ARTICLES

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Pd nanoparticles immobilized on graphite oxide modified with a base: Highly efficient catalysts for selective hydrogenation of citral

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In this work, the Pd-based catalysts were designed via immobilizing Pd nanoparticles on graphite oxide (GO) modified with organic base, 1,1,3,3-tetramethylguanidine (TMG), which was used for the selective hydrogenation of citral. These catalysts were characterized by various techniques including IR, X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy. It was demonstrated that the Pd particles with size less than 5 nm were uniformly distributed throughout the support, and they were in the electron-deficient state due to the strong interactions with the modified support. The resultant Pd-TMG/GO catalyst displayed high efficiency for the selective hydrogenation of citral with a turnover frequency of 7100 h^{-1} as well as superior selectivity to citronellal of 89.6%. Moreover, the catalyst can be reused for five times without obvious activity loss, which may result from its stable structure.

tetramethylguanidine, graphite oxide, palladium, citral hydrogenation

1 Introduction

Chemoselective hydrogenation of α , β -unsaturated aldehyde is widely used for the synthesis of fine chemicals [1–3]. Citral is a naturally occurring unsaturated aldehyde acting as a valuable intermediate for the production of flavors, fragrances, pharmaceuticals, vitamins, and nutrients [4–7]. Since there exist three different double bonds (a conjugated system composed of C=C and C=O groups as well as an isolated C=C bond) in a citral molecule, the reaction pathways of citral hydrogenation are complicated. Various products, such as citronellal, citronellol, geraniol, and nerol 3,7-dimethyl-1-octanal, may be produced simultaneously as a result of numerous parallel and consecutive hydrogenation of C=O and C=C bonds. In addition, cyclisation of citronellal or reaction between aliphatic aldehydes and alcoholic solvent can lead to formation of other products including isopulegol, menthol or acetals. Therefore, it is particularly challenging to control the product selectivity as well as the overall conversion in the citral hydrogenation. To selectively obtain desired products, several factors such as types of catalysts, promoters and solvents have been taken into consideration in the citral hydrogenation [7–24]. Citronellal is an important compound in flavoring and perfumery industries, and its production via selective hydrogenation of citral depends on the catalyst metal, the support material, and the auxiliary. For example, palladium catalyzed citral hydrogenations with basic promoters such as NaOH and NaCO₃, leading to higher selectivity toward citronellal, which increased with increasing pH values of the aqueous phase [10, 16]. In industrial applications, the selective hydrogenation of citral towards citronellal is catalyzed by palladium on carbon, and yields of citronellal > 90% were ob-

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tained by using methanol as the solvent and trimethylamine as a base (citral:CH₃OH:N(CH₃)₃ = 70:27:3, w/w) [25]. Recently, dicyanamide-containing ionic liquids as bases were reported to act very well as selectivity modifiers for citral hydrogenation towards citronellal on Pd supported catalysts [8, 9]. Despite recent advances in this regard, the design of the catalysts for selective hydrogenation of citral towards citronellal still remains an ongoing challenge.

