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Article

Geometric and electronic effects on the performance of a bifunctional Ru₂P catalyst in the hydrogenation and acceptorless dehydrogenation of *N*-heteroarenes

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ABSTRACT

The development of bifunctional catalysts for the efficient hydrogenation and acceptorless dehydrogenation of *N*-heterocycles is a challenge. In this study, Ru₂P/AC effectively promoted reversible transformations between unsaturated and saturated *N*-heterocycles affording yields of 98% and 99%, respectively. Moreover, a remarkable enhancement in the reusability of Ru₂P/AC was observed compared with other Ru-based catalysts. According to density functional theory calculations, the superior performance of Ru₂P/AC was ascribed to specific synergistic factors, namely geometric and electronic effects induced by P. P greatly reduced the large Ru-Ru ensembles and finely modified the electronic structures, leading to a low reaction barrier and high desorption ability of the catalyst, further boosting the hydrogenation and acceptorless dehydrogenation processes.

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1. Introduction

Saturated and unsaturated *N*-heterocyclic compounds are highly valuable building blocks in the pharmaceutical industry [1–6]. However, it is very challenging to achieve a reversible interconversion of *N*-heterocycles owing to the different adsorption/desorption ability requirements of related species [2,7]. Therefore, it is crucial to design catalysts with appropriate electronic [8] and geometric structures to achieve equilibrium among the saturated and unsaturated *N*-heterocyclic compounds on the catalyst surface.

Extensive studies have been conducted on the use of homogeneous catalysts for the reversible transformation of *N*-heteroarenes, mainly including Ir [9,10] and Fe [7] catalysts, which required long reaction times and harsh additives [11]. Compared with homogeneous catalysts, heterogeneous catalysts are preferred in the chemical industry because of the ease of catalyst separation and reuse. At present, supported metal

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nanocatalysts are generally used for hydrogenation [2,12–14] or dehydrogenation [5,15–18] reactions. However, the strong coordination of *N*-heterocyclic compounds to metal nanoparticles (NPs) disfavors the adsorption of other substrates, resulting in low activity and poor reusability. Apart from modifying the support [19], tuning the topology of the active sites [17,20] is also an effective and direct method to improve the metal properties. The fabrication of Pd_xAu_{1-x} bimetallic catalysts could lead to the selective adsorption of halogenated quinolines on Au rather than on Pd via a tilted orientation, which may protect the active sites of the catalysts [2]. Ru catalysts have been used in the chemoselective hydrogenation of quinolones [21]. Unfortunately, their poor reusability and strict reaction conditions made Ru-based catalysts not very good hydrogenation catalysts [22]. The incorporation of foreign atoms at the interstitial sites [23], such as transition metal carbides [24–26] and transition metal phosphides [27–30], might induce different geometric and electronic properties [31], which could regulate the reaction and desorption barriers of the substrate on the surface of the catalyst [32]. Herein, we demonstrated that ruthenium phosphide NPs supported on activated carbon (Ru₂P/AC) could be employed as an efficient bifunctional catalyst for direct reversible transformations between unsaturated and saturated *N*-heterocycles. The bifunctional properties were due to the phosphorus atom, which altered the intrinsic spatial structure and electronic distribution of ruthenium. It was revealed that the balance between reaction and desorption could be adjusted by the synergistic geometric and electronic effects, thereby achieving bifunctional properties.

2. Experimental

2.1. Materials

Activated carbon (AC; Jiuding Chemical (Shanghai) Technology Co., Ltd.), RuCl₃ (99.99% Bide Pharmatech Ltd.), NaH₂PO₂ (AR, 99.0% Aladdin Industrial Co., Ltd), H₃PO₄ (AR, ≥85.0%, Sinopharm Chemical Reagent Co., Ltd), ethanol (≥99.7%, Sinopharm Chemical Reagent Co., Ltd), and other quinoline reagents (Bide Pharmatech Ltd.) were purchased from commercial sources. Millipore deionized water was used to prepare all solutions.

