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COMMUNICATION

Thermoregulated phase-transfer iridium nanoparticle catalyst: highly selective hydrogenation of C=O bond for α, β-unsaturated aldehydes while C=C bond for α, β-unsaturated ketones

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In the same catalytic system, thermoregulated ligand $Ph_2P(CH_2CH_2O)_{22}CH_3$-stabilized iridium nanoparticles exhibited a totally different orientation for the hydrogenation of unsaturated carbonyl compounds, namely, highly selective hydrogenation of the C=O bond for α, β-unsaturated aldehydes while the C=C bond for α, β-unsaturated ketones.

Catalytic hydrogenation of α, β-unsaturated aldehydes and ketones is very important for the synthesis of fine chemicals.[1] The hydrogenated products are different (Fig. 1) by the presence of two functional groups with similar reactivity: C=O and C=C bond, thereby the chemoselective hydrogenation of α, β-unsaturated aldehydes and ketones has been a very prolific research field over the past few decades. Among these intensive studies, although the highly chemoselective hydrogenation remains as a challenging task, more difficulty is that one can orientate the different hydrogenated tendency for α, β-unsaturated aldehydes and ketones under the condition as similar as possible. For example, using different hydrogen donors and Ir (I) complexes, Farnetti et al. realized that unsaturated aldehydes could be hydrogenated to the unsaturated alcohols, while unsaturated ketones were selectively hydrogenated to the corresponding ketones.[2] In addition, Himeda reported that selective hydrogenations of the C=C bond of enone were observed under basic conditions and the ketone moieties can be hydrogenated under acidic conditions.[3] However, these studies mainly focused on the metal complex catalysis. Moreover, the major drawbacks of these catalytic systems are the use of supplementary ligands or reagents associated with difficulties such as product separation and metal catalyst recycling.

Soluble transition-metal nanoparticles have drawn much attention because of their high catalytic efficiency and unique physicochemical properties. Based on density functional theory (DFT) and the Langmuir-Hinshelwood (LH) mechanism, the reactive bonds in the case of catalytic hydrogenation are the ones involved in chemisorption on metal surface. Therefore, the problem of selective hydrogenation can be ascribed in a first rough approximation to the factors which control the adsorption mode of substrate molecules on the metal surface. In terms of catalytic hydrogenation of α, β-unsaturated aldehydes and ketones, the key factors, such as the nature of metallic catalyst,[4] support material,[5] particle size,[6] presence of a second metal,[7] preparation method,[8] or temperature,[9] have been proposed to influence the hydrogenation selectivity, but there is no report about the totally different hydrogenation orientations in case the catalytic system is the same.

The design of new catalytic process with both recyclability and chemoselectivity is desired because it does not require tedious separation procedures and yields fewer by-products. Based on the concept of thermoregulated phase-transfer catalysis (TRPTC), our group synthesized thermoregulated ligand $Ph_2P(CH_2CH_2O)_nCH_3$(n = 16 or 22)-stabilized noble metal (Rh, Pt, Ru, Ir, Pd, and Au) nanoparticles (NMNPs) and realized their thermoregulated phase-transfer function in the aqueous/alcoholic biphasic system.[10] The general principle of this catalytic process can be simply described as follows: The system consists of the upper 1-pentanol phase and the lower water phase. The as-prepared NMNPs are in the water phase at room temperature. Afterward, the water/1-pentanol mixture is heated gradually to a higher temperature under stirring, and then the as-prepared NMNPs are transferred into

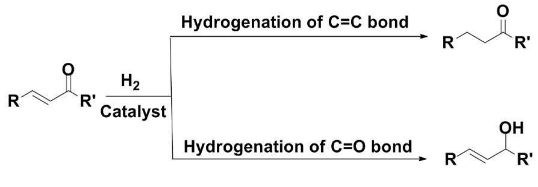

Fig. 1 Reaction pathways for the chemoselective hydrogenation of α, β-unsaturated aldehydes and ketones

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Table 1 The chemoselective hydrogenation of CAL using the as-prepared Ir-NPs.[a]

