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Introduction

important building blocks in organic synthesis, As N-heteroaromatics are extensively applied in the synthesis of natural products, bioactive molecules and pharmaceuticals.¹⁻³ One of the fundamental procedures to obtain heteroarenes is oxidative dehydrogenation reaction of the corresponding saturated N-heterocycles. Many homogeneous catalysts and catalytic systems have been developed and successfully employed, such as Lewis acid B(C₆F₅)₃,⁴ Ir-,⁵⁻⁷ Fe-,^{2,8} Rh-,⁹ Pd-,^{10,11} and Ru-complexes,¹² Ru-Co catalysts¹³ and metal/ quinone systems.¹⁴ In addition, photoredox catalysis using boron carbon nitride nanosheets and electrochemical processes using TEMPO as an organic electrocatalyst were both developed.^{15,16} In addition to aerobic oxidative dehydrogenation, acceptorless dehydrogenation has attracted much attention. Kazuya Yamaguchi and Takashi Toyao reported the acceptorless dehydrogenation of 1,2,3,4tetrahydroquinoline catalyzed by Pd and Pt, respectively.¹⁷

Aerobic oxidative dehydrogenation of N-heterocycles over OMS-2-based nanocomposite catalysts: preparation, characterization and kinetic study;

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OMS-2-based nanocomposites doped with tungsten were prepared for the first time and their remarkably enhanced catalytic activity and recyclability in aerobic oxidative dehydrogenation of N-heterocycles were examined in detail. Many tetrahydroquinoline derivatives and a broad range of other N-heterocycles could be tolerated by the catalytic system using a biomass-derived solvent as a reaction medium. Newly generated mixed crystal phases, noticeably enhanced surface areas and labile lattice oxygen of the OMS-2-based nanocomposite catalysts might contribute to their excellent catalytic performance. Moreover, a kinetic study was extensively performed which concluded that the dehydrogenation of 1,2,3,4-tetrahydroquinoline is a first-order reaction, and the apparent activation energy is 29.66 kJ mol⁻¹.

From a sustainability perspective, heterogeneous catalysts are more preferable due to the facile product separation, catalyst reusability and operational simplicity. Some existing heterogeneous catalysts for oxidative dehydrogenation of N-heterocycles are Rh-, Pd-, and Pt-based catalysts, Pd₃Pb, Au nanoparticles and Ru supported on metal oxide supports.^{12,13} Notably, most of the aforementioned systems are based on precious metals and display a narrow substrate scope. Thus, the preparation and development of non-noble and recyclable heterogeneous catalysts with high catalytic activities for the aerobic oxidative dehydrogenation of N-heterocycles are still challenging.

In recent years, some novel catalytic systems employing non-noble metal catalysts for oxidative dehydrogenation of N-heterocycles have been developed. Beller and co-workers reported an efficient Fe-based core-shell catalyst for the aerobic oxidative dehydrogenation of various N-heterocycles under high pressure oxygen in heptane.¹⁸ Besides, manganese was used to synthesize NiMn layered hydroxide compounds for the aerobic dehydrogenation of saturated N-heterocycles in mesitylene.¹⁹ In particular, for the first time, mesoporous manganese oxide was found to be an efficient heterogeneous catalyst for aerobic oxidative dehydrogenation using DMF as the reaction medium.²⁰ In the past years, our group has focused on the synthesis and modification of manganese oxide catalysts, especially manganese oxide octahedron molecular sieve (OMS-2), and their catalytic application towards the clean synthesis of heterocycles.²¹ OMS-2 being a 2 × 2 tunnel structure

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Paper

nanomaterial has been applied in catalysis, batteries, separation and environmental protection because of its properties including redox ability, structural stability, mixed valence of manganese, semi-conductivity and adsorption.^{22–25} As a solid catalyst, morphology modification, ion-exchange and preparation of its hybrid with carbon, g-C₃N₄, graphite and CuFe₂O₄ were studied, thereby improving its catalytic performance in certain oxidation reactions.^{25,26} Recently, we also reported that modified OMS-2-based materials could efficiently catalyze oxidative cyclization for the synthesis of benzoxazoles and benzimidazoles when biomass-derived dimethyl carbonate (DMC) was used as a green solvent.²⁷ Therefore, it is worth preparing novel and modified nonnoble OMS-2-based catalysts with significantly enhanced catalytic activity for clean synthesis in green reaction media.

Herein, we report the preparation of OMS-2-based nanocomposites containing two phases, OMS-2 and Mn₂O₃ hydrate, for the first time and describe their remarkably enhanced activity and recyclability in catalytic oxidative dehydrogenation of N-heterocycles. By the use of tungsten as the dopant for the modification of OMS-2, it was found that W was doped into frameworks of OMS-2, which makes the material have mixed crystal phases, newly generated catalytic active species, labile lattice oxygen and a significantly enhanced surface area ($\sim 204 \text{ m}^2 \text{ g}^{-1}$). The as-synthesized nanocomposites were fully characterized and could efficiently catalyze oxidative dehydrogenation of a wide range of heterocyclic compounds, such as indoline, isoquinoline, quinazoline, and quinoxaline derivatives, in DMC. In addition, the kinetics including the catalyst effect, reaction order and activation energy was carefully investigated.

Experimental section

General information

All reagents were purchased from commercial suppliers and used without further purification and DMC (CAS NO. 616-38-6, ReagentPlus®, 99%) was purchased from Sigma-Aldrich with the mark of Greener Alternative Product. All experiments were carried out under air or using an O_2/N_2 balloon. Flash chromatography was carried out with Merck silica gel 60 (200–300 mesh). Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃. Chemical shifts (δ) are reported in ppm using TMS as an internal standard, and spin–spin coupling constants (*J*) are given in Hz.