In this work, we intend to design catalysts for the selective hydrogenation of citral towards citronellal via immobilizing Pd nanoparticles onto the base-modified support. We selected graphite oxide (GO) as the catalyst support and 1,1,3,3-tetramethylguanidine (TMG) as the base to modify the GO surface for immobilizing Pd nanoparticles. GO is a graphite derivative with rich oxygen-containing functional groups (such as hydroxyl, epoxy, carbonyl and carboxyl groups) and is readily available and inexpensive. Up to date, GO has been widely used as a starting material to prepare reduced GO (RGO) or graphene-based nanomaterials, which have displayed unique performances due to their remarkable electronic, mechanical and chemical properties [26–30]. Especially, GO provides extraordinary potential in designing novel catalytic systems with enhanced performances. For example, Pd/GO displayed an extremely high activity and very low leaching of Pd species for Suzuki-Miyaura coupling reactions [26]. Pt/RGO hybrid exhibited good catalytic activity for methanol oxidation and hydrogen conversion reactions [30]. TMG as an organic base with a higher pK_a than typical amines has attracted considerable interest, especially as a highly efficient base catalyst [31-35]. Various metal nanoparticles such as Pd, Ru and Ru-Cu supported catalysts prepared with the aid of TMG and/or TMG-based ionic liquids exhibited high efficiency for hydrogenations of alkenes, hydrogenolysis of glycerol and Heck reactions [36-38]. Therefore, TMG with unique chemical structure and basic property, exhibited extraordinary potential in designing GO based catalytic systems with enhanced performances. Herein, the GO support was first surface-modified with TMG, and then dispersed in Pd(CH₃COO)₂ ethanol solution, followed by reduction via NaBH₄ aqueous solution, resulting in the GO supported Pd nanocatalysts. The resultant catalysts were characterized by infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The catalytic performances of the resultant catalysts for citral hydrogenation were investigated.

2 Experimental

2.1 Materials

Palladium acetate was supplied by Shanghai Jiuyue Co. Ltd. Graphite, TMG, citral, and citronellal were purchased from Alfa Aesar. Graphite oxide was prepared based on the procedures reported by Hummers and Offeman [39]. All chemicals used in this work were of analytical grade and used as supplied.

2.2 Synthesis of catalysts

The GO was first treated in TMG ethanol solution under Ar atmosphere via stirring at 90 °C for 24 h, followed by being washed with distilled water for three times, and then dried under vacuum at 60 °C overnight. The resultant sample was denoted as TMG/GO. In a typical experiment to immobilize Pd particles onto the TMG/GO support, 20 mg of TMG/GO was initially dispersed in 50 mL Pd(CH₃COO)₂ ethanol solution at a designated concentration of 8×10^{-5} M to form a uniform suspension via tip sonication (500 W, 20 kHz, 20% amplitude power output) for 4 min. Subsequently, 1 mL NaBH₄ (0.06 M) aqueous solution was dropped into the suspension under tip sonication within 2 min. Finally, the obtained sample was ultracentrifuged, washed repeatedly with absolute ethanol and distilled water, and then vacuum dried at 60 °C for 6 h. For comparison, Pd/GO was prepared by directly reducing Pd(CH₃COO)₂ with NaBH₄ in the GO suspension under tip sonication.

2.3 Characterization

XRD was carried out on a D/MAX-RC diffractometer operated at 30 kV and 100 mA with Cu K_{α} radiation. XPS was performed on an ESCAL Lab 220i-XL spectrometer at a pressure of ~3×10⁻⁹ mbar (1 mbar=100 Pa) using Al K_{α} as the excitation source ($h\nu$ = 1486.6 eV) and operated at 15 kV and 20 mA. The loading content of Pd in the catalysts was determined by ICP-AES (VISTA-MPX). The morphology and microstructure of the products were examined by TEM on a transmission electron microscope (JEOL JEM-2010) equipped with an energy dispersive X-ray spectrometer with 200 kV accelerating voltage. TG measurements were performed on a thermal analyzer (NETZSCH STA 409 PC/PG) with a heating rate of 10 °C/min under N₂. FTIR spectra of the samples were collected on a TENSOR 27 FTIR at a resolution of 4 cm⁻¹.

2.4 Citral hydrogenation

Hydrogenation reactions of citral were carried out in a high pressure stainless steel reactor of 7 mL equipped with a magnetic stirrer. Typically, a desired amount of the catalyst dispersed in 1 mL ethanol and 1.1 mmol of citral were loaded in the reactor. After the air inside the reactor was evacuated, the reactor was moved to an oil bath set at a desired temperature, and H₂ was introduced up to the pressure of interest. The H₂ pressure was kept constant by replenishing H₂ as the reaction proceeded. After desired reaction time, the reactor was cooled in ice water and the gas inside was

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vented slowly. The product was analyzed by gas chromatography (Agilent 4890D) equipped with an Innovax capillary column and a Varian FID-GC flame and gas chromatography/mass spectrometry (GC-MS, SHIMADZU-QP2010). 1-Butanol was used as an internal standard for GC measurement.

