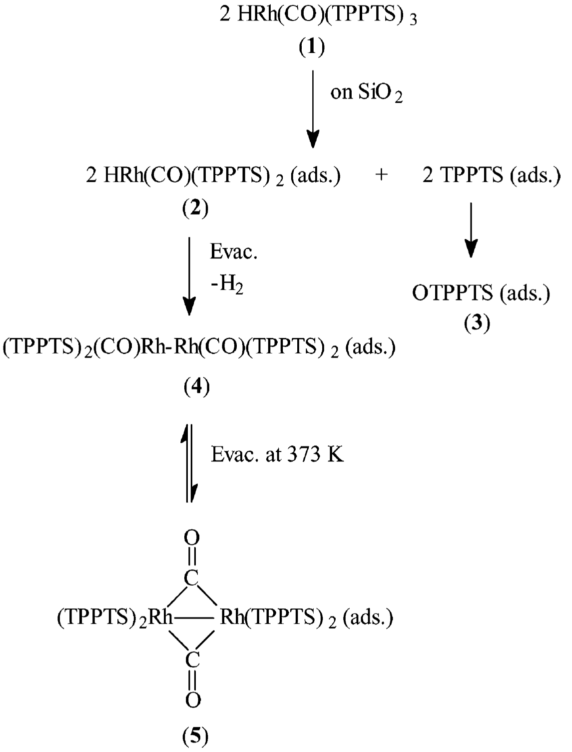
[b] The complex **1** was immobilized on SiO_2 after preimpregnation of the excessive TPPTS ligand.

were formed in-situ after starting of the reaction, which are considered as the catalytically active complex species responsible for hydroformylation. When the water-soluble complex **1** was immobilized on SiO_2, no typical twin phosphorus-31 chemical shifts at $\delta = 44.7, 43.9$ ppm, but new twin-peaks at $\delta = 32.1, 31.5$ ppm and significant increase in intensity at $\delta = 35$ for OTPPTS species were observed by the conventional solution $^{31}P(^1H)$ NMR (Fig. 2). The typical twin phosphorus-31 NMR chemical shifts could be detected while using SiO_2 preimpregnated with Na_2CO_3 or TPPTS (Na_2CO_3/SiO_2 or TPPTS/SiO_2) as supports (Fig. 3). The peaks at 32.1 and 31.5 ppm were estimated to be a TPPTS–Rh-complex containing phosphorus:rhodium ratio closely to 2:1, likely the species of $[Rh(CO)(TPPTS)_2]_n$ ($n = 1, 2$) at SiO_2 surface.

The acidic properties at the support surface were considered to be one of the main reasons that caused the structure change of the Rh-complex **1** while immobilization. Before loading the complex **1**, the SiO_2 support was pre-impregnated by TPPTS or Na_2CO_3, the $^{31}P(^1H)$ NMR spectra for the samples, thus, prepared, **1**/TPPTS/SiO_2 and **1**/Na_2CO_3/SiO_2, were found to be significant different from that for the **1**/SiO_2 as shown in Fig. 2b and c. The results suggested that use of TPPTS/SiO_2 and Na_2CO_3/SiO_2 as supports prevent the complex **1** from an interaction with the acidity at SiO_2 surface, leading to that the surface complex at **1**/TPPTS/SiO_2 and **1**/Na_2CO_3/SiO_2 could mainly remain the structure feature of the intact complex **1**. With the results of the pyridine–TPD for SiO_2 and Na_2CO_3/SiO_2, it is reasonable to deduce that the structure of **1** on support depends on the property of the support, particularly the acidity/polarity of the support.

We found that the Rh–TPPTS complex **1** could strongly interacted with unpretreated SiO_2 support, which resulted in the structure deformation while immobilization. The deformed complex at **1**/SiO_2 was suggested to be exited at the interfacial layer between the SiO_2 surface and the surface complex. Therefore, it becomes possible to determine the monolayer loading weight of the complex by solution $^{31}P(^1H)$ NMR technique by the observations of the structure changes. In the case of loading weigh less than 0.1 mmol Rh/γ-SiO_2, we found that the $^{31}P(^1H)$ NMR spectroscopy presented a signal at $\delta = 35.2$ ppm for OTPPTS and a signal at about $\delta = 30$ ppm for the species as shown in Fig. 5. The signals at 44.7 and 43.9 ppm for the complex **1** were appeared in the case of loading weight of 0.2 mmol Rh/γ-SiO_2, in which there were about 30 mol% of phosphorus species in the state of original complex **1**. It was estimated from the NMR results the monolayer loading of the Rh-complex **1** to be 0.14 mmol Rh/γ-SiO_2.

The coordination state of the Rh atom in the species of $[Rh(CO)(TPPTS)_2]_n$ was unsaturated in the case of $n = 1$. To understand the complex structure at SiO_2 more clearly, we measured the IR spectra of **1**/SiO_2 at different treatment conditions as shown in Fig. 6. The FTIR spectra for the **1**/SiO_2 shown that there were two peaks at 1992 and 1870 cm^{-1}. After evacuation at 373 K for 2 h, the relative intensity of the peak at 1987 cm^{-1} increased a little. By comparison to the FTIR data of the complex **1**, the peaks at 1992 and 1870 cm^{-1} at the **1**/SiO_2 might be due to the de-coordination of the ligands from the complex [19] and then the dimerization to a dinuclear complex as shown in the Scheme 1. The broad peak at



Scheme 1. A possible structure transformation of the complex **1** at SiO_2 surface.

