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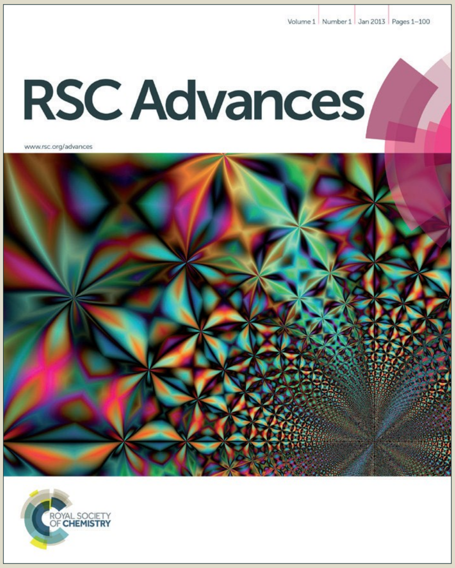

Selective Hydrogenation of α-Pinene to Cis-pinane over Ru Nanocatalysts in Aqueous Micellar Nanoreactors

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Abstract: D-α-tocopheryl polyethylene glycol 1000 succinate (TPGS-1000) stabilized Ru(0) nanoparticles were prepared and characterized. These nanoparticles were employed to selectively hydrogenate α-pinene to cis-pinane, with a small amount of Na_2CO_3 present, reaction rates could be increased significantly, and the reaction media could be readily recycled. TEM, CLSM, IR and leaching experiments were employed to quantify the advantages of catalytic system. The procedure is environmentally friendly. It offers a reference for the catalytic hydrogenation of other hydrophobic natural products.

Key words: α-pinene; hydrogenation; micelle; nanoreactor; water

1. Introduction

Metal nanoparticles have attracted a growing interest in the international scientific community in the last few decades. Such nanoparticles exhibit many novel chemical and physical properties that differ from their bulk counterparts.[1] These novel properties are attributed to the surface effect, quantum size effect and quantum tunneling effect. They are widely used in various kinds of catalytic reactions and fuel cells due to their large surface area, small size and high-activity,[2] such as hydrogenation, hydrogenolysis, oxidation, biomass conversion and Fischer-Tropsch synthesis reaction.[3] Therefore, synthesis of metal nanoparticles has attracted a tremendous amount of attention from researchers over the past two decades. Micellar method is one of important ways widely used to prepare nano-metal catalyst with accurately controlled particle sizes and shapes.[4]

Micelles formed by addition of amphiphiles to an aqueous reaction medium. The hydrophilic chains extended into the water and the lipophilic chains pointed to the interior. Then the surfactant assembled into micelles with a lipophilic 'core'.[5] For the fabrication of metal nanoparticles, the use of micelles for nanoparticle synthesis has attracted much interest because of its potential advantages. The reaction is restricted in the lipophilic core, the growth of the obtained metal nanoparticles can be controlled by the size of the nonpolar core, and the metal nanoparticles can be stabilized. Metal nanoparticles protected by micelles can be thought as micellar catalysis.[6] Micellar catalysis in water can play an important contributing role in green chemistry. Early review papers on the subject of micellar catalysis date back to the late 1970s.[7] Since that time, this area has witnessed a rapid growth. Today, many valued reactions take place within the lipophilic core of self-aggregated nanomicelles. This type of catalyst, which combines the advantages of both homogeneous and heterogeneous catalysts, can be regarded as a ‘‘semi-homogeneous catalyst’’: the metal nanoparticles are heterogeneous in nature but, similar to homogeneous catalysts, their high degree of dispersion in the solvent facilitates the access of reactant molecules.[8] Furthermore, a high local concentration of the reactants in the nanometer-sized micelles leads to accelerated transformations and increased selectivities.

Compared to traditional “soaps”, the vitamin E derived amphiphiles TPGS offer outstanding properties in terms of reactivity, selectivity, and catalyst recycling in many transition-metal-catalyzed reactions.[9] Such as asymmetric hydrosilylation reactions, cross-couplings, Trifluoromethylation of heterocycles , asymmetric intramolecular hydrocarboxylations. Could all be carried out in ≤5 wt % TPGS/water micellar catalysis at room temperature.[10] However, nanoparticles prepared using TPGS micelles as a stabilizer have seldom been reported. In this paper, we designed a catalyst of Ru(0) nanoparticles protected by TPGS-1000 micelles in aqueous solution. The catalytic system was used in the hydrogenation of α-pinene to produce cis-pinane, which is highly desirable materials for fine chemistry, numerous derivatives, such as linalool, dihydromyrcenol and other terpenes series spices have been prepared from such intermediates.[11]

2. Results and discussions

2.1 Impact of surfactant concentration

Table 1 Screening of the weight percent of TPGS-1000 for the conversion of α-pinene [a]

