Insoluble Wilkinson catalyst RhCl(TPPTS)$_3$ supported on SBA-15 for heterogeneous hydrogenation with and without supercritical CO$_2$

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The insoluble Wilkinson catalyst RhCl[P(m-$C_6H_4SO_3$)Na)$_3$]$_3$ changes from inert to very active by supported on mesoporous material SBA-15, and the catalyst is stable, easy to separate from products, clean, and can be reused directly. This catalyst combines the advantages of homogeneous catalysts and heterogeneous catalysts very well.

KEY WORDS: hydrogenation; Wilkinson; support; homogeneous heterogeneous catalysts.

1. Introduction

Homogeneous catalysts are molecularly dissolved in the reaction fluids, which provide easy access to the catalytic sites. Therefore, homogeneous catalysts have some attractive properties, such as high activity and selectivity. However, many homogeneous catalytic systems cannot be commercialized because of the difficulties associated with separation of the products and the catalyst [1]. On the other hand, heterogeneous catalysts – usually solids – are in a different phase from the reactants, which reduces separation problems, but their activity is usually lower due to the limited access to the catalytic sites. Combination of the advantages of homogeneous and heterogeneous catalysts has been an interesting topic for years, and many successful examples have been reported. One of the effective routes to achieve this is to immobilize homogeneous catalysts on solid supports [1,2].

Hydrogenation reactions play an important role in chemical industry. Wilkinson catalyst RhCl(PPh$_3$)$_3$ is the most familiar homogeneous catalyst for hydrogenation of alkenes. But catalyst separation is a main problem to solve. Recently, some new approaches of catalyst immobilization were reported. For example, Jessop *et al.* [3] reported a poly(ethylene glycol) and supercritical (SC) CO$_2$ biphasic Wilkinson catalytic system for catalyst separation and recycling. Mehnert *et al.* [2a] reported an ionic liquid supported Wilkinson catalytic system. Tumas *et al.* [4] studied a RhCI(TPPDS)$_3$ water/CO$_2$ emulsion catalytic system for hydrogenation of alkenes. Some other water/organic biphasic Wilkinson catalytic systems were also investigated [5]. Quasi Wilkinson catalysts immobilized on porous SiO$_2$ have also been used for the hydrogenation of alkenes [6], and satisfactory result was obtained.

As far as we know, all the Wilkinson catalysts supported on the solid supports are anchored on the solid surface by special interaction between the catalyst and the solid, such as hydrogen bonding, and the catalysts themselves are soluble in the reaction fluids if they are not supported, which is favorable to the effective contacting of the reactants and the catalysts. It can be imaged that an insoluble Wilkinson catalyst immobilized on a solid surface is not easy to be leached by the reaction fluid because of the insoluble nature. In other words, the catalyst will be more stable, and the product will not contain the catalyst. In this work, we performed experiments to test the activity of an insoluble Wilkinson catalyst supported on a molecular sieve. SBA-15, which was a mesoporous silica material with tunable pore diameter, surface area and pore volume [7], was used as a solid support, and RhCl(TPPTS)$_3$ was used as the catalyst. The ligand TPPTS was (3, 3′, 3″-phosphinidynetris (benzenesulfonic acid) trisodium salt), TPPTS = P(m-$C_6H_4SO_3Na$)$_3$, which is insoluble in hydrocarbon, but is soluble in water [8]. It was demonstrated that if not supported, the activity of catalyst was very low for hydrogenation of olefins without solvent or in SC CO$_2$. But the supported catalytic system was very active, selective, stable, reusable, and easy to separate from products, and clean. The catalyst combined the advantages of both homogeneous and heterogeneous catalysts very well.

2. Experimental

The SBA-15 silica was synthesized as reported by Zhao *et al.* [7] using Pluronic P123 triblock copolymer