2.2. Synthesis of Ru₂P/AC

The synthesis of Ru₂P/AC [27] is shown in Scheme 1. Specifically, 1 mL of an aqueous solution of RuCl₃ (Ru³⁺: 10 mg/mL) and (AC 500 mg) was added to 50 mL of deionized water, and the mixture was stirred vigorously overnight at

Scheme 1. Schematic of the Ru₂P/AC preparation process along with the hydrogenation and dehydrogenation of quinolines based on Ru₂P/AC.

room temperature. Then, the solution was evaporated at 80 °C to afford the Ru precursor. NaH₂PO₂ was added to the Ru precursor, and the mixture was fully ground in an agate mortar. The P/Ru mole ratio was adjusted to 1:1, and NaH₂PO₂ (8.51 mg) was pestled with the Ru precursor. The as-collected powder was carbonized at 600 °C (heating rate of 5 °C/min) under a N₂ atmosphere. The crude Ru₂P/AC catalyst was washed sequentially with 50 mL of deionized water and 30 mL of ethanol 3 times to remove the by-products. The Ru₂P/AC catalyst was then dried in an oven at 60 °C overnight under vacuum.

2.3. Synthesis of P_AC

A P_AC sample was prepared by a two-step thermal annealing process [33]. First, 200 mg of AC, 200 μL of phosphoric acid, and 200 mL of deionized water were mixed, treated by ultrasonication for 12 h, and freeze-dried. Second, the as-collected sample was carbonized at 800 °C under a N₂ atmosphere for 2 h at a ramp rate of 5 °C/min to afford P_AC.

2.4. Synthesis of P/AC

For the synthesis of P/AC, 10 mg of NaH₂PO₂ and 500 mg of AC were added to a quartz mortar, and the mixture was fully ground. The as-collected powder was carbonized at 600 °C (heating rate of 5 °C/min) under a N₂ atmosphere. The crude P/AC catalyst was washed sequentially with 50 mL of deionized water and 30 mL of ethanol 3 times to remove the by-products. The P/AC catalyst was dried in an oven at 60 °C overnight under vacuum.

2.5. Synthesis of Ru/AC

A 1 mL of an aqueous solution of RuCl₃ (Ru³⁺: 10 mg/mL) and 500 mg of AC were added to 50 mL deionized water, and the mixture was stirred vigorously overnight at room temperature. Then, the volatiles were removed by evaporation at 80 °C, and the dried sample was treated at 600 °C for 5 h at a ramp rate of 5 °C/min under a N₂ atmosphere to afford Ru/AC.

2.6. Synthesis of Ru/P_AC

This process was similar to that used for the synthesis of Ru/AC. Thus, 1 mL of an aqueous solution of RuCl₃ (Ru³⁺: 10 mg/mL) and 500 mg of P_AC were added to 50 mL of deionized water, and the mixture was stirred vigorously overnight at room temperature. Then, the volatiles were removed by evaporation at 80 °C, and the dried sample was treated at 600 °C for 5 h at a ramp rate of 5 °C/min under a N₂ atmosphere to afford Ru/P_AC.

2.7. Synthesis of RuO₂/AC

Ruthenium oxide was prepared by a mild hydrothermal reaction [34]. Typically, 200 μL of a RuCl₃ solution (Ru³⁺: 10 mg/mL) and 100 mg of AC were added to 30 mL of deionized water under magnetic stirring. Subsequently, the suspension

was transferred into a Teflon-lined autoclave and kept at 180 °C for 24 h. After cooling to room temperature, the precipitates were separated by centrifugation and washed with water several times until the pH was ~7. The product was dried at 60 °C overnight.

2.8. Synthesis of RuS₂/AC

A 1 mL of an aqueous solution of RuCl₃ (Ru³⁺: 10 mg/mL) and 500 mg of AC were added to 50 mL of deionized water, and the mixture was stirred vigorously overnight at room temperature. Then, the volatiles were removed by evaporation at 80 °C to leave the precursor. Sulfur was added to the black powder, and the mixture was fully ground in an agate mortar. The S/Ru mole ratio was adjusted to 2:1, and S (6.33 mg) was pestled with the Ru precursor. The as-collected powder was treated at 600 °C (heating rate of 5 °C/min) under a N₂ atmosphere. The crude RuS₂/AC catalyst was washed sequentially with 50 mL of deionized water and 30 mL of ethanol 3 times to remove the by-products. The RuS₂/AC catalyst was dried in an oven at 60 °C overnight under vacuum.

