

A multinuclear MAS NMR study on the stability of Ph₃P-Rh/SBA-15 catalysts for hydroformylation of propylene

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ABSTRACT

Multinuclear MAS NMR together with XRD and N₂ adsorption were employed to characterize the local structures of heterogeneous Ph₃P-Rh/SBA-15 and supported homogeneous HRh(CO)(PPh₃)₃/SBA-15 catalysts. It is found that Ph₃P-Rh complex can be tightly grafted on SBA-15 through the Si-O-Rh bonds while much less such bonds are formed in the supported homogeneous counterpart. This can be correlated to the longer catalytic life of heterogeneous PPh₃-Rh/SBA-15 for propylene hydroformylation.

1. INTRODUCTION

Hydroformylation of propylene yielding *n*-butanal and *iso*-butanal is one of the most important processes in the industrial application, representing approximately 75% of the world consumption of oxo chemicals [1, 2]. However, the practical application has been limited by difficulties in the catalyst-product separation [3]. We have reported that the heterogeneous catalyst Rh/SBA-15 modified by PPh₃ showed higher selectivity and stability for propylene hydroformylation than the supported homogeneous catalyst HRh(CO)(PPh₃)₃/SBA-15 [4]. In this study, multinuclear solid-state NMR is used to elucidate the local structures of the above catalysts. This includes the less routine ¹⁷O MAS NMR to illustrate the variations of the framework structures of the support. ²⁹Si and ¹H MAS NMR are carried out to understand different hydroxyls on the support and their interactions with the rhodium species. In this paper we report the investigation results of the interaction between the support SBA-15 and the rhodium species. Combining with other techniques such as XRD, N₂ adsorption, etc. the structure differences of these two types of catalysts have been revealed, which can be correlated to the higher stability of heterogeneous Ph₃P-Rh/SBA-15 catalyst in propylene hydroformylation.

2. EXPERIMENTAL

2.1 Sample preparation

The natural abundance of ^{17}O is only 0.037 %. In order to carry out the ^{17}O MAS NMR experiments, the ^{17}O enriched SBA-15 support (from Changchun Jilin University High Tech. Co. Ltd.) was prepared by heating the dehydrated sample in $^{17}\text{O}_2$ gas (Isotec) at 853 K for 12 h [5]. Catalysts $\text{PPh}_3\text{-Rh/SBA-15}$ and $\text{HRh(CO)(PPh}_3)_3\text{/SBA-15}$ with 1 wt % Rh were prepared according to the procedures in literature [4]. The support was impregnated with an aqueous solution of rhodium chloride (Shanghai July Chemical Co. Ltd.) using the incipient wetness method. After impregnation, the samples were dried at 373 K firstly, then calcined at 673 K in a quartz tube and finally reduced by H_2 at 673 K. The precursor was introduced into the PPh_3 solution in toluene and stirred for 0.5 h. The solvent was removed under vacuum at room temperature, and the resultant catalyst $\text{PPh}_3\text{-Rh/SBA-15}$ was stored in the argon atmosphere. $\text{HRh(CO)(PPh}_3)_3$ complex was synthesized as that reported in reference [6], and dissolved in toluene. Then SBA-15 was introduced into this solution and the mixture was stirred for 0.5 h. Finally the solvent toluene was removed under vacuum, and the catalyst $\text{HRh(CO)(PPh}_3)_3\text{/SBA-15}$ was obtained. All these experiments were finished in the argon protection.

2.2 NMR measurements

All MAS NMR measurements were carried out on a VARIAN Infinityplus-400 spectrometer using 7.5 and 4 mm probeheads. The ^{29}Si MAS NMR spectra with high power proton decoupling were recorded at 79.4 MHz with the samples spun at 4 kHz, $\pi/4$ pulse width of 1.9 μs , 360 s recycle delay and 120 scans. Before the ^1H MAS NMR experiments, samples were dehydrated at 473 K and a pressure below 10^{-2} Pa for 20 h. ^1H MAS NMR spectra were collected at 399.9 MHz with the samples spun at 10 kHz, $\pi/4$ pulse width of 1.3 μs , 4.0 s recycle delay and 200 scans. To obtain quantitative results from ^1H MAS NMR, all samples were weighed and the spectra were calibrated by measuring a known amount of 1,1,1,3,3,3-hexafluoro-2-propanol under the same conditions [7]. Chemical shifts of the ^{29}Si and ^1H NMR spectra were referenced to DSS. ^{17}O MAS NMR spectra were collected at 54.2 MHz with the samples spun at 15 kHz, $\pi/4$ pulse width of 0.9 μs , 1.0 s recycle delay and 30,000 scans and the chemical shift was referenced to water. The deconvolution of the spectra was conducted using dmfit software.