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(EO_{20} $PO_{70}EO_{20}$). In the experiment, 4.0 g Pluronic P123 was dissolved in 150 g of 1.6 M HCl solution. Then, 8.50 g of tetraethyl orthosilicate (TEOS) and 3.0 g 1,3,5-trimethylbenzene (TMB) was added. The resulting mixture was stirred for 5 min and then kept at 308 K for 24 h without stirring, and then aged for 2 days at 353 K. The solid product was filtered, and dried in an oven for 4 h at 413 K. To completely remove organic materials, the as-synthesized product was subsequently calcined in air for 6 h at 823 K. The surface area, pore diameter, and pore volume were 910 m^2 g^{-1}, 22.6 nm, and 1.9 cm^3 g^{-1}, respectively. The catalyst was prepared by an incipient-wetness procedure without any pretreatment of SBA-15. Firstly, 0.06 mmol TPPTS was added to 10 mL water, then 0.01 mmol $Rh_2(CO)_4Cl_2$ was added to the solution, and a yellow solution was obtained. One gram of SBA-15 was added into the solution. After 5 h stirring, the solution turned to mild yellow, and the SBA-15 turned to a yellow solid. The solid was dried by a rotatory evaporator and then in a vacuum oven at 323 K for 10 h. After cooled, the supported Wilkinson solid catalyst was obtained, and placed into a nitrogen-protected vessel. The CO in $Rh_2(CO)_4Cl_2$ was substituted completely by the ligand TPPTS, and $RhCl(TPPTS)_3$ was formed and supported on SBA-15. This was confirmed by the FTIR spectra of $Rh_2(CO)_4Cl_2$ (figure 1a) and the prepared catalyst (figure 1b) determined in this work. The four peaks of CO [9] at 2021, 2036, 2080, 2102 cm^{-1} in the spectrum of $Rh_2(CO)_4Cl_2$ (figure 1a) can be observed. These peaks disappeared in the spectrum of the prepared catalyst. The surface of the SiO_2 is full of hydroxyl groups, which can interact with the TPPTS via hydrogen bonding, as was evidenced by the change of the absorption of hydroxyl at 3436 cm^{-1}, [10] which is shown in figure 1b. The possible structure of the catalyst prepared in this work is given in figure 2.

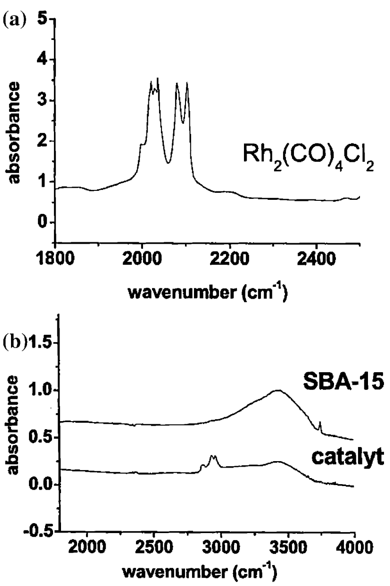

Figure 1. FTIR spectra of $Rh_2(CO)_4Cl_2$ (a) and SBA-15 and catalyst $RhCl(TPPTS)_3$ supported on SBA-15 (b).

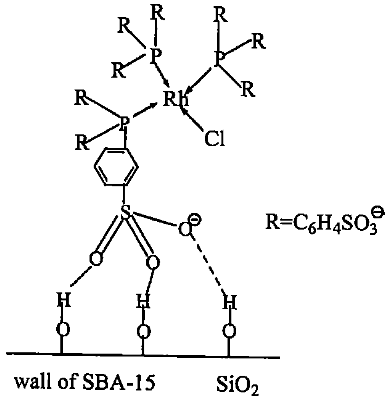

Figure 2. Immobilization of $RhCl(TPPTS)_3$ on the SBA-15 via hydrogen bonding.

The hydrogenation was carried out in a 100 mL stainless steel autoclave with a diameter of 40 mm. In a typical solvent free experiment, 0.5 g catalyst (contain 0.01 mmol Rh) and 0.10 mol interested olefin were charged into the autoclave, and the air in the autoclave was replaced by H_2 of 2.0 MPa for 3-times. The reaction system was stirred by a mechanical stirrer (1000 rpm) at 293.2 K, and the pressure of hydrogen was maintained at 4.0 MPa for the solvent free reactions. The composition of the reaction mixture was monitored frequently by GC (Agilent 4890D). The catalyst deposited at the bottom of the autoclave after the stirrer was stopped, and the catalyst could be directly reused after removing the product. For the reaction in SC CO_2, the initial pressure of hydrogen was 5.0 MPa at 308.2 K and the initial total pressure was 16.0 MPa after CO_2 was charged, and hydrogen was not added in the reaction process, In order to compare the results with and without SC CO_2, the initial pressure of hydrogen was also 5.0 MPa for the solvent free reaction at 308.2 K.