2.9. General hydrogenation procedure

In a 50 mL stainless steel autoclave purchased from Anhui Kemi Machinery Technology Co., Ltd., quinoline (0.5 mmol) and Ru₂P/AC (15 mg) were mixed with 2 mL of ethanol. Subsequently, hydrogen was injected to replace the air twice in the autoclave, which was pressurized with hydrogen at 5 bar. Then, the autoclave was heated at 60 °C using an oil bath block. After 5 h, the autoclave was rapidly cooled to room temperature and hydrogen was released. The crude reaction mixture was centrifuged at a speed of 6000 r/min to afford 1,2,3,4-tetrahydroquinoline and further analyzed by GC-MS.

2.10. General procedure for acceptorless dehydrogenation

Acceptorless dehydrogenation (dehydrogenation) is a conventional anhydrous anaerobic transformation. In a round bottom flask equipped with a condensing tube (50 mL), 1,2,3,4-tetrahydroquinoline (0.25 mmol) and Ru₂P/AC (30 mg) were mixed with 3 mL of mesitylene. The flask was flushed with a nitrogen balloon twice. Then, the flask was placed in an oil bath block, and the reaction was performed at 145 °C. After 24 h, the reaction was completed, the flask was cooled to room temperature, and the crude reaction mixture was centrifuged at a speed of 6000 r/min to afford quinoline and further analyzed by GC-MS.

2.11. Recycling of the catalysts

To avoid loss of the catalysts during the regeneration process, the reaction vials were directly centrifuged at 6000 rpm to demulsify and remove the liquid phase. The used catalysts were then washed three times with ethanol. Finally, the washed catalysts along with the vials were dried under vacuum (60 °C) and then used for the next cycle.

2.12. DFT calculations

All the calculations involving the quinoline (C₉H₇N) hydrogenation and 1,2,3,4-tetrahydroquinoline (C₉H₁₁N) dehydrogenation were performed using the Vienna ab initio simulation program (VASP) [35,36]. The Perdew-Burke-Ernzerhof (PBE) [37], which is one of the most common functional in the generalized gradient approximation (GGA), was employed to describe the exchange-correlation energy. Considering the importance of the van der Waals interactions for organics [38,39], the DFT-D3 method [40,41] was introduced in both the geometric optimization and transition state research process. The projector-augmented-wave (PAW) method [42,43] of plane-wave basis was utilized to describe the interaction of the core-valence electrons. The cut-off energy was 400 eV. In the calculation, four different models were built, including (1) A (3 × 5) unit cell of Ru(101) surface with the lattice constants $A = 15.2 \text{ \AA}$, $B = 13.5 \text{ \AA}$, and $C = 21.5 \text{ \AA}$, (2) A (3 × 3) unit cell of RuS₂(200) surface with the lattice constants $A = 16.8 \text{ \AA}$, $B = 16.8 \text{ \AA}$, and $C = 25.6 \text{ \AA}$, (3) A (5 × 3) unit cell of RuO₂(110) surface with the lattice constants $A = 15.6 \text{ \AA}$, $B = 19.2 \text{ \AA}$, and $C = 27.8 \text{ \AA}$, and (4) A (2 × 2) unit cell of Ru₂P(112) surface with the lattice constants $A = 21.0 \text{ \AA}$, $B = 19.8 \text{ \AA}$, and $C = 23.4 \text{ \AA}$. For the Ru(101) and RuS₂(200) surfaces, Monkhorst pack *k*-point mesh sampling was used as 2 × 2 × 1, while the other surface mentioned above was set as 2 × 1 × 1. All surfaces were built in four layers periodically with the bottom two layers fixed, while the top two layers were relaxed in the 15 Å vacuum space. The BFGS minimization scheme was used to relax the ionic degrees of freedom until the Hellman-Feynman forces on each ion were less than 0.05 eV/Å. A constrained optimization scheme was used to search the transition states (TSs) [44–46]. Two rules were used for confirming the transition states: (1) all forces on the atoms were optimized as to be less than 0.05 eV/Å; (2) the total energy was the largest along the reaction coordinate, but the smallest with respect to all other degrees of freedom. Vibrational frequency analysis is vital to confirm the integrity of the states in the transition state research.