Entry	Weight percent (%)	Average Diameter (nm) [b]	Size (nm) [c]		Viscosity (Cp) [d]	Zeta potencial (mV)	Conv. (%)	Select. (%)
			TPGS	Ru(0)/TPGS				
1	0	-	-	-	1.12	-	6.0	96.7
2	0.25	2.63 ± 0.15	12.3	17.3	1.28	12.2	52.5	98.5
3	0.50	2.47 ± 0.07	10.6	15.1	1.32	23.5	61.3	99.2
4	1.00	2.19 ± 0.09	10.5	14.2	1.43	29.3	59.0	99.0
5	1.50	2.63 ± 0.16	10.0	13.6	1.50	31.2	50.7	98.9

[a] Conditions: substrate (2 mmol), catalyst (0.01mmol), H_2 (0.5 MPa), temperature (50 °C), time (1.5 h). [b] Measured using TEM, the results represent error margin of 95% confidential intervals. TEM images were shown in Fig. S3. [c] Measured using DLS. [d] Measured at 16 °C.

The results from varying the amount of TPGS-1000 from 0 to 1.5 weight percent for the reaction were shown in Table 1. The conversion and selectivity were poor in the control experiment performed ‘on water’ (entry 1), this confirmed the importance of micellar catalysis in facilitating hydrogenation in aqueous media. The conversion of α-pinene increased with the weight percent of TPGS-1000 (entries 2 and 3), and decreased with further increased in TPGS-1000 percent (entries 4 and 5). This could be ascribed to a combination of the following factors: On one hand, Ru(0) particle size decreased with increasing the amount of TPGS-1000, and the catalyst activity increased. Ru(0)/TPGS-1000 micelle size also decreased from 17.3 nm to 13.6 nm, the zeta potential of Ru(0)/TPGS-1000 micelle increased with increasing the amount of TPGS-1000, these leaded Ru(0) nanoparticles became more stable.[12] Furthermore, the number of micelles increased with the amount of TPGS-1000 rose further, the interfacial area between two phases would also increase.[13] As a result, the reaction was accelerated. However, the decreased activity observed as the weight percent of TPGS-1000 exceeded a certain value. It was probably due to micelle sizes were decreased, which left less room for the substrate to diffuse into micelles. Furthermore, the viscosity of the mixture was increased with the amount of TPGS-1000 increased (1.25 Cp to 1.50 Cp), which may have interfered with the impingement of the reactant molecules.[14] Hence, we selected 0.5% TPGS-1000/H_2O for subsequent experiments.

2.2 Effects of metal salts on α-pinene hydrogenation

Table 2 Effects of metal salts on the conversion of α-pinene [a]

Entry	Salt	Weight (mg)	Size (nm) [b]	Conv. (%)	Select. (%)
1	$H_3O_{40}PW_{12}$	2.5	15.9	50.3	99.0
2	$CoCl_2$	2.0	16.3	51.5	98.8
3	NaCl	2.0	17.1	58.0	99.1
4	Na_2CO_3	2.0	19.7	99.7	98.8
5	Na_2CO_3	10.0	39.8	99.1	98.3
6	NaOH	2.0	18.7	95.6	97.5

[a] Conditions: substrate (2 mmol), catalyst (0.01mmol), H_2 (0.5 MPa), temperature (50 °C), time (1.5 h). [b] Measured using DLS.