Entry	Temp. (℃)	Time (min)	P_{H2} (MPa)	Conv. (%)[b]	Sel. (%)[b,c]
1	50	60	1	73	>99
2	60	60	1	93	>99
3	70	60	1	>99	>99
4	80	60	1	>99	95
5	90	60	1	>99	87
6	70	20	1	68	>99
7	70	40	1	80	>99
8	70	80	1	>99	96
9	70	60	0.5	94	>99
10	70	60	1.5	>99	96
11	70	60	2	>99	93

[a] Reaction conditions: 1-pentanol 4 mL, water 4 mL containing 6.7×10^{-3} mmol Ir-NPs ($Ph_2P(CH_2CH_2O)_{22}CH_3$/Ir = 1 (molar ratio)), CAL/Ir = 100 (molar ratio), 50 mg of *n*-decane as internal standard. [b] Determined by GC and GC-MS. [c] Selectivity for cinnamyl alcohol and the main by-product was 3-phenyl-1-propanol.

Table 2 The reusability of the as-prepared Ir-NPs for the chemoselective hydrogenation of CAL.[a]

Entry	Time(h)	Conv.(%)[b]	Sel.(%)[b,c]
1	1	>99	>99
2	1	>99	98
3	1	87	97
4	3	90	98
5	4	93	98
6	6	93	95
7	10	97	95

[a] Reaction conditions: 1-pentanol 4 mL, water 4 mL containing 6.7×10^{-3} mmol Ir-NPs ($Ph_2P(CH_2CH_2O)_{22}CH_3$/Ir = 1 (molar ratio)), CAL/Ir = 100 (molar ratio), 50 mg of *n*-decane as internal standard, T = 70 ℃, 1 MPa H_2. [b] Determined by GC and GC-MS. [c]Selectivity for cinnamyl alcohol and the main by-product was 3-phenyl-1-propanol.

the upper 1-pentanol phase, in which the reaction proceeds homogeneously. As soon as the reaction is completed and the system is cooled to room temperature, the as-prepared NMNPs could return to the aqueous phase. Therefore, by simple phase separation the as-prepared NMNPs can be easily separated from products. It is noteworthy that the phase transfer efficiency of NMNPs from 1-pentanol to aqueous or vice versa isn't less than 99.9%. Herein, we employed the as-prepared Ir-NPs as catalyst for the hydrogenation of α, β-unsaturated aldehydes and ketones. The catalytic activity, selectivity and reusability of the catalyst, the substrate scope as well as the possible hydrogenation mechanism were explored.

For the study reported here, cinnamaldehyde (CAL) was firstly chosen as the model substrate for the hydrogenation of α, β-unsaturated aldehydes and ketones in the water/1-pentanol biphasic system. Various reaction conditions were studied and the results were summarized in Table 1(see ESI† for full experimental details). The effect of reaction temperature was investigated in the range of 50-90 ℃ at 1 MPa H_2 for 60 min (Table 1, entries 1-5). It was noteworthy that the conversion of CAL reached a maximum value (>99%) as the reaction temperature increased to 70 ℃, whereas the selectivity to C=O group began to decrease when the reaction temperature exceeded 70 ℃. As can be observed therein (Table 1, entries 3, 6-8), longer reaction time hindered the enhancement of the selectivity towards the cinnamyl alcohol. Generally, increasing pressure may lead to the decrease of the selectivity in the selective catalytic hydrogenation. As shown in Table 1 (entries 3, 9-11), Ir-NPs exhibited the best selectivity towards cinnamyl alcohol at 1 MPa H_2 along with comparative high conversion. As a consequence, we established the optimal reaction conditions (1 MPa H_2, 70℃, 60 min) for the chemoselective hydrogenation of CAL in the water/1-pentanol biphasic system.

Considering that the lifetime is an important aspect for a catalyst, the reusability of Ir-NPs was examined. After each reaction, the upper organic phase was separated from the lower catalyst-containing phase. And the lower catalyst-containing phase was directly reused in the next reaction run. The results were summarized in Table 2. Although the conversion began to decrease in the third cycle (Table 2, entry 3), prolonging the reaction time can make the conversion ≥ 90%. (Table 2, entries 4-7).