2.3 XRD and BET measurements

X-ray diffraction patterns were obtained at room temperature on a Rigaku D/Max-RB diffractometer using $\text{Cu K}\alpha$ radiation. Powder diffractograms of the samples were recorded over a range of 2θ values from 0.5 to 10 degrees under the conditions of 40 kV and 50 mA at a scanning rate of 0.5 deg min^{-1} . The nitrogen adsorption experiments were performed at 77 K on an ASAP 2000 system. The samples were outgassed at 473 K for 10 h before the measurements.

3. RESULTS AND DISCUSSION

Fig. 1 shows the low-angle XRD patterns of the samples. It can be seen that all the samples have three reflection peaks that can be indexed to the (1 0 0), (1 1 0) and (2 0 0) diffraction lines characteristic of the hexagonal structure. The ordered mesostructure of SBA-15 support is maintained after loading Rh- PPh_3 or Wilkinson complex $\text{HRh(CO)(PPh}_3)_3$. The intensity

of three reflections gradually decreases with loading the Rh complexes, which indicates the pore filling of the host SBA-15 support because pore filling can reduce the scattering contrast between the pores and the walls of the mesoporous material. Table 1 lists the BET surface areas of the samples, which are calculated from the N₂ physisorption isotherms. The surface area of SBA-15 decreases obviously after loading the rhodium complex. However, the BET surface area of supported homogeneous HRh(CO)(PPh₃)₃/SBA-15 decreases less than that of heterogeneous PPh₃-Rh/SBA-15. This may be due to the inhomogeneous dispersion of the Wilkinson complex on the SBA-15 support prepared by the impregnation method. These also indicate the inclusion of Rh complexes into the channels of SBA-15 and interactions may occur between the rhodium species and the SBA-15 support.

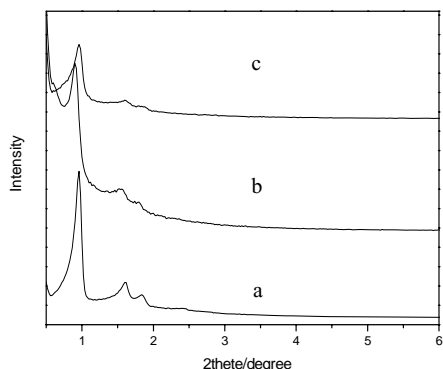


Fig.1. Low-angle XRD Patterns of SBA-15(a); PPh₃-Rh/SBA-15(b);HRh(CO)(PPh₃)₃/SBA-15 (c).

High-resolution ¹H MAS NMR is a useful and direct method for characterizing the hydroxyls in porous materials. Compared with IR, it can provide quantitative information on the interaction between the metal ions and the hydroxyl species on the support without the difficulties of extinction coefficients. The ¹H MAS NMR spectra of the catalysts are shown in Fig. 2. ¹H MAS NMR spectrum of SBA-15 exhibits two hydroxyl groupings i.e. single and hydrogen-bonded silanols at 1.7 and 2.4 ppm, respectively. Two new resonance peaks at about 3.2 ppm and 7.0 ppm can be seen, after loading heterogeneous catalyst PPh₃-Rh or impregnating homogeneous catalyst. The newly resonance peak at 7.0 ppm is assigned to PPh₃ and the peak at about 3.2 ppm can be attributed to the spillover hydrogen or physisorbed water [8]. After quantification, the total amount of hydroxyls on SBA-15 is about 2.0 mmol g⁻¹ after calibration by the external standard. The amount of single silanols at 1.7 ppm decreases more readily from 1.1 to 0.57 mmol g⁻¹ when loading heterogeneous catalyst PPh₃-Rh, and have no obvious change after impregnating homogeneous catalyst HRh(CO)(PPh₃)₃ (see Table 1). This indicates that the silanols on SBA-15 may react easily with the RhCl₃ precursors to form Si-O-Rh species, which immobilizes the heterogeneous PPh₃-Rh complex in SBA-15 support.