Procedure for the preparation of OMS-2 nanocomposites

All the OMS-2-based composites in the present research were prepared through a reflux method. Taking OMS-2 doped with sodium phosphotungstate (1 mol% to the amount of KMnO₄) as an example, 52 mmol (8.8 g) $MnSO_4$ ·H₂O was dissolved in 30 mL deionized water, and 3 mL HNO₃ was added to the MnSO₄ solution. Then, 0.37

mmol (1.09 g) sodium phosphotungstate was added into the above mixed solution to form solution A. 37 mmol (5.89 g) KMnO₄ was dissolved in 100 mL deionized water to prepare solution B. Then, solution B was added dropwise to solution A under vigorous stirring at room temperature. After the resulting solution was refluxed at 100 °C for 24 h, the resulting solid was collected by filtration, washed with deionized water and dried in air at 80 °C for 8 h to afford 4.2 g of OMS-2-based nanocomposite which was denoted as 1 [PW]-OMS-2. The molar percentage of dopant/KMnO₄ was adjusted by changing the amount of sodium phosphotungstate, and the samples with different dopant/KMnO₄ ratios are referred to as 0.1 [PW]-OMS-2, 1 [PW]-OMS-2, 2 [PW]-OMS-2, 5 [PW]-OMS-2, and 10 [PW]-OMS-2.

Characterization

ICP-AES measurements were conducted on a Varian Vista MPX. Samples were first calcined in air at 600 °C for 30 min, then digested in concentrated HNO3 and diluted to desired concentrations. Nitrogen adsorption-desorption measurements were performed at 76 K using an ASAP 2020 M analyzer utilizing the BET model for the calculation of specific surface areas. The morphology images were recorded using a Tecnai G2 F20 S-Twin 200 kV high-resolution transmission electron microscope and an EVO 18 scanning electron microscope, respectively. The crystal phase and composition were determined by powder X-ray diffraction using an X-Pert PRO X-ray diffractometer with Cu Ka radiation in the 2θ range of 10–90°. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos AXIS Ultra DLD high performance electron spectrometer using a nonmonochromatized Al Ka excitation source (hv = 1486.6 eV). Binding energies were calibrated by using the contaminant carbon (C1s = 284.8 eV). The elemental composition analysis of the catalyst was carried out by inductively coupled plasma emission spectroscopy and the test was based on ILSR/FF-14-03. The reducibility of the catalysts was measured by the hydrogen temperatureprogrammed reduction (H2-TPR) technique. 50 mg of OMS-2, 0.1 [PW]-OMS-2, 1 [PW]-OMS-2, and 2 [PW]-OMS-2 was placed in a quartz reactor that was connected to a TPR instrument and the reactor was heated from r.t. to 550 °C with a heating rate of 10 °C min⁻¹. The reducing atmosphere was a mixture of H_2 and N_2 with a total flow rate of 30 mL \mbox{min}^{-1} and the amount of H₂ uptake during the reduction was measured by a thermal conductivity detector (TCD). Electron paramagnetic resonance (EPR) was performed on a Bruker spectrometer at the X-band at room temperature, with a field modulation of 100 kHz. The microwave frequency was kept at 9.401 GHz. Raman spectroscopy was performed at 514 nm with a Renishaw 2000 Raman microscope system, which included an optical microscope and a CCD camera for multichannel detection. Raman spectra of the samples were collected at 64 scans with a scan rate of 126 min⁻¹.

Aerobic dehydrogenation of 1,2,3,4-tetrahydroquinoline

Typically, a mixture of 0.20 mmol 1,2,3,4-tetrahydroquinoline, x [PW]-OMS-2 (20 mg) and 1.0 mL DMC in a reaction tube was magnetically stirred at 80 °C under 1 atm of oxygen. The reaction was monitored and analyzed through a gas chromatograph (Agilent 7890A) with a flame ionization detector (FID). After completion of the reaction, the reaction mixture was cooled and the catalyst was separated by filtration to recycle it. After being washed with deionized water and dried at 80 °C for 12 h, the retrieved catalyst was reused under the same conditions. The conversion and the selectivity of the reaction were obtained on the basis of GC analysis (dodecane was used as the internal standard reference). A pure product was obtained by silica gel chromatography with petroleum ether/ethyl acetate (5:1 v/v) as the mobile phase.

Catalytic dehydrogenation of other N-heterocyclic aromatic compounds

A mixture of N-heterocyclic aromatic compounds (0.20 mmol), 2 [PW]-OMS-2 (20 mg) and 1.0 mL DMC in a reaction tube was magnetically stirred at 80 °C under 1 atm of oxygen for the indicated time. After completion of the reaction, the reaction mixture was cooled, filtered and washed with EtOAc. The resulting solution was concentrated under reduced pressure to give the crude product which was purified by silica gel chromatography to yield the pure product.