3. Results and discussion

The results of the solvent free hydrogenation of cyclohexene, 1-hexene, and styrene are listed in Table 1 (Entry 2–7). The catalyst showed very high activity for the hydrogenation reactions. After reaction, the products were collected and analyzed by AAS (atomic absorption spectrum) method for Rh atom, and Rh was not detectable (the limitation was 5 ppm). In other words, the leaching of catalyst by the reaction fluids was negligible. This is easy to understand because, besides the hydrogen bonding of catalyst with the surface of the support, the catalyst is not soluble in the reactants or products. This is one of the advantages to use the insoluble catalyst. The catalyst after being used once

Table 1
Performance of the insoluble Wilkinson catalyst for hydrogenation

Entry	Substrate	H_2 Pressure (MPa)	Time (min)	Temperature (K)	Conv.[a] (%)	TOF [b] (min^{-1})
1[c]	cyclohexene	4.0	40	293	<1	
2[d]	cyclohexene	4.0	40	293	93	233
3[d]	cyclohexene	4.0	70	293	>99	143
4[d]	styrene	4.0	30	293	90	300
5[d]	styrene	4.0	60	293	>99	167
6[d]	1-hexene	4.0	20	293	92	460
7[d]	1-hexene	4.0	40	293	>99	250
8[d]	cyclohexene	5.0	30	308	>99	333
9[c]	cyclohexene	5.0	25	308	>99	400
10[f]	cyclohexene	5.0	40	308	<2	
11[g]	cyclohexene	4.0	40	293	5	

Reaction conditions: 0.5 g catalyst containing 0.01 mmol RhCl(TPPTS)$_3$ for Entries 2–9, and the added Rh complexes were also 0.01 mmol for Entries 1 and 10; substrate 0.10 mol; stirrer speed 1000 rpm; for Entries 1–7 hydrogen pressure was maintained at 4.0 MPa in the reaction process; for Entries 8–10 initial hydrogen pressure was 5.0 MPa and hydrogen was not added in the reaction process.

[a] Substrate conversion.

[b] TOF defined as mole hydrogenation product per mole (rhodium) per minute.

[c] complex RhCl(TPPTS)$_3$ was used without support for the solvent free reaction.

[d] supported catalyst was used the solvent free reactions.

[e] reaction was carried out in SC CO_2 using the supported catalyst.

[f] reaction was carried out in SC CO_2 using the unsupported catalyst.

[g] the catalyst after used once was washed by 2 ml water for three times.

was washed for 3-times by water and it exhibited very low catalytic activity (Entry 11), which excludes the existence Rh metal nanoparticles as catalyst.

In order to confirm the function of immobilization, we also carried out the hydrogenation of cyclohexene using unsupported RhCl(TPPTS)$_3$ as the catalyst directly (Entry 1) [11] and other conditions were the same as those for Entry 2 in Table 1. The conversion was $< 1\%$. The very low activity may result from the fact that the catalyst was insoluble in the reactant. The main reason for the high activity of the catalyst supported onto the porous material is that the SBA-15 used has large surface area (910 $m^2\ g^{-1}$). The catalyst can be considered as a "heterogeneous" catalyst with molecular nature in the sense that it is insoluble and is highly dispersed on a porous material with large surface area. In other words, the hydrogenations are heterogeneous but the catalyst has the molecular nature.

The work by Cole-Hamilton and coworkers [12] demonstrated that the unsupported rhodium complexes with suitable ligands had high activity and selectivity for the hydroformylation of 1-hexene in SC CO_2, although the catalysts were insoluble in SC CO_2. Hydrogenations of hydrocarbons in SC CO_2 have been extensively investigated. [12] In this work, we also conducted hydrogenation of cyclohexene reaction in SC CO_2 using the supported and the unsupported catalysts prepared in this work, and the results are also listed in (Entries 9,10). The immobilized catalyst showed high activity, while that of the unsupported catalyst was not active. Entries 8 and 9 indicate that supported catalyst is more active in SC CO_2. The main reason is that the diffusivity of SC CO_2 is much larger [13].

As discussed above, the catalyst could be separated easily from the hydrogenation products and reused after the reaction. In this work, the catalyst was reused 20-times for the hydrogenation of cyclohexene without any solvent, and its deactivation was not detectable.

In summary, the insoluble Wilkinson catalyst RhCl(TPPTS)$_3$ immobilized on SBA-15 is very active for the hydrogenation of alkenes, while the unsupported catalyst shows very low activity. Thus, the inert catalyst is converted into a highly active heterogeneous catalyst, and the leaching of the catalyst was negligible due to its insoluble nature. The products can be separated easily from the catalyst, and the catalyst can be reused directly.

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