It is known that the size of TPGS-derived micelles can be strongly increased in the presence of metal salt, leading to faster reactions in cross-coupling and ring-closing olefin metathesis.[15] To establish whether this effect can also be utilized in hydrogenation reaction catalyzed by Ru(0) nanoparticle catalyst, dynamic light scattering (DLS) measurements of a Ru(0)/TPGS-1000 solution were carried out (Table 2). Interestingly, the addition of salt to the Ru(0)/TPGS-1000 solution made the micellar sizes become larger. But the impact on the conversion was different. When adding a small amount of acidic salts and neutral salts, the conversion were decreased (entries 1,2,3 compared with entry 3 in Table 1). However, the limited conversion could be increased dramatically by adding 2mg of Na_2CO_3 (entry 5) or NaOH (entry 7). With further increased the amount of Na_2CO_3, the conversion and selectivity were declined to some degree (entry 6). Attempted to figure out the cause of the increased conversion, we designed a series of experiments to explore this phenomenon. The research started with the evaluation of pH effects on the hydrogenation of α-pinene over Ru catalyst (As Ru catalyst was resistant to corrosion and oxidation, it provided reliable results over the whole pH range) [16]. Experiments were carried out at a pH range from 0.51 to 12.9, adjusted with HCl to obtain an acidic and NaOH for a basic reaction medium. The results were presented in Fig. 1. Without the addition of acid or base the reaction mixture has an initial pH of 2.1. A decrease of the pH to 0.95 and 0.51 led to a decrease of the conversion from 61.3% to 47.5% and 43.1%. By a sharp contrast, changed the pH to higher values of 10.2 and 11.2 induced a markedly increased in the conversion of α-pinene. Even higher pH of 11.5 and 12.9 led to a gradually reduced conversion was also observed. Nevertheless, the conversion of α-pinene was almost unchanged when the reaction system was free of TPGS-1000 micelles. These results indicated high pH had no directly impact on Ru(0) nanoparticles and α-pinene, but it was favorable to hydrogenation of α-pinene in micellar system. The Ru(0) nanoparticles before the reaction (Fig.S3) and after the reaction (Fig. 4B) were measured using TEM, the results showed that there were almost no change in the sizes of the Ru(0) nanoparticles after adding 2 mg Na_2CO_3 in the hydrogenation (pH=11.2). Furthermore, The infrared spectroscopy was also used to characterize the change of Ru(0) nanoparticles under higher pH (Fig. 2). The appearance of the shoulder peak around 1600 cm^{-1} suggested that the interactions between Ru(0) and TPGS-1000 were enhanced, and Ru(0) nanoparticles became more stable in the micelles.[17] Hence, the acceleration by Na_2CO_3 could be ascribed to a combination of the following factors: On one hand, TPGS-1000 micelles were enlarged, and the internal volume capacity of the lipophilic 'core' increased. This could accommodate more substrates in the reaction. On the other hand, Na_2CO_3 was added to the reaction system and provided an alkaline environment. Alkaline environment was favorable to hydrogenation of α-pinene in micellar system. Furthermore, alkaline conditions could improve the mobility of lipophilic chain. The mass transfer rate between aqueous phase and lipophilic 'core' was accelerated, which was affects both reaction rate and product separation procedure.[18] In addition, after Na_2CO_3 was added in the hydrogenation reaction, Ru(0) nanoparticles were uniformly dispersed in aqueous (Fig S4), provided an effective catalytic system. Moreover, α-pinene also dispersed evenly in the semi-homogeneous catalyst during hydrogenation (Fig S5). The biphasic interface area was significantly increased, and the energy barrier of phase transfer was effectively minimized.[19] The combination of the aforementioned factors created highly advantageous conditions for acceleration of the reaction.

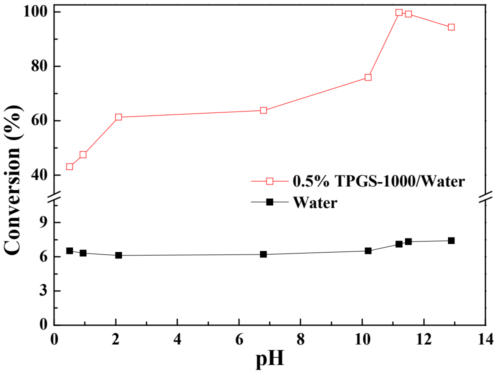


Fig. 1 Conversion of the hydrogenation of α-pinene over Ru(0) nanoparticles as a function of pH. Reaction condition: H_2 (0.5 MPa), temperature (50 °C), time (1.5 h), 0.5 mol% Ru.

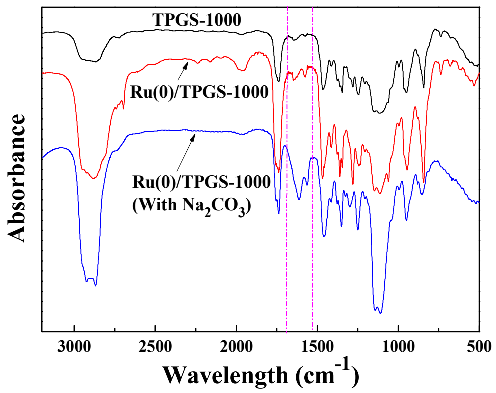


Fig. 2 IR spectra of the Ru(0)/TPGS-1000.