3 Results and discussion

The samples prepared in this work including GO, TMG/GO, and Pd-TMG/GO were examined by different techniques. Figure 1 shows the FTIR spectra of GO, TMG and TMG/ GO in the wavenumber length from 4000 to 800 cm^{-1} . The FTIR spectrum of GO demonstrates typical peaks at 3382 cm⁻¹ (the H-bonded associated -OH), 1717 cm⁻¹ (C=O carboxyl stretching vibration), 1621 cm⁻¹ (aromatic C=C and O-H bending), 1383 cm⁻¹ (C-OH stretching), 1238 cm⁻¹ (epoxy C-O stretch) and 1057 cm⁻¹ (alkoxy C-O stretch), respectively, which suggests that the as-prepared GO possessed these polar groups on its surface, identical to the reported results [40]. Compared with the spectrum of GO, the peaks at 1400–1040 cm⁻¹ in the spectrum of TMG/GO became weak and a new band at 1562 cm⁻¹ appeared, which was attributed to N-H stretching vibration [41]. This group originated from TMG, suggesting the presence of TMG in the sample, which is also supported by a lower peak intensity band at 3300-3600 and by the emergence of a new peak at 3425 cm⁻¹ belonging to the N-H stretching. In addition, the bands at 1441, 2933 and 2858 cm⁻¹ assigned to -CH₃ were also from TMG, further confirming the successful attachment of TMG in these samples. The immobilization of TMG onto the GO surface may result from amidation between carboxylic group and guanidine group, and the reaction of guanidine group with epoxy group. Since these oxygen-containing groups were present throughout the GO support, the distribution of TMG on the



Figure 1 IR spectrum of GO and TMG/GO and TMG.

surface of the GO sheets can be supposed to be uniform.

Typical TG curves of GO and TMG/GO under nitrogen atmosphere are shown in Figure 2. The weight loss of GO started around 100 °C, and a sudden weight loss (about 30%) occurred from 150 to 250 °C, which was mainly attributed to the removal of the labile oxygen-containing functional groups, suggesting that the GO support was not stable at high temperature. In comparison, the weight loss of TMG/GO started at a relatively high temperature, and continued to about 350 °C. This suggests that TMG/GO was thermally stable compared with GO.

Figure 3 gives the XRD patterns of GO and TMG/GO. The XRD of GO showed a sharp peak at 11.86°, indicating the layered structure of GO with an interlayer distance of approximately 0.75 nm, which is more susceptible to intercalation of hydroxyl, epoxy, and carboxyl groups. The XRD pattern of TMG/GO showed a distinct sharp peak at 10.80°, corresponding to a larger interlayer distance of 0.82 nm compared with GO, which may be ascribed to the TMG molecule inserted into the intergallery space of GO via the strong interactions between TMG molecules with the oxygen-containing groups present on the GO surface. In addition, new broad peaks appeared at around 24°, which is closer to the typical (002) diffraction peak of graphite ($2\theta =$



Figure 2 Typical TG curves of GO and TMG/GO under nitrogen atmosphere.



Figure 3 XRD patterns of GO and TMG/GO.

 26.4°) [42]. This indicates that GO was partially reduced into graphite in the process to surface modification with TMG.