Results and discussion

Characterization of the [PW]-OMS-2 composite catalysts

Structural characterization of the [PW]-OMS-2 materials was carried out using various methods. First of all, ICP-AES was used to examine the actual dopant loading of sodium phosphotungstate for [PW]-OMS-2. As shown in Table 1, the results show that P and Na ions were not detected for all [PW]-OMS-2 materials, while W was detected and its actual loadings were consistent with the theoretical loadings. On the other hand, W was detected and its actual loadings were consistent with the theoretical loadings were consistent with the theoretical loadings were consistent with the theoretical loadings. Then, from the analysis of the XRD spectra, the diffraction peaks of 0.1 [PW]-OMS-2 and 1 [PW]-OMS-2 were the same as those of OMS-2 and they both had a pure and typical cryptomelane phase

(JCPDS file #29-1020). When the loading of dopant increased to 2 mol%, the diffraction peaks of Mn₂O₃ hydrate (JCPDS file #74-1049) became increasingly observed with obvious diffraction peaks of OMS-2 remaining. For 5 [PW]-OMS-2, however, the crystal phase became much more complex although the diffraction peaks of Mn₂O₃ hydrate became stronger. Moreover, α-MnOOH (JCPDS file #88-648) and other MnOx peaks appeared clearly, and the diffraction peaks of OMS-2 became much weaker. When the dopant loading was further increased to 10 mol%, the diffraction peaks of OMS-2 became much sharper and narrower, which means the crystallinity of OMS-2 and its particle size were remarkably enhanced, and 10 [PW]-OMS-2 still had complex multiple crystal phases (Fig. 1). However, the diffraction peaks of WO₃ were not detected no matter how much dopant was used. We noticed that doping with a large amount of tungsten would destroy the crystal structure of OMS-2 resulting in an amorphous phase reported by Zhang's group.²⁸ In our study, the cryptomelane phase of OMS-2 remained very well even when the amount of dopant was increased to 10 mol%. Thus, it is believed that sodium phosphotungstate was decomposed into sodium tungstate dihydrate and phosphoric acid in heated solution. Sodium tungstate possibly played a role as a dopant to modify the catalyst and phosphoric acid provided an acidic environment.

Subsequently, the BET surface areas and porosities of the [PW]-OMS-2 materials were determined by N₂ adsorptiondesorption, and the results are concluded in Table 1 and Fig. 2. It is obvious to summarize that the doping reagent could significantly affect the BET surface area of OMS-2. The surface area of doped OMS-2 could increase from 67 m² g⁻¹ to the highest 204 m² g⁻¹, while the surface area of doped OMS-2 decreased if tungsten was doped too much (Fig. 2). These results were in agreement with the XRD patterns, which indicates that the BET surface area over impure crystal phases of the as-synthesized materials could decrease. Generally, the surface area is highly related to catalytic activity and a higher surface area tends to expose more catalytic active sites. Moreover, the pore volume of [PW]-OMS-2 also increased and the pore size decreased gradually with increased loadings of the dopant (Table 1). Then, the morphologies of the [PW]-OMS-2 materials were carefully observed by TEM (Fig. 3. For the SEM images, see ESI[†] Fig. S1) In general, the materials with low loadings of dopant

Table 1 Textural properties of OMS-2 and the [PW]-OMS-2 catalysts								
	Surface	Pore volume	Pore		Molar ratio ^b			
Catalyst	area $(m^2 g^{-1})$	$(cm^3 g^{-1})$	size (nm)	AOS ^a	K/Mn	W/Mn		
OMS-2	67	0.37	28	3.83 ^c	0.106			
0.1 [PW]-OMS-2	115	0.55	22	3.75	0.089	0.004		
1 [PW]-OMS-2	122	0.52	19	3.55	0.075	0.042		
2 [PW]-OMS-2	204	0.59	13	3.65	0.081	0.082		

^{*a*} Average oxidation state (AOS) of Mn was calculated according to the binding energy difference (ΔE) of Mn 3s in XPS through an empirical formula, *i.e.* AOS = 8.956 – 1.126 × ΔE . ΔE : the splitting width (Δ) of the XPS spectra in the Mn 3s region. ^{*b*} Calculated from the ICP-AES result. ^{*c*} AOS determination by the magnetic method.²⁹



Fig. 1 XRD patterns of the catalysts made via different pathways.





(0.1–2 mol%) both showed a typical and uniform nanorod morphology, which means that W-doping does not change the structure and morphology of OMS-2. When the doping amount exceeded 2 mol%, the nanorod-like structure of catalytic materials changed greatly; the nanorod-like



Fig. 3 TEM images of (a) OMS-2, (b) 0.1 [PW]-OMS-2, (c) 1 [PW]-OMS-2, (d) 2 [PW]-OMS-2, (e) 5 [PW]-OMS-2, and (f) 10 [PW]-OMS-2; (g-i) HRTEM images of 2 [PW]-OMS-2 {200}.

structures became shorter and thicker, or even lost their nanorod-like structure and became granular, like in 10 [PW]-OMS-2. These results from XRD and TEM indicate that the morphologies of the doped OMS-2 materials change gradually from rod-like to granular particles with the formation of impure multiple crystal phases, like MnOx and α -MnOOH. From the HRTEM observation (Fig. 3g–i) and measurements of the lattice fringes, 2 [PW]-OMS-2 favorably exposed the (200) plane.

The surface elemental analysis was performed by X-ray photoelectron spectroscopy (Fig. 4 and Tables 2 and 3). Firstly, Mn 2p3/2 could be deconvoluted into three peaks for all [PW]-OMS-2 and OMS-2 materials (Fig. 4a). Among them, 2 [PW]-OMS-2 exhibited the highest content of Mn^{3+} (63.9%), which generally means that it has the most abundant oxygen vacancies for electrostatic balance. Combined with the analysis of EPR characterization results (Fig. 6), 2 [PW]-OMS-2 features a g value of 2.0040, which is larger than 1.94 of fully oxidized MnO₂ in the literature,³⁰ which indicates the presence of defect sites. Compared to that of original OMS-2, the $\Delta H = 14.58$ mT of 2 [PW]-OMS-2 is smaller, which is ascribed to the contents of Mn^{3+} and Mn^{4+} being relatively higher. This result is consistent with the XPS spectra analysis of 2 [PW]-OMS-2 (AOS = 3.65, $Mn^{3+}\%$ = 63.9%). It can be inferred that tungsten incorporated into the 2 [PW]-OMS-2 framework resulted in the increase of Mn3+ content, and lattice oxygen becomes more active and is more likely to produce oxygen vacancy defects, thus improving catalytic activity. The labile lattice oxygen and oxygen vacancies play a vital role in the formation of quinoline. The probable mechanisms of 1,2,3,4-tetrahydroquinoline adsorption and oxidation over 2 [PW]-OMS-2 is discussed in Scheme S2.†