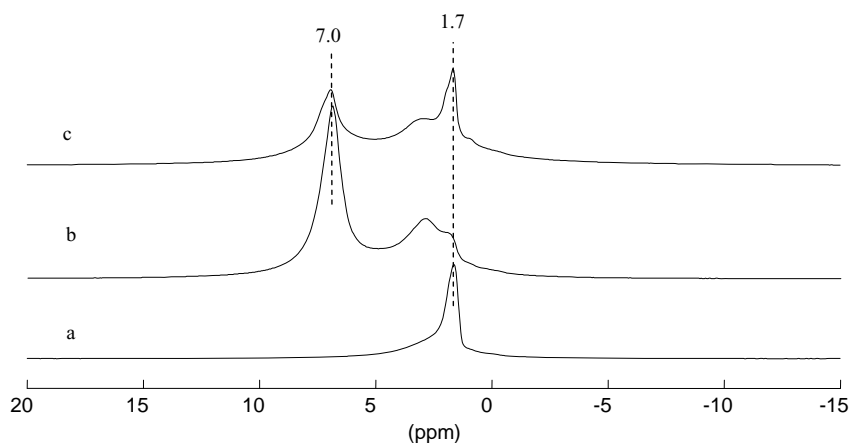


Fig. 2. ^1H MAS NMR spectra of SBA-15 (a); $\text{PPh}_3\text{-Rh/SBA-15}$ (b); $\text{HRh(CO)(PPh}_3)_3\text{/SBA-15}$ (c).

Fig. 3 displays the ^{29}Si MAS NMR spectra of the samples. There are three resonance peaks at -92 ppm, -101 ppm and -111 ppm, which can be assigned to Q^2 [$\text{Si(OSi)}_2(\text{OH})_2$], Q^3 [$\text{Si(OSi)}_3\text{OH}$] and Q^4 [Si(OSi)_4], respectively. After loading heterogeneous catalyst $\text{PPh}_3\text{-Rh}$, a new resonance peak centered at *ca.* -104 ppm is observed after deconvolution of the spectrum. It may be assigned to the [$\text{Si(OSi)}_3\text{ORh}$] species in terms of the chemical shift range, which may come from the interaction between the support SBA-15 and the rhodium species as shown by the ^1H MAS NMR measurement. However, for the supported homogeneous catalyst $\text{HRh(CO)(PPh}_3)_3$, this peak is relatively weak, which indicates that few [$\text{Si(OSi)}_3\text{ORh}$] species may be formed in this catalyst.

Table 1
Surface areas and the silanol concentrations of the catalysts.

| | SBA-15 | $\text{PPh}_3\text{-Rh/SBA-15}$ | $\text{HRh(CO)(PPh}_3)_3\text{/SBA-15}$ |
|---|--------|---------------------------------|---|
| BET surface area/ m^2g^{-1} | 702 | 395 | 503 |
| support | | | |
| Single silanol concentration/ mmolg^{-1} | 1.1 | 0.57 | 1.09 |
| support ^a ($\pm 5\%$) | | | |

^a. silanol concentrations were determined from ^1H MAS NMR measurement using $\text{CF}_3\text{CH(OH)CF}_3$ as the external standard.