2.3 Recyclability of the catalyst

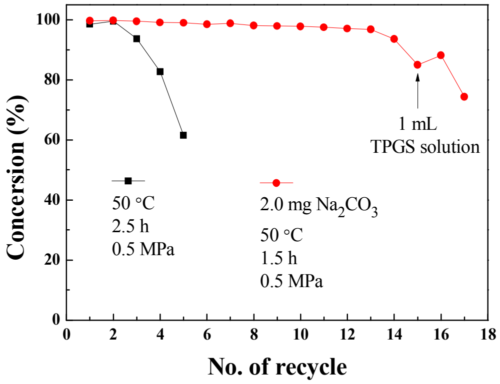


Fig. 3 Recycling of the aqueous reaction mixture for the conversion of α-pinene

Another characteristic of this process was the opportunity to recycle the contents of the entire reaction mixture. When the reaction was complete, the product was extracted with a single organic solvent (ethyl acetate) in reactor (5×0.5 mL). The organic phase was removed with syringe to ensure the product and any starting materials were removed as completely as possible (Fig. S5). Remaining in the water were the surfactant, Na_2CO_3, Ru(0) catalyst and thimbleful of ethyl acetate. Addition of fresh α-pinene (0.2730 g) and H_2 (0.5 MPa), a new reaction could be conducted as described for the initial run. As illustrated in Fig. 3, this process could be repeated more than ten times with a small decrease in conversion. However, when there was no Na_2CO_3 in the mixture, this process could be repeated only one cycle. The reduced conversion may be related to the particle size of the Ru(0) nanoparticles. TEM was employed to measure particle size and shape. As shown in Fig. 4, after one catalytic cycle, the particle size of the Ru(0) nanoparticles increased, and aggregation occurred without Na_2CO_3 in the mixture. Some of Ru(0) nanoparticles gathered into clumps (Fig. 4A), presumably leading to the decrease in catalytic activity during the recycling experiments. Ru(0) nanoparticles gathered into clumps also could be observed in the catalyst phase after reaction (Fig. S4). Nevertheless, when Na_2CO_3 was added in the mixture and the reaction system was in alkaline environment, Ru(0) nanoparticles displayed a homogeneous distribution after one catalytic cycle (Fig. 4B). Even after fifteen cycles, only a small part of Ru(0) nanoparticles aggregation occurred (Fig. 4C). Furthermore, this gradually decreased conversion was probably due to diffusion of ethyl acetate into the micelles, which left less room for the substrate.[20] This problem can be solved either by removal of excess ethyl acetate under reduced pressure or by extending the time for phase separation. We also tested the catalyst for Ru(0) leaching, which is an important criterion in terms of recyclability. 1 g of extraction was dissolved in aqua regia and tested by ICP-AES analysis. Over the 1 cycle, no Ru(0) leaching was observed. Only 0.2% of the Ru(0) catalyst was lost in the 17 cycles. This result demonstrated the high stability of the Ru(0) catalyst in hydrogenation of α-pinene under alkaline environment.

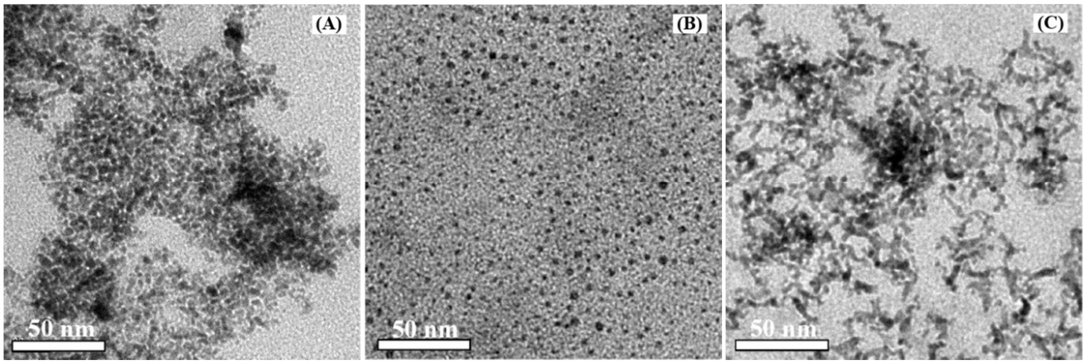


Fig. 4 TEM images of Ru(0) nanoparticles in various recycle stages. A: after 1 cycle without Na_2CO_3. B: after 1 cycle. C: after 15 cycles.

2.4 Hydrogenation of α-pinene at room temperature

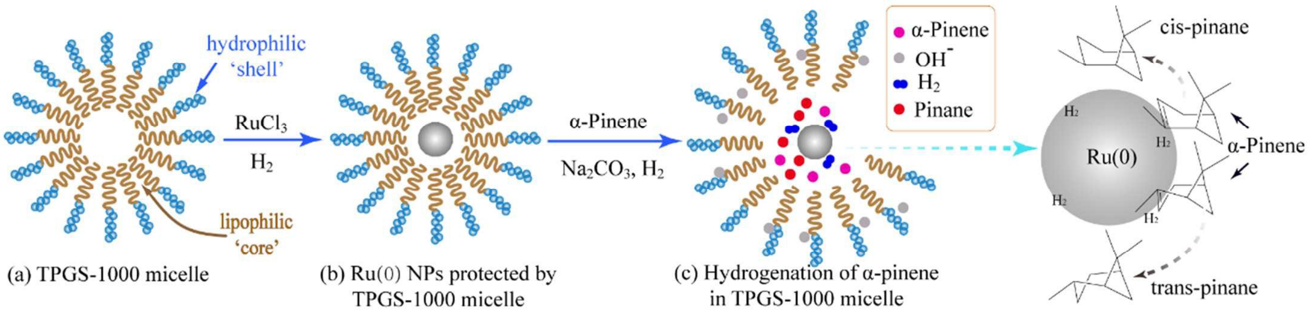
Moreover, unlike most hydrogenation of α-pinene that occur best at high temperatures and high H_2 pressure,[21] these procedure also could proceed smoothly at normal pressure and room temperature. The results of α-pinene hydrogenation at ambient temperature were summarized in Table 3. The conversion of α-pinene was poor at ambient temperature (entry 1), but increased significantly with Na_2CO_3 was added (entries 2 and 3). Some examples previously studied by Nowicki and co-workers were directly compared (entries 4 and 5).[22] The TOF were improved, while reaction times are comparable. We also compared to a classical catalyst such as Pd/C (entry 6), Ru(0)/TPGS-1000 had a better result on selectivity for cis-pinane than Pd/C. This illustrated that Ru(0)/TPGS-1000 was an efficient catalyst for hydrogenation of α-pinene under alkaline environment.