Also, the high percentage of Mn^{3+} is believed to come from the existence of Mn_2O_3 hydrate species in 2 [PW]-OMS-2. After analysis of the Mn 3s XPS spectra, the average oxidation state (AOS) of Mn was calculated based on the following formula: AOS = $8.956 - 1.126 \times \Delta E$, where ΔE is the binding energy difference between the doublet Mn 3s peaks as shown in Fig. S2.† The AOS of Mn decreased with small amounts of dopant, while it increased slightly with increased amounts of dopant. Next, O 1s was fitted into two peaks including surface adsorbed unsaturated oxygen species with high binding energy and saturated lattice oxygen with low binding energy (Fig. 4b and Table 3). After doping with



Fig. 4 (a) The Mn2p XPS patterns of as-synthesized; (b) The O1s XPS patterns of as-synthesized.

Table 2 The Mn2p XPS data of the as-synthesized materials

	Binding energy of Mn 2p (eV)			Manganese species (%)		
Catalyst	Mn ⁴⁺	Mn ³⁺	Mn ²⁺	Mn^{4+}	Mn ³⁺	Mn ²⁺
OMS-2	643.36	642.44	641.04	60.0	35.6	4.4
0.1 [PW]-OMS-2	643.76	642.34	640.79	38.9	57.3	3.7
1 [PW]-OMS-2	643.97	642.51	642.20	28.3	57.8	13.9
2 [PW]-OMS-2	643.71	642.17	640.66	34.4	63.9	1.7

Table 3 The O 1s XPS data of the as-synthesized materials

	Binding ene O 1s (eV)	ergy of	Oxygen species (%)		
Catalyst	Surface O	Lattice O	Surface O	Lattice O	
OMS-2	531.12	530.03	33.6	66.4	
0.1 [PW]-OMS-2	531.43	529.85	21.9	78.1	
1 [PW]-OMS-2	531.44	529.93	25.2	74.8	
2 [PW]-OMS-2	531.43	529.94	19.6	80.4	



Fig. 5 (a) $H_2\text{-TPR}$ of OMS-2 and 2 [PW]-OMS-2; (b) $H_2\text{-TPR}$ of 0.1 [PW]-OMS-2, 1 [PW]-OMS-2 and 2 [PW]-OMS-2.

sodium phosphotungstate, we can see clearly shifting of the lattice oxygen peak compared with that of pure OMS-2, which means that the doping causes weaker interactions between Mn and O atoms and improves the reactivity of lattice oxygen. Moreover, 2 [PW]-OMS-2 showed the highest content of lattice oxygen species (80.4%) compared to others. The W 4f XPS spectra of 0.1 [PW]-OMS-2, 1 [PW]-OMS-2 and 2 [PW]-



Fig. 6 EPR spectra of 0.1 [PW]-OMS-2, 1 [PW]-OMS-2, 2 [PW]-OMS-2 and OMS-2.

OMS-2 are shown in Fig. S3.† The W 4f spectra could be fitted into two peaks, the lower binding energy peak was assigned to W^{5+} and the higher one was assigned to W^{6+} . As shown in Table S2,† the contents of W^{5+} and W^{6+} were calculated with their peak areas, respectively. The results show that the content of W^{6+} is higher in 0.1 [PW]-OMS-2, 1 [PW]-OMS-2 and 2 [PW]-OMS-2. Among them, W^{6+} accounts for 69.1% in 2 [PW]-OMS-2.

The Raman spectrum of the original OMS-2 sample shows a characteristic peak at ~636 cm⁻¹ and the [PW]-OMS-2 samples show peaks at ~580 cm⁻¹ and ~636 cm⁻¹ (Fig. 7). The strong peak at ~636 cm⁻¹ corresponded to Mn–O lattice vibrations perpendicular to the MnO₆ octahedra. The weak peak at ~580 cm⁻¹ corresponded to the Mn–O stretching vibration along the chains of the edge-sharing MnO₆ octahedra.³¹ With the increase of doping amount, the peak strength at ~636 cm⁻¹ becomes stronger. The main peaks of WOx like WO₃ at 710 and 800 cm⁻¹, WO₄²⁻ compounds at 909 cm⁻¹, and WO₂ at 790 and 881 cm⁻¹ were not observed in all spectra, indicating that no separate tungsten oxides were observed.^{32,33}

The redox ability of the doped OMS-2 materials was measured by temperature programmed reduction with H₂ (H2-TPR), while original OMS-2 was also examined for comparison. For all OMS-2-based materials, the reduction of MnO₂ to MnO proceeds in two different steps (MnO₂ to Mn₃O₄ to MnO) generally, but these processes overlap sometimes. As shown in Fig. 5a, the overlapping peak (a) from 369 °C to 395 °C was ascribed to the reduction of MnO₂ to MnO of OMS-2. For 2 [PW]-OMS-2, four reduction peaks (α , β , b and b') are shown and all shifted to lower temperatures compared with that of original OMS-2, implying the remarkable enhancement of redox ability. Specifically, the two main reduction peaks (b and b') which were split obviously and demonstrated at 342 °C and 394 °C at lower temperatures suggest that the lattice oxygen of 2 [PW]-OMS-2 is more reactive and mobile. Furthermore, two new peaks (α and β) appeared at temperatures in the range of 150–250 °C. The α peak probably corresponded to the reduction of surface labile oxygen species adsorbed by oxygen vacancy defects. The β and b peaks resulted from the reduction of



Fig. 7 Raman spectra of 0.1 [PW]-OMS-2, 1 [PW]-OMS-2, 2 [PW]-OMS-2 and OMS-2.