The morphology of Pd-TMG/GO and Pd/GO was examined by TEM, and their typical TEM images are shown in Figure 4. It can be observed that numerous nanoparticles with sizes less than 5 nm were uniformly deposited throughout the support in sample Pd-TMG/GO with Pd content of 1.94%, while relatively large Pd particles with a wider size distribution were present on the surface of GO in Pd/GO sample with Pd content of 2.38%. Therefore, it can be deduced that the modification of GO with TMG played an important role in stabilizing the Pd nanoparticles. The above analysis indicates that oxygen-containing groups including -OH, -COOH, and epoxy groups were present in GO, which can stabilize metal nanoparticles in the Pd/GO sample. However, it should be noted that only some of these polar groups can act as stabilizing agents for Pd particles, which resulted in the uneven distribution of Pd nanoparticles depending on the distribution of the stabilizing groups. In sample Pd-TMG/GO, TMG may be uniformly distributed on the surface of GO due to the strong interactions of TMG with all the residue oxygen-containing groups present on the GO surface. Since TMG has good stabilizing ability for metal particles, in Pd-TMG/GO the uniform distribution of TMG on the GO surface may lead to even decoration of Pd nanoparticles with small size and narrow size distribution.

The XPS analysis was used to examine the oxidation state of all species in the composites. As shown in Figure 5, it is obvious that element N was present in the survey spectrum of Pd-TMG/GO, which originated from TMG in the sample. Figures 6 (a, b) show the C 1s spectrum of GO and Pd-TMG/GO, respectively. The C1s core level XPS spectrum of the GO support can be deconvoluted into four peaks at 284.4, 286.2, 287.2, and 288.6 eV, which are assigned to C=C/C-C and C-O in hydroxyl or epoxy forms, C=O and O=C-O, respectively, suggesting the presence of these groups in GO. As compared with the C 1s spectrum of GO, the peaks assigned to the oxygen-containing groups were greatly weakened in intensity in the C 1s XPS spectrum of Pd-TMG/GO, suggesting the removal of the oxygen-containing groups. The appearance of a new peak at 285.7 eV attributed to C bound to N [43] and the N 1s peak at 399.8 eV assigned to N species bound to =C and -C (Figure 6(c)) originated from TMG, further confirming the



Figure 4 TEM images of Pd-TMG/GO (a) and Pd/GO (b).



Figure 5 Survey XPS spectra of GO and Pd-TMG/GO.

presence of TMG in the sample.

The XPS spectrum of Pd in Pd-TMG/GO is shown in Figure 6(d). The Pd 3d core level XPS pattern fitted with the expected 3:2 peak area ratio, and the 5.3 eV peak separation exhibited asymmetric peaks with a doublet structure. Compared with the binding energy (BE) value (335.1 eV) of Pd 3d in bulk Pd metal [44], the relatively low BE set of doublet at 335.5 and 340.8 eV was attributed to Pd(0) species and the other set of doublet at 337.5 and 342.8 eV belonged to Pd(II) species. Since excessive NaBH₄ was used to reduce Pd ions during the synthetic process, the Pd(II) species may be ascribed to Pd oxide due to the slight oxidation of Pd nanoparticles upon exposure to ambient air. Compared with the BE of the bulk Pd (335.1 eV) [44], the BEs of Pd particles in Pd-TMG/GO shifted to higher values, suggesting that the Pd particles were in the electron-deficient state. The small size of Pd particles as well as the interaction between the Pd particles and the supports should be responsible for the shift.

The as-prepared catalysts including Pd-TMG/GO and Pd-GO were used to catalyze citral hydrogenation under mild conditions, and the results are listed in Table 1. The reactions were carried out in ethanol at 50 °C and under H₂ pressure of 2 MPa. Ethanol was used as the solvent due to its several merits such as low cost, being environmentally benign, and good hydrogen solubility. The products of citral hydrogenation over the Pd-TMG/GO catalysts mainly included citronellal and dihydrocitronellal, while when Pd/GO was used as the catalyst, a relatively large amount of isopulegol was detectable in the product. Pd-TMG/GO showed high activity for the citral transformation, and the turnover frequency (TOF) with respect to citral conversion reached 7100 h⁻¹ under the experimental conditions (Table 1, entry 1), much higher than that of the carbon supported Pd catalyst promoted with dicyanamide-containing ionic liquid [9]. The Pd particles in Pd-TMG/GO displayed the electron-deficient state due to the small size and/or strong