Table 3 Direct comparisons with other catalysts at room temperature [a]

Entry	Catalyst	Salt	Reaction medium	*P* (MPa)	*T* (°C)	Time (h)	Conv. (%)	Select. (%) [b]	TOF (h^{-1}) [c]
1	Ru(0)	-	TPGS-1000 [d]	0.1	20	12	22.0	98.6	3.7
2	Ru(0)	Na_2CO_3	TPGS-1000 [d]	0.1	20	5	64.3	98.5	25.7
3	Ru(0)	Na_2CO_3	TPGS-1000 [d]	0.1	20	9	99.5	98.7	22.1
4 [e]	Ru(0)	-	Me-γ-CD [d]	0.1	20	9	>99.9	95	11.1
5 [e]	Ru(0)	-	HEA16Cl [d]	0.1	20	30	>99.9	88	3.3
6 [f]	Pd/C	-	water	0.1	20	9	57.2	80.8	-

[a] Conditions: substrate (2 mmol), catalyst (0.01mmol), Na_2CO_3 (2 mg). [b] Selectivity: The percentage of cis-pinane in the product. [c] Turnover frequency defined as converted number of mol of substrate per mol of ruthenium per hour. [d] The surfactant was dissolved in water. [e] The data were referenced from literature 22. [f] 2 mg of Pd/C substituted for Ru(0)/TPGS-1000 in the hydrogenation.

2.5 The mechanism of reaction



Scheme 1 Mechanism of the hydrogenation of α-pinene

During the preparation of Ru(0) nanoparticles, amphiphilic surfactant TPGS-1000 was dissolved in aqueous. The hydrophilic heads were extended into the water. The lipophilic ends were pointed to the interior and shielded from water. Then, the amphiphilic surfactant TPGS-1000 was assembled into spherical micelles with lipophilic cores (Scheme 1(a)). When the hydrophilic Ru(III) was reduced to lipophilic Ru(0), Ru(0) nanoparticles were embedded into the lipophilic cores and protected by micelles (Scheme 1(b)). In the procedure of hydrogenation of α-pinene, α-pinene and H_2 were easily solubilized in the lipophilic cores.[5] In this micro-circumstance, micelles could be considered as nanoreactors. Reactions were divided and limited into the nanoreactors ((Scheme 1(c)).[23] These nanoreactors were beneficial for promoting the substrate to interact with the Ru(0) catalyst, and the reaction was accelerated.[24] Furthermore, α-pinene dispersed evenly in the semi-homogeneous catalyst (Fig S5), and the biphasic interface area was significantly increased. Under such conditions, the energy barrier of phase transfer was effectively minimized, and the reaction rate was greatly improved.

In an effort to determine the source of hydrogen atoms in the product pinanes, hydrogenation of α-pinene was carried out under our standard conditions replacing water with D_2O (Scheme S1). Hydrogenation in D_2O afforded the nondeuterated cis-pinane and trans-pinane. This indicated that both hydrogen atoms were arose from H_2, and the aqueous medium plays no role in providing H_2. In addition, this also suggested that hydrogenation of α-pinene were took place in the lipophilic core between the metal and the hydrogen-containing micelles ((Scheme 1(c)).[5]

2.6 The scope of the catalyst

Table 4 Scope of the hydrogenation in TPGS-1000 micelles [a]