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 MnO_2 from MnO_6 - \Box (\Box means vacancy) species and MnO_2 from MnO_6 -K species, respectively,³⁷ and the b' peak corresponded to the reduction of Mn_3O_4 to MnO. On the other hand, OMS-2 doped with sodium phosphotungstate all showed enhanced reducibility compared with original OMS-2, while the reducibility of [PW]-OMS-2 increased gradually with the increasing dopant loading (Fig. 5b).

Catalytic activity of the [PW]-OMS-2 composite materials

Optimization of the reaction conditions. To examine the activity of the prepared catalysts for selective oxidative dehydrogenation of heterocycles, we initially tested the different [PW]-OMS-2 materials with 1,2,3,4tetrahydroquinoline as the model substrate. Firstly, a blank experiment was performed to gain insight into the activity of the [PW]-OMS-2 materials (Table 4, entry 1). There is no substrate conversion without a catalyst. However, when [PW]-OMS-2 with different dopant loadings, OMS-2 and commercial α-MnO₂ were used as the catalyst respectively, different conversions and selectivities to 2a were obtained (Table 4, entries 2-8). Delightfully, 2 [PW]-OMS-2 facilitated the reaction with the highest catalytic activity and 2a was obtained at 99% conversion with >99% selectivity (Table 4, entry 6). The results might arise from the special physicochemical properties of 2 [PW]-OMS-2, such as its mixed crystal phases, newly generated catalytic active species, noticeably enhanced surface area, labile lattice oxygen and enhanced reducibility. In addition, it was found that the content of dopant from 1 mol% to 2 mol% had no obvious difference towards catalytic performance for the oxidative dehydrogenation of 1a (Table 4, entries 5 and 6). Next, we decided to use 2 [PW]-OMS-2 as the best catalyst to further optimize the reaction conditions. It was found that the reaction worked better in O2 while it worked much worse in N2, which means that the reaction was aerobic oxidation (Table 4, entries 9 and 11). From the perspective of oxidants, we tried to use oxygen, hydrogen peroxide and air as an oxidant, respectively, to explore the conversions and selectivities to the product, and we found that the highest conversion of 1a was obtained in an oxygen atmosphere (Table 4, entries 9-11). Then, different biomass-derived solvents and water were tested in the model reaction, including DMC, 2-MeTHF, ethyl lactate, propylene carbonate, ethylene carbonate and EtOH, under the standard conditions and it was found that DMC was the best solvent (Table 4, entries 6 and 12-18). Full conversion of 1,2,3,4tetrahydroquinoline and high selectivity to quinoline were observed in DMC. Then, it was found that the reaction temperature affected the reaction greatly. The reaction rate markedly increased at higher temperature and the dehydrogenation could finish in 6 h at 80 °C. However, when the temperature was decreased to 60 °C, 40 °C and 20 °C, the conversion dropped down to 80%, 48% and 21%, respectively (Table 4, entries 19-21). Lastly, the amount of catalyst was optimized under the standard conditions (Table S4 in the ESI†). When 20 mg of 2 [PW]-OMS-2 was used for 0.2 mmol of substrate, the highest conversion and selectivity to 2a were

Table 4	Optimization of the reaction co	onditions ^a				
			oxidant			
			N cat., solvent	N [×] N		
		1a	Н	2a		
Entry	Catalyst	Temp.	Solvent	Oxidant	$\operatorname{Con.}^{b}(\%)$	Sel. ^b (%)
1	_	80	DMC	O_2	N.R.	_
2	α -MnO ₂	80	DMC	O_2	31	99
3	OMS-2	80	DMC	O_2	61	>99
4	0.1 [PW]-OMS-2	80	DMC	O_2	55	99
5	1 [PW]-OMS-2	80	DMC	O_2	95	>99
6	2 [PW]-OMS-2	80	DMC	O_2	99	>99
7	5 [PW]-OMS-2	80	DMC	O_2	44	99
8	10 [PW]-OMS-2	80	DMC	O_2	25	99
9 ^c	2 [PW]-OMS-2	80	DMC	Air	38	98
10^d	2 [PW]-OMS-2	80	DMC	H_2O_2	47	99
11^e	2 [PW]-OMS-2	80	DMC	N_2	32	99
12	2 [PW]-OMS-2	80	H2O	O_2	N.R.	—
13	2 [PW]-OMS-2	80	EtOH	O_2	32	99
14	2 [PW]-OMS-2	80	2-MeTHF	O_2	51	99
15	2 [PW]-OMS-2	80	Ethyl lactate	O_2	27	99
16	2 [PW]-OMS-2	80	DEC	O_2	72	>99
17	2 [PW]-OMS-2	80	PC	O_2	56	99
18	2 [PW]-OMS-2	80	Ethylene carbonate	O_2	73	99
19 ^{<i>f</i>}	2 [PW]-OMS-2	60	DMC	O_2	80	>99
20^g	2 [PW]-OMS-2	40	DMC	O_2	48	99
21^h	2 [PW]-OMS-2	20	DMC	O_2	21	99

^{*a*} Reaction conditions: **1a** (0.2 mmol), 2 [PW]-OMS-2 (20 mg), solvent (1 mL), O₂ balloon, 80 °C, 6 h. ^{*b*} The conversions and selectivities were obtained by GC using dodecane as an internal standard. ^{*c*} Under air. ^{*d*} H₂O₂ (50 μL). ^{*e*} N₂ balloon. ^{*f*} At 60 °C. ^{*g*} At 40 °C. ^{*h*} At 20 °C.

obtained. Further increasing the amount of catalyst did not increase the yield and conversion of the reaction.