In the reusability experiments, we also investigated the factors, which resulted in the decrease of catalyst activity. Firstly, the leaching of Ir in the upper 1-pentanol phase was studied by ICP-AES. The results were shown in Table S1. We can know that the leaching of Ir, in each cycle, gradually decreased as the number of cycle experiments increased. After three cycles, the amount of Ir leaching was 10 wt. %. In order to investigate the influence of Ir leaching, the fresh catalyst (90 wt.%, relative to the initial Ir-NP catalyst) was used to catalyze the hydrogenation of CAL in the same reaction conditions, and the conversion was 89% (The real conversion for the Ir-NP catalyst after three cycles was only 68% within 1 h). So, we further investigated the size and the morphology of Ir-NPs by TEM test after the third cycle (see Fig. S1). Careful analysis of the diameter revealed that the size of Ir-NPs changed to 2.1 nm (2.1±0.2 nm, Fig. S1) with respect to the freshly prepared Ir-NPs (1.9±0.3 nm, Fig. S2). Within the range of allowable error, the size remained almost the same. However, the morphology of Ir-NPs was different and became more agglomerated, indicating that the stabilizer could not maintain the stabilization of Ir-NPs very well. So we evaluated the loss of thermoregulated ligand after one cycle with the aid of ICP-AES. The result showed that the loss of thermoregulated ligand was up to 12 wt.%. Subsequently, we added fresh thermoregulated ligand (12 wt. %) to the solution of catalyst after one cycle. The result showed that the selectivity to C=O bond was restored

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to > 99%. In addition, we also recycle the catalyst nearby 75% conversion (see Table S2). Similar results were observed compared with >99% conversion. From the above-mentioned experiment data, we could infer that the reason for deactivation of the catalyst may result from the loss of Ir and the morphology change of Ir-NPs. Moreover, thermoregulated ligand played an important role on the catalyst's reactivity and selectivity.

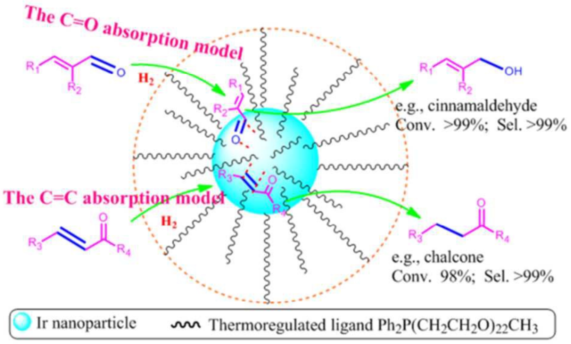
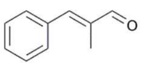
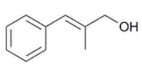
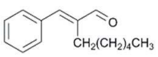
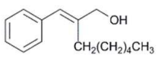
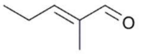
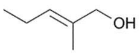
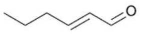
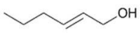
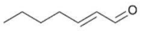
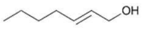
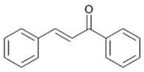
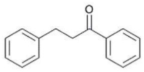
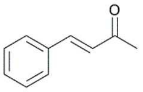
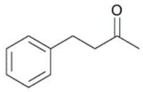
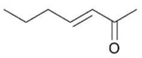
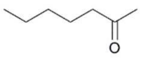
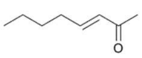
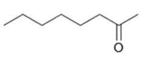
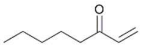
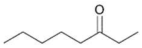


Fig. 2 Two different hydrogenation orientations for α, β-unsaturated aldehydes and ketones.