Entry	Substrate	Salt	Conv. (%) [b]	Product (Select. %) [b]	Time (h)	TOF (h^{-1})
1	Octene	-	84.1	Octane (>99)	1.0	168.2
2		Na_2CO_3	99.9	Octane (>99)	1.0	199.8
3	Toluene	-	81.2	Methylcyclohexane (>99)	1.5	108.3
4		Na_2CO_3	99.9	Methylcyclohexane (>99)	1.5	133.2
5	Styrene	-	95.6	Ethylbenzene (91.3) Ethylcyclohexane (8.7)	1.5	127.5
6		Na_2CO_3	99.9	Ethylbenzene (6.4) Ethylcyclohexane (93.6)	2.0	99.9
7	Nitrobenzene	-	5.2	Aniline (>99)	1.5	6.9
8		Na_2CO_3	10.6	Aniline (>99)	1.5	14.1
9[c]	Nitrobenzene	-	85.8	Aniline (98.8) Cyclohexylamine (1.2)	1.5	114.4
10[c]		Na_2CO_3	98.9	Aniline (>99)	1.5	131.9
11	Phenol	-	89.5	Cyclohexanol (98.5) Cyclohexanone (1.5)	1.5	119.3
12		Na_2CO_3	99.9	Cyclohexanol (>99)	1.5	133.2
13	Cyclohexene	-	77.3	Cyclohexane (>99)	1.0	154.6
14		Na_2CO_3	99.9	Cyclohexane (>99)	1.0	199.8

[a] Conditions: substrate (2 mmol), Ru(0) catalyst (0.01mmol), H_2 (0.5 MPa), temperature (50 °C), Na_2CO_3 (2 mg). [b] Determined by GC-MS. [c] Ru(0) was replaced with Pd(0), the detailed information was placed in S1.2.

Lastly, to further demonstrate the potential for this mild, green catalyst to be used in other hydrogenation reactions, an expanded study was undertaken examining several types of arene derivatives and terminal olefin. The results were summarized in Table 4. Remarkably, all the hydrogenation reactions were accelerated by Na_2CO_3. Cyclohexene (entries 13,14) and octene (entries 1,2) were completely transformed in a very short time. Some interesting results in term of selectivity have been obtained in the hydrogenation of styrene, the aromatic ring was hydrogenated after added Na_2CO_3 (entry 6). This indicated that the regioselective hydrogenation of the exocyclic C–C double bond in the case of styrene was possible (entry 5 and entry 6). In the hydrogenation process of nitrobenzene, Ru(0) (entries 7,8) nanoparticles were inert to these hydrogenation conditions. Pd(0) (entries 9,10) has much higher activity than Ru(0) nanoparticles.[25] Interestingly, the aqueous phase was clear and colorless after hydrogenation of phenol (entry 11). This was presumably due to the phenol destroyed the structure of micelles. Ru(0) nanoparticles were absolutely aggregated into clumps and deposited in the bottom of the reactor. However, this damage was greatly weakened after added Na_2CO_3 (entry 12). Ru(0) nanoparticles were dispersed evenly in the aqueous phase after reaction.

3 Conclusions

In summary, hydrogenation of α-pinene could be performed in water typically at room temperature by employing nanoreactors formed from the commercial available surfactant TPGS-1000. This procedure was environmentally friendly, limited amounts of water were used as the reaction media, and only an in-reactor extraction with a minimal amount of a single, recoverable organic solvent. Additionally, with as little as 2 mg of Na_2CO_3 present, reaction rates could be increased significantly, and the reaction media could be readily recycled. Lastly, these reactions took place in high yields and stereoselectivity, thereby offering considerable potential for applications to other hydrophobic natural products in hydrogenation reactions.