With the establishment of optimized conditions, various tetrahydroquinoline derivatives were investigated in the catalytic system (Table 5). When the aromatic ring of tetrahydroquinoline was substituted, the substrates were fully converted in 6 h and good to excellent conversions and selectivities to functional quinolines were readily obtained (Table 5, entries 1–6). The turnover numbers (TONs)

represent the efficiency of the catalyst, and the 2 [PW]-OMS-2 reaction system gave a high TON of 7.2 in 6 h under optimized conditions, which is higher than 1.7 for similar reaction systems.^{18,37} Moreover, alkyl and cycloalkyl substrates were introduced into the investigation, and moderate conversions and excellent selectivities to the corresponding products were obtained (Table 5, entries 7 and 8). The high reactivity of the catalytic system encouraged us to test the dehydrogenation of selected interesting bioactive

Entry	Substrate	Product	Conv. (%)	Sel. (%)	TON^b
1			99	>99	7.2
	1a	2a			
2	Me	Me	98	>99	7.2
	1b	2b			
3	Ph N H	2c	78	98	5.7
4	1c	20	70	00	
4	G		78	99	5./
-	1d	2d	-4	00	5.0
5		wie	/1	98	5.2
	н 1е	2e			
6	Br	Br	91	95	6.7
	н 1f	2f			
7	n-Bu	п-Ви	84	98	6.2
	₩ N H	2g			
8			82	>99	6.0
		لر المراجع الم 2h			
9		$\langle \rangle$	61	>99	4.5
	H 1:	2i			

^{*a*} Reaction conditions: substrate (0.2 mmol), 2 [PW]-OMS-2 (20 mg), DMC (1 mL), O₂ balloon, 80 °C, 6 h. ^{*b*} Turn over number, TON = moles of amines converted/moles of catalyst. Formula weight of OMS-2 (KMn₈O₁₆·*n*H2O) is 734.6 g mol⁻¹ (excluding the water).³⁸

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Table 6 Oxidative dehydrogenation of other N-containing compounds over 2 [PW]-OMS-2^a

Entry	Substrate	Product	Conv. (%)	Sel. (%)	TON ^c
1	NH NH OMe	N N OMe	98 $(49)^b$	99 (92) ^b	$7.2 (3.6)^{b}$
2	3a		93 (43) ^b	99 (95) ^b	$6.8(3.2)^b$
3	3b		72 (37) ^b	99 (89) ^b	$5.2 (2.7)^{t}$
4	3c		89 $(32)^b$	99 $(95)^b$	$6.5 (2.4)^{b}$
5			95	98	6.8
6	3e		68	95	4.8
7	3f	$ \begin{array}{c} 4f \\ \swarrow \\ \searrow \\ \searrow \\ \searrow \\ \swarrow \\ \swarrow \\ \swarrow \\ \swarrow \\ \swarrow \\ \swarrow \\ $	46	82	3.4
8	3g		93	98	6.8
9	⊐ 3h ∭Me	4h	70	98	5.1
10	3i Br	4i Br	83	95	6.1
11	3j O ₂ N		80	97	5.9
12	3k ℂナ→	$\overset{\mathbf{4k}}{\underset{\mathbb{H}}{\overset{OH}}{\overset{OH}}{\overset{OH}}{\overset{{}}{\overset{{}}{{OH}}}{\overset{{OH}}}{\overset{{OH}}}}}{\overset{{OH}}{{}}}}}}}}}}$	93	>99	6.8
13	$\begin{array}{c} 3l \\ \overbrace{{}_{N} \leftarrow {}_{H}}^{N} \end{array}$		95	>99	7.0
14	3m	4m MeO OMe	99	>99	7.3
15		Me Nr Me 4n	92	>99	6.8

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Table 6 (continued)

Entry	Substrate	Product	Conv. (%)	Sel. (%)	TON ^c
16	MeO MeO Me Me H Me	MeO MeO Me Me Me	92	>99	6.8
17	3p Meo Meo Meo Meo Meo Meo Meo	4p Meo Me Me	81	97	5.9
18	3q 3q ⊖N 3r H	$ \begin{array}{c} \mathbf{4q} \\ \overset{N}{\underset{N}{\underset{Ar}{\overset{Ar}}{\overset{Ar}{\overset{Ar}{\overset{Ar}}{\overset{Ar}{\overset{Ar}{\overset{Ar}{\overset{Ar}{\overset{Ar}{\overset{Ar}{\overset{Ar}{\overset{Ar}{\overset{Ar}{\overset{Ar}{\overset{Ar}{\overset{Ar}{\overset{Ar}}{\overset{Ar}{\overset{Ar}{\overset{Ar}{\overset{Ar}}{\overset{Ar}{\overset{Ar}}{\overset{Ar}{\overset{Ar}}{\overset{Ar}{\overset{Ar}}{\overset{Ar}{\overset{Ar}}{\overset{Ar}{\overset{Ar}}{\overset{Ar}{\overset{Ar}}{\overset{Ar}{\overset{Ar}}{\overset{Ar}{\overset{Ar}}{\overset{Ar}{\overset{Ar}}{\overset{Ar}}{\overset{Ar}}{\overset{Ar}{\overset{Ar}}{\overset{Ar}{\overset{Ar}}}{\overset{Ar}{\overset{Ar}}}{\overset{Ar}{\overset{Ar}}{\overset{Ar}}{\overset{Ar}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}$	98	>99	7.2
19	3r		99	>99	7.3
20	3s	4s 4t 4t	58	>99	4.3