3. Results and discussion

3.1. Materials characterization

Initially, a detailed characterization of Ru₂P/AC was conducted. The Ru content of Ru₂P/AC was found to be 1.024 wt%, as determined by ICP-MS (Table S1). This indicated that the Ru content in Ru₂P NPs did not decrease compared with the raw Ru/AC sample. The morphology of the samples was investigated by transmission electron microscopy (TEM). The Ru₂P NPs were uniformly deposited on an AC surface (Fig. 1(a)), and the mean particle size was found to be 2.25 nm according to the statistics of more than 200 individual NPs. As shown in the high-resolution transmission electron microscopy (HRTEM) image (Fig. 1(b)), clear lattice fringes with an interlayer spacing of ~0.235 nm were observed and assigned to the (112) plane of Ru₂P, which may display different structural properties compared to the Ru metal. Moreover, the dark-field TEM and ener-

Fig. 1. (a) TEM image, inset shows the size distribution histogram; (b) HRTEM image; (c) Corresponding EDS elemental (C, P, and Ru) mapping, and (d) Elemental line profile of Ru and P.

gy dispersive X-ray spectroscopy (EDXS) (Fig. S1) elemental mapping profiles (Fig. 1(c)) revealed that Ru and P were uniformly distributed throughout the catalyst skeleton. The elemental mapping of Ru₂P/AC revealed overlapping distributions of P (Fig. S2(c)) and Ru (Fig. S2(d)), further verifying the interaction of the P atoms surrounding the Ru. Elemental line-scans across several linear NPs revealed that the atomic ratio of Ru and P was close to 2:1 (Fig. 1(d)). This trend was consistent with the HRTEM results.

Next, the chemical nature of Ru₂P/AC was studied by X-ray photoelectron spectroscopy (XPS) (Fig. S3). The Ru 3 $p_{3/2}$ and Ru 3 $p_{1/2}$ peaks of Ru-P were located at 461.7 and 483.9 eV (Fig. 2(a)), respectively, and thus blue-shifted by 0.2 eV from the Ru 3 $p_{3/2}$ of metal Ru (461.5 and 483.7 eV, Fig. S4(a)). This phenomenon was attributed to the P-Ru bonding structures, in which the electron density of the outer layer of Ru was reduced, thus weakening the shielding effect and increasing the binding energy. Moreover, the relatively slight shift of Ru₂P might be caused by the small amount of P [47]. On the other hand, Ru hydroxide and oxidized Ru-P species could be observed at 464.7 and 487.9 eV, respectively. Correspondingly, the P 2 $p_{3/2}$ peak at 129.1 eV (Fig. 2(b)) was assigned to Ru-P, which was red-shifted by 1.0 eV from the neutral peak (130.1 eV for 2 $p_{3/2}$). This mainly originates from the negatively charged P ions of the Ru-P bond. It should be noted that the main peak located at 132.2 eV was attributed to the P-O bonds at the surface phosphate-related groups due to surface oxidation [47]. To further verify the composition of the catalyst, X-ray diffraction (XRD) investigations were performed; however, no peaks corresponding to Ru₂P were found (Fig. S5) due to the low loading of these elements on the composites [27].

3.2. Catalytic hydrogenation and acceptorless dehydrogenation

To investigate the role of P on the catalytic activity, we

Fig. 2. (a) XPS spectrum of Ru 3 $p_{3/2}$ and Ru 3 $p_{1/2}$; (b) XPS spectrum of P 2 p .