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References

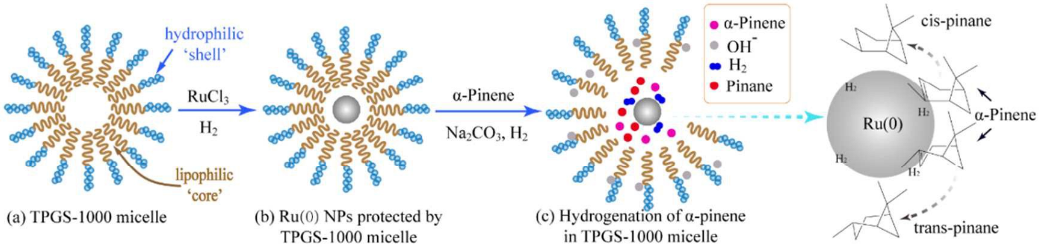
1. (*a*) M. H. Liu, J. Zhang, J. Q. Liu and W. W. Yu, *J. Catal.*, 2011, **278**, 1. (*b*) X. Q. Huang and N. F. Zheng, *J. Am. Chem. Soc.*, 2009, **131**, 4602.
2. (*a*) D. S. Wang and Y. D. Li, *Adv. Mater.*, 2011, **23**, 1044. (*b*) N. Yan, J. G. Zhang, Y. Y. Tong, S. Y. Yao, C. X. Xiao, Z. C. Li and Y. Kou, *Chem. Commun.*, 2009, **29**, 4423. (*c*) B. Hua, M. Li, Y. F. Sun, Y. Q. Zhang, N. Yan, J. Chen, J. Li, T. Etsell, P. Sarkar and J. L. Luo, *J. Mater. Chem. A*, 2016, **4**, 4603. (*d*) B. Hua, N. Yan, M. Li, Y. Q. Zhang, Y. F. Sun, J. Li, T. Etsell, P. Sarkar and J. L. Luo, *Energy Environ. Sci.*, 2016, **9**, 207.
3. (*a*) S. Bulut, Z. Fei, S. Siankevich, J. Zhang, N. Yan and P. J. Dyson, *Catal. Today*, 2015, **247**, 96. (*b*) J. Zhang，M. Ibrahim，V. Collière，H. Asakura，T. Tanaka, K. Teramura, K. Philippot and N. Yan, *J. Mol. Catal. A-Chem.*, 2016, Doi:10.1016/j.molcata.2016.01.014. (*c*) X. D. Mu, D. G. Evans and Y. Kou, *Cat. Lett.*, 2004, **97**,151. (*d*)H. Wang, W. Zhou, J. X. Liu, R. Si, G. Sun, M. Q. Zhong, H. Y. Su, H. B. Zhao, J. A. Rodriguez, S. J. Pennycook, J. C. Idrobo, W. X. Li, Y. Kou and D. Ma, *J. Am. Chem. Soc.*, 2013, **135**, 4149. (*e*) G. X. Chen, Y. Zhao, G. Fu, P. N. Duchesne, L. Gu, Y. P. Zheng, X. F. Weng, M. S. Chen, P. Zhang, C. W. Pao, J. F. Lee and N. F. Zheng, *Science*, 2014, **344**, 495. (*f*) Y. Z. Wang, S. De and N. Yan, *Chem. Commun.*, 2016, **52**, 6210.
4. (*a*) N. Semagina, E. Joannet, S. Parra, E. Sulman, A. Renken, L. Kiwi-Minsker, *Appl. Catal. A. Gen.*, 2005, **280**, 141. (*b*) D. J. Gavia, M. S. Maung and Y. S. Shon, *ACS Appl. Mater. Inter.*, 2013, **5**, 12432. (*c*) M. J. MacLeod and J. A. Johnson, *J. Am. Chem. Soc.*, 2015, **137**, 7974.
5. E. D. Slack, C. M. Gabriel and B. H. Lipshutz, *Angew. Chem.*, 2014, **126**, 14275.
6. G. L. Sorella, G. Strukul and A. Scarso, *Green Chem.*, 2015, **17**, 644.
7. E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, 1970, **8**, 271.
8. (*a*) H. H. Duan, D. S. Wang, Y. Kou and Y. D. Li, *Chem. Commun.*, 2013, **49**, 303. (*b*) N. Yan, Y. Yuan, P. J. Dyson, *Dalton Trans.*, 2013, **42**, 13294.
9. (*a*) B. H. Lipshutz, S. Ghorai, A. R. Abela, R. Moser,T. Nishikata, C. Duplais, A. Krasovskiy, R. D. Gaston and R. C. Gadwood, *J. Org. Chem.*, 2011, **76**, 4379. (*b*) B. H. Lipshutz and S. Ghorai, *Green Chem.*, 2014, **16**, 3660.
10. (*a*) S. L. Huang, K. R. Voigtritter, J. B. Unger and B. H. Lipshutz, Synlett, 2010, **13**, 2041. (*b*) A. Krasovskiy, C. Duplais and B. H. Lipshutz, *J. Am. Chem. Soc.*, 2009, **131**, 15592. (*c*) J. C. Fennewald

and B. H. Lipshutz, *Green Chem.*, 2014, **16**, 1097. (*d*) S. Handa, D. J. Lippincott, D. H. Aue and B. H. Lipshutz, *Angew. Chem. Int. Ed.*, 2014, **53**, 10658.