^{*a*} Reaction conditions: substrate (0.2 mmol), 2 [PW]-OMS-2 (20 mg), DMC (1 mL), O₂ balloon, 80 °C, 6 h. ^{*b*} The data in brackets were obtained using OMS-2 (20 mg) as the catalyst. ^{*c*} Turn over number, TON = moles of amines converted/moles of catalyst. Formula weight of OMS-2 (KMn₈O₁₆·nH₂O) is 734.6 g mol⁻¹ (excluding the water).³⁷

compounds. As an example, both dehydrogenation and oxygenation of the benzylic group occurred when **1i** was employed as a substrate which provided a 61% conversion with >99% selectivity. This heterocycle is an important motif in numerous biologically active compounds (Table 5, entry 9).¹⁶

To further examine the tolerance of the present catalytic system, more N-containing compounds were employed. The results in Table 6 indicate that the current catalytic system tolerates various N-containing aromatic heterocycles. For comparison of the catalytic activity, undoped OMS-2 was also checked in the reactions firstly (Table 6, entries 1-4). The conversions from 32% to 49% of 3a-3d were obtained over OMS-2, while good to excellent conversions of 3a-3d were isolated over 2 [PW]-OMS-2. The enhancement of catalytic activity of the doped OMS-2 composite catalyst is obvious. Then, more 1,2,3,4-tetrahydroquinazoline derivatives were tested in the system, and the corresponding dehydrogenation products were obtained in good conversions and selectivities, although the heterocyclic substituted one did not show good tolerance (Table 6, entries 5-7). The concerning 1H-indoline and its derivatives could also proceed well under the present conditions (Table 6, entries 8-12), and 2,3-dihydro-1Hpyrrolo[2,3-b]pyridine was catalyzed smoothly and gave a 95% yield of the desired product (Table 6, entry 13). The oxidation of the Hantzsch ester derivatives gave the corresponding dehydrogenation products with excellent yields in a short reaction time (Table 6, entries 14-17), which might be due to their strong tendency toward forming a stable aromatic ring.

With a similar structure to 1,2,3,4-tetrahydroquinazoline, 1,2,3,4-tetrahydroquinoxaline and 9,10-dihydroacridine could also give perfect yields (Table 6, entries 18 and 19). Finally, a moderate yield of isoquinoline could be obtained in the case of 1,2,3,4-tetrahydroisoquinoline (Table 6, entry 20).

Kinetic study. According to the current research results, the kinetics of 1,2,3,4-tetrahydroquinoline aerobic dehydrogenation on 2 [PW]-OMS-2 was carefully examined in dimethyl carbonate. The pore diffusion limitation inside the pores of the catalyst was investigated before the kinetic study.



Fig. 8 (a) Kinetic profiles under standard conditions. (b) Initial rates with respect to substrate concentration. (c) Initial rates with respect to catalyst quantity. (d) Calculation of reaction activation energy parameters.

Based on the internal diffusion, the Weisz–Prater rule was deduced,^{34–36,39} which represents the ratio of the rate of reaction to the rate of diffusion in the pores, as shown in the following formula:

$$\Phi_{\mathrm{WP}} = rac{r_{\mathrm{a}}R_{\mathrm{P}}^2}{C_{\mathrm{s,A}}D_{\mathrm{eff}}}$$

 $\Phi_{\rm WP}$ = the dimensionless WP parameter,

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 $r_{\rm a}$ = observed reaction rate per catalyst volume, [mol cm⁻³ s⁻¹ s],

 $R_{\rm P}$ = radius of the catalyst particle [cm],

 $C_{S,A}$ = gas-phase concentration of 'A' at the particle surface [m cm⁻³],

 $D_{\rm eff}$ = effective diffusivity of 'A' [cm² s⁻¹].

For similar liquid phase reactions, the calculation was carried out by referring to ref. 37, and the specific calculation procedures are shown in the ESI.† The value of Φ_{WP} for each $(\Phi_{WP|O_2} = 1.125 \times 10^{-4}; \Phi_{WP|1,2,3,4\text{-tetrahydroquinoline} = 3.009 \times 10^{-4})$ is less than 0.3, which can prove that there was no obvious pore diffusion limitation in the oxidative dehydrogenation of 1,2,3,4-tetrahydroquinoline in dimethyl carbonate under the standard reaction conditions.³⁷ Experiments using the Weisz–Prater criterion verified that there was no mass transfer limitation in the reaction.

The reaction conditions was continuously sampled and analyzed by GC, as shown in Fig. 8. As the reaction progresses, the concentration of product 2a increases. It can be seen from the figure that there is no obvious induction period. The initial reaction rate was determined by measuring the change of product concentration with time, and the relationship between substrate and catalyst concentrations and initial reaction rate was obtained. As shown in Fig. 8b and c, in the dehydrogenation system of 1,2,3,4-tetrahydroquinoline to quinoline, the initial reaction rate increases with the increasing concentrations of substrate 2a and catalyst, showing a good linear relationship (Fig. S5 and S6 in the ESI[†]). The results showed that the dehydrogenation of 1,2,3,4-tetrahydroquinoline is a first-order reaction, which was similar to the result for a mesoporous manganese oxide catalyst.38

The kinetic properties of the oxidative dehydrogenation system of the 1,2,3,4-tetrahydroquinoline reaction were studied by time-dependent experiments at different temperatures (Fig. S7 in the ESI†).