Table 3 The chemoselective hydrogenation of different α, β-unsaturated aldehydes and ketones.[a]

Entry	Substrate	Product	Time (h)	Conv. (%)[b]	Sel. (%)[b,c]
1			3	96	>99
2			7	90	>99
3			7	72	98
4			3	>99	96
5			3.5	>99	94
6			9	98	>99
7			2.5	76	90
8			3.5	>99	>99
9			4	>99	>99
10			1	>99	>99

[a] Reaction conditions: 1-pentanol 4 mL, water 4 mL containing 6.7×10^{-3} mmol Ir-NPs (Ph$_2$P(CH$_2$CH$_2$O)$_{22}$CH$_3$/Ir = 1 (molar ratio)), Substrate/Ir = 100 (molar ratio), 50 mg of *n*-decane as internal standard, T = 70 ℃, 1 MPa H$_2$. [b] Determined by GC and GC-MS. [c] The main by-product was the fully hydrogenated product.

Once the best reaction conditions were established, we applied it to the catalytic hydrogenation of chalcone, surprisingly, a completely different hydrogenation orientation towards the C=C group occured. Through simply prolonging the reaction time, the conversion of chalcone was up to 98 % together with a very high chemoselectivity (> 99%) (Table 3, entry 6). Inspired by this exciting preliminary result, we further explored the catalytic hydrogenation of different α, β-unsaturated aldehydes and ketones. From Table 3, we knew that α, β-unsaturated aldehydes were selectively hydrogenated to the unsaturated alcohols (Table 3, entries 1-5), while α, β-unsaturated ketones were hydrogenated to the corresponding ketones (Table 3, entries 6-10). It was noteworthy to mention that chemoselectivity for unsaturated alcohols/saturated ketones was not less than 96%, except that trans-2-octenal and benzylideneacetone showed a relatively low selectivity but still had a value of 94% and 90%, respectively (Table 3, entries 5 and 7).

To our knowledge, among the reported catalytic hydrogenation of α, β-unsaturated aldehydes and ketones in the same catalytic system,[11] thermoregulated ligand Ph$_2$P(CH$_2$CH$_2$O)$_{22}$CH$_3$-stabilized Ir-NPs exhibited a totally different hydrogenation orientation, namely, highly selective hydrogenation of the C=O bond for α, β-unsaturated aldehydes while the C=C bond for α, β-unsaturated ketones. The excellent selectivity towards unsaturated alcohol to some extent was not surprising, because relevant studies and calculations had shown that Ir-NP catalyst could facilitate the C=O adsorption in the hydrogenation of α, β-unsaturated carbonyl compounds.[12] Herein, we did not add any supplementary ligands or reagents to change the properties of Ir-NP catalyst, yet the hydrogenation orientations were totally different, thus we supposed two different adsorption models to illustrate the reason: one was the C=O adsorption model for α, β-unsaturated aldehydes and the other was the C=C adsorption model for α, β-unsaturated ketones (see Fig.2). In the former, the C=O bond would be preferentially hydrogenated over the C=C bond, leading to the high selectivity to unsaturated alcohols.Several recent works had directly or indirectly proposed the similar C=O adsorption model for the chemoselective hydrogenation of cinnamaldehyde.[13] However, the situation would be different in the case of α, β-unsaturated ketones. This may be due to the fact that thermoregulated ligand Ph$_2$P(CH$_2$CH$_2$O)$_{22}$CH$_3$ around the nanoparticle surface constrained the geometry of metal active sites, permitting only the best favorable

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adsorption models to access. Assuming a simple geometric model did not illustrate well the real reaction manner, but it could guide our next work to get more information. So, further studies are under way in our laboratory.

Conclusions

In summary, thermoregulated phase-transfer iridium nanoparticles stabilized by thermoregulated ligand $Ph_2P(CH_2CH_2O)_{22}CH_3$ were very active and easily recyclable for the chemoselective hydrogenation of cinnamaldehyde in the water/1-pentanol biphasic system. More encouragingly, the Ir-NP catalyst, in the same catalytic system, exhibited a totally different hydrogenation orientation, namely, α, β-unsaturated aldehydes can be selectively hydrogenated to the unsaturated alcohols, meanwhile α, β-unsaturated ketones can be selectively hydrogenated to the corresponding ketones.

Acknowledgements

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Insert Table of Contents Graphic and Synopsis Here

Thermoregulated phase-transfer iridium nanoparticles exhibited a totally different hydrogenation orientation for *α, β*-unsaturated aldehydes and ketones.