11. (a) S. Tanielyan, N. Biunno, R. Bhagat and R. Augustine, *Top Catal.*, 2014, **57**, 1564. (*b*) X. Yang, S. W. Liu, C. X. Xie, S. T. Yu and F. S. Liu, *Chin. J. Catal.*, 2011, **32**, 643. (*c*) M. L. Casella, G. F. Santori, A. Moglioni, V. Vetere, J. F. Ruggera, G. M. Iglesias and O. A. Ferretti, *Appl. Catal. A. Gen.*, 2007, **318**, 1. (*d*) S. L. Hou, C. X. Xie, H. Zhong and S.T. Yu, *RSC Adv.*, 2015, **5**, 89552. (*e*) S. L. Hou, X. Y. Wang, C. R. Huang, C. X. Xie and S.T. Yu, *Catal. Lett.*, 2016, **146**, 580.
12. Y. Zhao, J.A. Baeza, N. Koteswara Rao, L. Calvo, M. A. Gilarranz and L. Lefferts, *J. Catal.*, 2014, **318**, 162.
13. (*a*) D. Sinou, C. Rabeyrin and C. Nguefack, *Adv. Synth. Catal.*, 2003, **345**, 357. (*b*) Y. Y. Yu, W. W. Zhu, H. Li, H. M. Wang and Z. S. Hou, *J. Colloid. Interf. Sci.*, 2014, **415**, 117.
14. (*a*) J. H. Li, X. F. Li, Y. P. Ma, J. S. Wu and J. G. Deng, *RSC Adv.*, 2013, **3**, 1825. (*b*) F. Wang, H. Liu, L. F. Cun, J. Zhu, J. G. Deng and Y. Z. Jiang, *J. Org. Chem.*, 2005, **70**, 9424. (*c*) F. Trentin, A. M. Chapman, A. Scarso, P. Sgarbossa, R. A. Michelin, G. Strukul and D. F. Wass, *Adv. Synth. Catal.*, 2012, **354**, 1095.
15. (*a*) G. P. Lu, C. Cai and B. H. Lipshutz, *Green Chem.*, 2013, **15**, 105. (*b*) P. Klumphu and B. H. Lipshutz, *J. Org. Chem.*, 2014, **79**, 888. (*c*) N. A. Isley, S. Dobarco and B. H. Lipshutz, *Green Chem.*, 2014, **16**, 1480. (*d*) S. R. K. Minkler, N. A. Isley, D. J. Lippincott, N. Krause and B. H. Lipshutz, *Org. Lett.*, 2014, **16**, 724.
16. H. Konnerth, J. G. Zhang, D. Ma, M. H. G. Prechtl, N. Yan, *Chem. Eng. Sci.*, 2015, **123**, 155.
17. F. Lu, J. Liu and J. Xu, *Adv. Synth. Catal.*, 2006, **348**, 857.
18. M. Schwarze, J. S. Milano-Brusco, V. Strempel, T. Hamerla, S. Wille, C. Fischer, W. Baumann, W. Arlt and R. Schomäcker, *RSC Adv.*, 2011, **1**, 474.
19. (*a*) M. S. Goedheijt, B. E. Hanson, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. V. Leeuwen, *J. Am. Chem. Soc.*, 2000, **122**, 1650. (*b*) L. Wang, H. X. Ma, L. Song, L. Li and H. D. Wang, *RSC Adv.*, 2014, **4**, 1567. (*c*) H. Y. Fu, M. Li and H. Chen. *J. Mol. Catal. A: Chem.*, 2006, **259**, 156.
20. S. R. K. Minkler, B. H. Lipshutz and N. Krause, *Angew. Chem. Int. Ed.*, 2011, **50**, 7820.
21. (*a*) V. A. Semikolenov, I. I. Ilyna and I. L. Simakova, *Appl. Catal. A: Gen.*, 2001, **211**, 91. (*b*) I. L. Simakova, Y. Solkina, I. Deliy, J Wärnå and D. Y. Murzin, *Appl. Catal. A: Gen.*, 2009, **356**, 216. (*c*) A. Milewska, A. B. Osuna, I. M. Fonseca and M. N. Ponte, *Green Chem.*, 2005, **7**, 726.
22. (*a*) A. D. Nowicki, A. Ponchel, E. Monflier and A. Roucoux, *Dalton Trans.*, 2007, **48**, 5714. (*b*) S. Noël, B. Léger, A. Ponchel, K. Philippot, A. D. Nowicki, A. Roucoux and E. Monflier, *Catal. Today*, 2014, **235**, 20.
23. J. Lu, J. Dimroth and M. Weck, *J. Am. Chem. Soc.*, 2015, **137**, 12984.
24. (*a*) T. Dwars, E. Paetzold and G. Oehme, *Angew. Chem. Int. Ed.*, 2005, **44**, 7174. (*b*) J. Li, Y. M. Zhang, D. F. Han, J. Q. Jia, J. B. Gao, L. Zhong and C. Li, *Green Chem.*, 2008, **10**, 608.
25. P. Serna and A. Corma, *ACS Catal.*, 2015, **5**, 7114.

ABSTRACT

D-α-tocopheryl polyethylene glycol 1000 succinate (TPGS-1000) stabilized Ru(0) nanoparticles were prepared and characterized. These nanoparticles were employed to selectively hydrogenate α-pinene to cis-pinane, with a small amount of Na_2CO_3 present, reaction rates could be increased significantly, and the reaction media could be readily recycled. TEM, CLSM, IR and leaching experiments were employed to quantify the advantages of catalytic system. The procedure is environmentally friendly. It offers a reference for the catalytic hydrogenation of other hydrophobic natural products.



Hydrogenation of α-pinene were took place in the lipophilic core between the metal and the hydrogen-containing micelles.