Scheme 1 Control experiments.



Fig. 9 Hot filtration test. Reaction conditions: 1,2,3,4-tetrahydroquinoline (1.0 mmol), 2 [PW]-OMS-2 (100 mg), DMC (5 mL), O_2 balloon, 80 °C.

For the experiments at different temperatures, the *k* values can be correlated by an Arrhenius-type expression, as shown in the following formula:

$$\ln k = -\frac{\mathrm{Ea}}{RT} + \ln A_0,$$

where Ea is the energy of activation (kJ mol⁻¹), A_0 is the preexponential factor (min⁻¹), which can be derived from the graph of ln *k* to 1/T depicted in Fig. 8(d). Through the multiple regression analysis of the constants in Fig. 8(d), this showed that the apparent activation energy (Ea) is 29.66 kJ mol⁻¹. Compared with that of the similar reaction system of mesoporous MnOx catalyst (34.6 ± 0.2 kJ mol⁻¹),³⁸ the apparent activation energy value is lower. Under the standard conditions, the reaction rate of the catalytic system is higher and the result is better.

Discussion of the mechanism. Although the mechanism of dehydrogenation catalyzed by Mn- and Fe-based catalysts have been proposed by Beller's,¹⁸ Xiao's and Suib's groups^{19,22} respectively, some control experiments were conducted (Scheme 1). Firstly, the reaction of **5a** did not occur at all, which proves that an adjacent conjugated functional group, like benzene, is necessary perhaps due to its electron-rich properties. As expected, 2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline **6a** did not participate in the reaction, which means that the α -C–H proton is critical for



Fig. 10 Oxidation of 1,2,3,4-tetrahydroquinoline: recycling of the 2 [PW]-OMS-2 catalyst. Reaction conditions: 1a (0.2 mmol), 2 [PW]-OMS-2 (15 mg), DMC (1 mL), O_2 balloon, r.t., 6 h for each cycle. Conversions and selectivities were determined by GC.

the substrate and a cyclic imine intermediate would be formed firstly. The detailed discussion of the proposed mechanism is found in the ESI.[†]

Surprisingly, *N*-substituted indole 7a could proceed through the reaction successfully and the corresponding dehydrogenated product 7b was collected in 60% yield (Scheme 1). From the results from other research studies, the C==C linkage in 7b generally is hard to directly form and the N-H motif is favorable for the adsorption of the substrate on their solid catalysts.^{18,38} Nevertheless, our results from the reaction of 7a indicate that the C==C linkage in 7b could directly form and possibly, the C-C bond in 7a could adsorb on the surface of as-synthesized 2 [PW]-OMS-2 due to its mixed crystal phases and newly generated catalytic active species.

The stability and recyclability of [PW]-OMS-2. Lastly, we used 1a as the substrate; a hot filtration experiment was firstly performed to probe the stability of the catalyst. After 20 min (at about 60% conversion of 1a), the catalyst was separated by filtration and the filtrate without catalyst was kept stirring for the next 70 min, and no further conversion of the substrate was detected (Fig. 9). In heterogeneous catalysis, it is still challenging to avoid aggregation and leaching of the active metal during the reaction, which often results in deactivation of the catalysts. To further check the leaching of metals, the reaction filtrate was analyzed by ICP-AES. The results show that the manganese and tungsten species were hardly detected, and the amounts of W and Mn ions in the filtrate were only 0.000069% and 0.00085%, respectively, so the catalysis in our study is truly heterogeneous.

The recyclability of 2 [PW]-OMS-2 has also been studied. In order to ensure the reliability of the catalyst stability test, we correspondingly reduced the amount of catalyst used and decreased the reaction temperature to room temperature (other conditions were maintained as those in the standard reaction conditions). Firstly, the catalytic reaction proceeded smoothly when the reaction scale was decreased to 0.2 mmol of 1a with 15 mg of catalyst in 1 mL of DMC. The results indicate that the catalyst after five cycles showed similar catalytic activity as the fresh one under the same reaction conditions (Fig. 10). Moreover, the conversion rate of 1,2,3,4tetrahydroquinoline was stable at about 39%, and the selectivity remained at 99%. The changes of the retrieved catalyst were measured by XRD, which confirms that the cryptomelane/Mn2O3 hydrate phases and crystallinity were retained after five recycles (see ESI† Fig. S4). Next, N2 adsorption/desorption measurements were performed to explore the change of the textural parameters of used 2 [PW]-OMS-2. The S_{BET} , pore volume, and average pore diameter were all maintained after five recycles (see ESI[†] Table S3), suggesting that 2 [PW]-OMS-2 has good structural stability. In addition, we compared various catalytic activities in a similar reaction system of 1,2,3,4-tetrahydroquinoline dehydrogenation, and we found that 2 [PW]-OMS-2 showed the best catalytic performance (see ESI[†] Table S1).

Conclusions

In conclusion, sodium phosphotungstate doped OMS-2 and applied nanocomposites were prepared as а heterogeneous catalyst in oxidative dehydrogenation of N-heterocycles. The as-synthesized catalyst showed great substrate tolerance, highly enhanced catalytic activity (compared with undoped OMS-2) and great recyclability. Moreover, the new catalyst was fully characterized and it was found that it had newly generated mixed crystal phases, an enhanced surface area and labile lattice oxygen. The kinetic study concluded that the dehydrogenation of 1,2,3,4tetrahydroquinoline was a first-order reaction with an apparent activation energy of 29.66 kJ mol⁻¹. It is believed that the doped OMS-2 nanocomposite catalyst has more potential towards other oxidation processes due to its exclusive physicochemical properties.

Conflicts of interest

There are no conflicts to declare.

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