interaction with the TMG/GO support, which may be responsible for its high catalytic activity for citral hydrogenation. Over the Pd-TMG/GO catalyst, citral was almost completely converted within 4 min with a selectivity toward citronellal of 89.6% (Table 1, entry 1). While prolonging the reaction time to 10 min resulted in further hydrogenation of citronellal to dihydrocitronellal with the selectivity of citronellal dramatically declining to 54.6%. From the above results, it can be deduced that citronellal or dihydrocitronellal can be controllably obtained from citral hydrogenation by tuning the reaction time. In addition, when increasing the amount of the reactant to 2 mmol, Pd-TMG/GO catalyst maintained good activity and selectivity toward citronellal of 84.1% at a conversion of 94.2% within 7 min (Table 1, entry 2). In comparison, the Pd-GO catalyst was less active (e.g., TOF 2400 h⁻¹), giving citronellal as the main product with a selectivity of 75.3% (Table 1, entry 4) at a citral conversion of 82.1% under the similar

conditions. The lower activity mainly originated from the relatively large Pd particles with a wider size distribution.

Citronellal can be isomerized to isopulegol in the citral hydrogenation (Scheme 1). In this work, little amount of isopulegol was detected as Pd-TMG/GO was used as the catalyst, while more isopulegol was obtained when Pd/GO was used as the catalyst. This indicates that the surface modification of GO with TMG played an important role in the performances of the catalysts. The basic promoters such as NaOH and Na₂CO₃ are usually used in the selective hydrogenation of citral towards citronellal [10,16]. In this work, the TMG in the catalyst may serve as a basic promoter to hamper the formation of isopulegol, resulting in the good selectivity towards citronellal.

The Pd-TMG/GO catalyst kept a good catalytic activity after being reused for four times (Table 1, entry 3), suggesting the stable performances, which should result from its stable structure. As confirmed by the TEM observation,



Figure 6 C 1s core level XPS patterns of GO (a) and Pd-TMG/GO (b), N 1s core level XPS pattern of Pd-TMG/GO (c) and Pd 3d core level XPS pattern of Pd-TMG/GO (d).

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Entry	Catalyst	Time (min)	Citral conv. (%) —	Selectivity (%)		TOE ^b (t-1)
Entry				Citronellal	Dihydrocitronellal	- 10F ⁽ⁿ⁾
1	Pd-TMG/GO	4	100	89.6	9	7100
2 ^{c)}	Pd-TMG/GO	7	94.2	84.1	14.4	7000
3 ^{d)}	Pd-TMG/GO	4	99.1	90.3	8.4	7000
4	Pd-GO	12	82.1	75.3	14	2400

a) 1.1 mmol citral, 2.3×10^{-3} mmol Pd, 1 mL ethanol, 323 K, 2 MPa H₂; b) TOF of citral conversion (mol citral converted per mol Pd per h); c) 2 mmol citral, 2.3×10^{-3} mmol Pd, 1 mL ethanol, 323 K, 2 MPa H₂; d) the catalyst reused for the fifth time.



Scheme 1 Reaction pathways of citral hydrogenation.

the morphology of the Pd-TMG/GO catalyst was almost unchanged without any aggregation of Pd nanoparticles after the catalyst was reused for five times.

4 Conclusions

In summary, a two-step approach was presented to prepare GO supported Pd nanocatalysts. The modification of GO with TMG made the distribution of Pd nanoparticles on the GO support uniform with small particle size and narrow size distribution. The Pd-TMG/GO catalyst exhibited high activity with a turnover frequency (e.g., $7100 h^{-1}$) as well as superior selectivity to citronellal (e.g., 89.6%) under green and mild conditions. Moreover, the catalyst can be reused for five times without obvious activity loss, which resulted from the stable structure of the catalyst. This method may also be extended to prepare other noble metal nanoparticles (such as Au and Pt) immobilized catalysts on GO, and further work is underway.

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