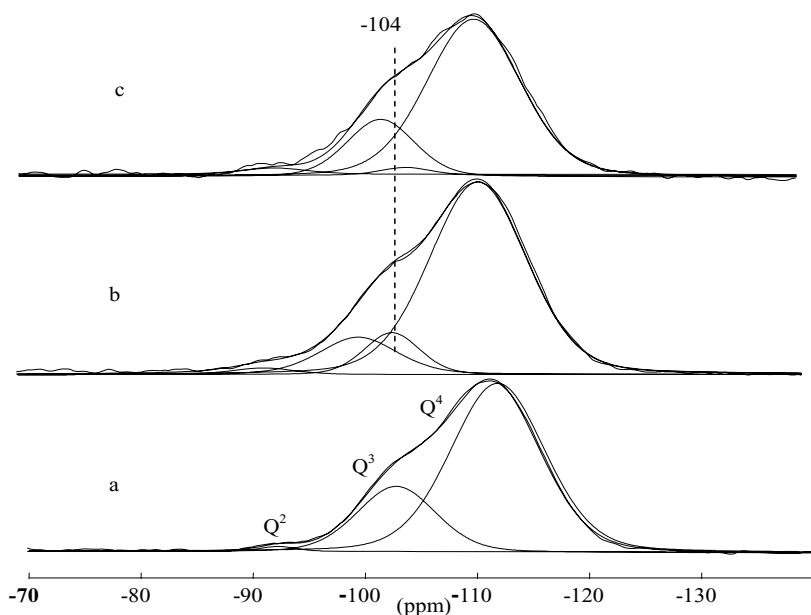


Fig. 3. Deconvoluted ^{29}Si MAS NMR spectra of SBA-15 (a); $\text{PPh}_3\text{-Rh/SBA-15}$ (b); $\text{HRh(CO)(PPh}_3)_3\text{/SBA-15}$ (c).

In order to further confirm the Si-O-Rh species, the unusual ^{17}O MAS NMR experiments were conducted. The oxygen constitutes a major part of the zeolite framework and it is via the oxygen atoms that many loading (adsorbed) species bind to the zeolite framework. There few works have been performed in this field due to both the very low natural abundance, and the broad ^{17}O resonances typically observed for the framework sites caused largely by the 2nd order-quadrupolar interaction. In metal silicate gels the formation of M-O-Si bonds can be clearly detected by ^{17}O NMR and makes structural modelling much less ambiguous than that based on ^{29}Si MAS NMR alone [9]. Fig. 4 shows the ^{17}O MAS NMR spectra of the support SBA-15 and the catalyst $\text{PPh}_3\text{-Rh/SBA-15}$. After deconvolution of the spectra, we can assign the resonance peaks individually. The broad quadrupolar lines 1 and 2 in the spectrum of SBA-15 can be assigned to Si-O-Si and Si-O-H species, respectively [10].

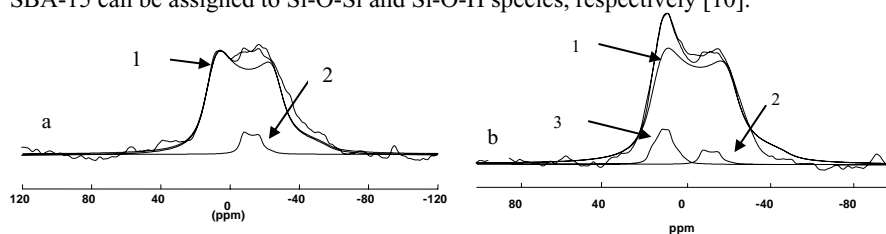


Fig. 4. Deconvoluted ^{17}O MAS NMR spectra of SBA-15 (a); $\text{PPh}_3\text{-Rh/SBA-15}$ (b).

After loading the heterogeneous catalyst $\text{PPh}_3\text{-Rh}$, there is a new resonance line 3 appeared in the deconvoluted spectrum, which can be related to Si-O-Rh species [10]. However, this peak could not be well resolved in the supported homogeneous catalyst

HRh(CO)(PPh₃)₃/SBA-15 under the same conditions, which indicates few Si-O-Rh species presented in this sample.

4. CONCLUSIONS

These results indicate that Rh complexes can be included into the mesochannels of SBA-15. The silanols on SBA-15 may interact with RhCl₃ to form Si-O-Rh species. Thus, Ph₃P-Rh complex can be tightly grafted on SBA-15 through the Si-O-Rh bonds. Therefore, the heterogeneous catalyst PPh₃-Rh/SBA-15 is more stable than the supported homogeneous catalyst HRh(CO)(PPh₃)₃/SBA-15. This may be the reasons why the heterogeneous catalyst PPh₃-Rh/SBA-15 has longer catalytic life for propylene hydroformylation than the supported homogeneous catalyst HRh(CO)(PPh₃)₃/SBA-15 [4].

ACKNOWLEDGEMENTS

We thank Prof. C. P. Grey and Dr. L. Peng of SUNY at Stony Brook for the preparation of the ¹⁷O enriched SBA-15. We also are grateful for the financial support of the National Natural Science Foundation of China (No. 20673111) and the Ministry of Science and Technology of China.

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