1992 cm^{-1} may be due to the contributions from following species: the Rh–H stretching at the mononuclear complex **2** and the linear carbonyl species, and also the linear carbonyl species at dinuclear complex **4**. The overlaps of above species caused the broadness of the peak at 1992 cm^{-1}. The peak at 1870 cm^{-1} may be due to the contribution of bridge carbonyl in the dinuclear complex **5**. The treatment at 373 K caused further dehydrogenation to dimerization, thus, resulted in an increase in the peak intensity at 1870 cm^{-1}.

The results obtained indicate that there are de-coordination of the ligand TPPTS from **1** and oxidation of ligand TPPTS while deposition of the complex **1** onto SiO_2 due to the strong interaction of basic ligand TPPTS with acidic surface of the carrier silica–gel, forming a surface complex containing two phosphine ligands, which was further dehydrogenation and dimerization to dinuclear surface Rh–TPPTS complex most probably $[Rh(CO)(TPPTS)_2]_2$ (with the $^{31}P(^1H)$ NMR peak at ~32.1, 31.5 ppm). The dinuclear species were in-situ and readily activated to form a catalytic active species of $[Rh(CO)(TPPTS)_2]$ at the SiO_2 surface during hydroformylation condition. The deformed complexes with a ratio of Rh:TPPTS = 1:2 were stable enough during the propene hydroformylation (Fig. 5). The experiments also demonstrated that the de-coordination and oxidation could be partially/principally depressed when using Na_2CO_3/SiO_2 or $TPPTS/SiO_2$ as supports, which were supported by the NMR data for the complex **1** in the presence of NaOH and acids (Figs. 7 and 8). Higher catalytic activities for the hydroformylation of propene were achieved over **1**/SiO_2 than that on **1**/Na_2CO_3/SiO_2 due to the easier generation of the

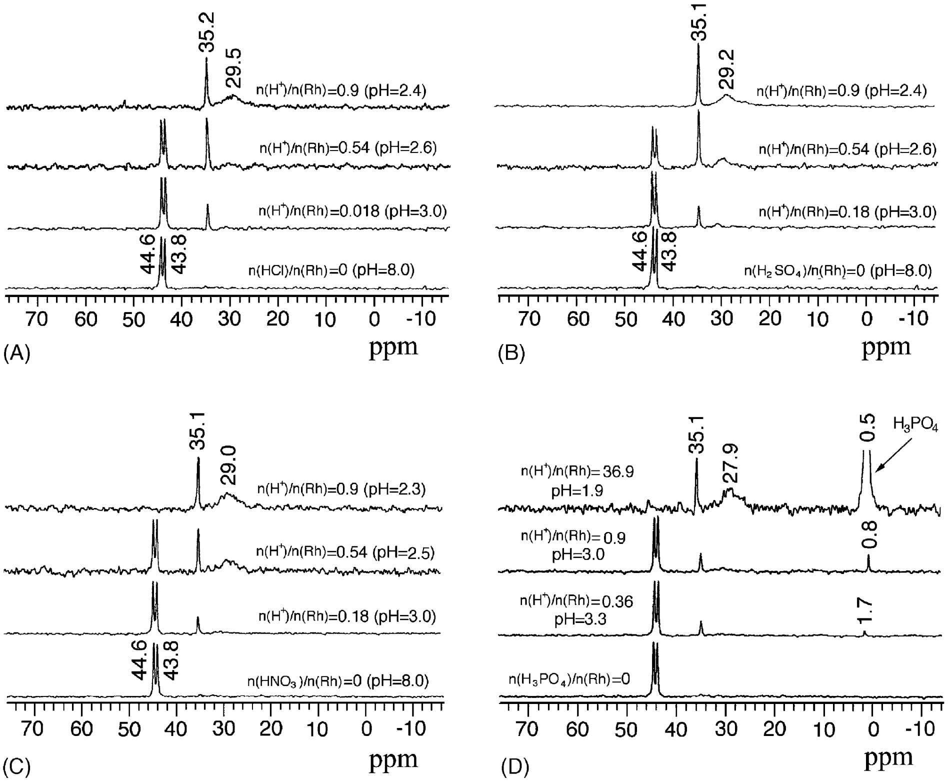


Fig. 8. (A–D) $^{31}P(^1H)$ NMR spectra for **1** in the presence of solution acids.

coordination unsaturated species $[Rh(CO)(TPPTS)_2]$ at **1**/SiO_2.

5. Conclusions

1. The strong interaction between the complex **1** and SiO_2 support surface was due to a interaction through the basic ligands TPPTS and the acidity at the SiO_2 surface, which resulted in the liberation of the coordinated TPPTS and the deformation of the complex **1** at SiO_2 by dehydrogenation and dimerization to form a new species of $[Rh(CO)(TPPTS)_2]_2$.
2. The de-coordination and oxidation could be partially/principally depressed when using Na_2CO_3/SiO_2 or TPPTS/SiO_2 as supports for immobilizing the complex **1**.
3. A higher catalytic activity in the propene hydroformylation was obtained on **1**/SiO_2 than that on **1**/Na_2CO_3/SiO_2.

Acknowledgements

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