evaluated the catalytic hydrogenation and dehydrogenation performance of the Ru₂P/AC bifunctional catalyst using quinoline and tetrahydroquinoline as model reactants, respectively. A series of catalysts prepared under different feed ratios of P and Ru were tested in the reversible reaction, and the related characterization is displayed in Fig. S6. It was found that all catalysts prepared with different feeding ratios exhibited excellent hydrogenation and dehydrogenation performance (Table S3). The hydrogenation and dehydrogenation reaction conditions were screened for the most active catalyst (Figs. S7–S10 and Table S4). The catalytic behavior of the carbon, P-doped carbon (P-AC), phosphate and carbon (P/AC), Ru/P-AC, Ru₂P/AC, RuO₂/AC, and RuS₂/AC catalysts is illustrated in Table 1. No catalytic hydrogenation product was observed for AC, P-AC, and P/AC. However, P-AC could activate the dehydrogenation process and a 62.9% conversion was observed. This can be explained by the fact that the P-AC material possessed a higher work function than normal carbon materials, which led to higher activity in catalytic aerobic oxidation reactions [48]. Moreover, the phosphate in P/AC did not exert any catalytic activity in this reversible reaction. Ru/AC and Ru/P-AC displayed low activity for the hydrogenation of quinoline within 5 h unless the reaction temperature and H₂ pressure were increased to 80 °C and 10 bar, respectively. However, the performance for the dehydrogenation to quinoline reached 50.9%, which seemed that the dehydrogenation was likely a ruthenium-catalyzed process. Remarkably, Ru₂P/AC exhibited a superior TOF value for both hydrogenation and dehydrogenation processes than previously reported results (Table S5). More importantly, the chemoselectivity of both reactions approached 99.9%, and the content of byproducts was below the detection limit of gas chromatography-mass spectrometry (GC-MS). This may be due to the formation of phosphide, which makes the Ru electron-deficient because of the electron transfer from Ru to phosphorus. The decreased electron density of the active transition metal may enhance the adsorption of electron-rich aromatic rings. Then, RuO₂/AC was used as catalyst, which could hardly catalyze the hydrogenation of quinoline, but displayed excellent dehydrogenation activity due to the higher valence Ru in RuO₂/AC. RuS₂/AC also displayed a lower conversion in the hydrogenation reaction than Ru₂P/AC; however, the dehydrogenation activity was exceptional. Ru₂P/AC emerged as an optimal bifunctional catalyst, which allowed a reversible reaction to reach completion under relatively mild experimental conditions.

Table 1Reversible transformation between **1a** and **2a** via hydrogenation-acceptorless dehydrogenation reactions catalyzed by a variety of catalysts.

		1a			2a		
Entry	Catalyst	Hydrogenation ^a			Dehydrogenation ^b		
		Conversion (%)	Selectivity ^c (%)	TOF ^d (h ⁻¹)	Conversion (%)	Selectivity ^e (%)	TOF ^f (h ⁻¹)
1	Ru ₂ P/AC	98.7	>99.9	164.4	98.0	>99.9	22.5
2	AC	0.0	0.0	—	0.0	0.0	—
3	P_AC	0.0	0.0	—	62.9	>99.9	—
4	P/AC	0.0	0.0	—	0.0	0.0	—
5	Ru/AC	65.7	98.9	47.3	47.9	99.2	2.2
6	Ru/P_AC	5.9	98.1	3.64	61.4	99.3	2.8
7	RuO ₂ /AC	0.0	0.0	—	99.2	>99.9	4.6
8	RuS ₂ /AC	32.6	99.6	19.8	99.7	94.6	4.5

^a Hydrogenation conditions unless otherwise mentioned: 0.5 mmol substrate **1a**, 15 mg catalyst, H₂ (5 bar), EtOH 2 mL at 60 °C for 5 h; ^b Dehydrogenation conditions unless otherwise mentioned: 0.25 mmol substrate **2a**, 20 mg catalyst, N₂ (1 bar), 3 mL mesitylene at 145 °C for 24 h; ^c Selectivity of product **2a**, as determined by GC-MS; ^d TOF = [moles of reactants reacted]/[(moles of metal used)*(reaction time)]; ^e Selectivity of product **1a**, as determined by GC-MS.

3.3. Catalytic mechanism

To understand the mechanism of the enhanced performance of foreign elements, especially P, DFT models for a series of Ru-based catalysts (Ru (101), RuS₂ (200), RuO₂ (110), and Ru₂P (112)) were constructed based on the XRD standard card and lattice fringes of HRTEM (Figs. S5 and S11). At the geometric configuration level, the dispersion distance between two adjacent Ru atoms substantially affected the chemisorption energy of the intermediates. It was found that the dispersion distance on Ru was 2.61 Å, which was much shorter than that on the other three surfaces (Figs. S12 and S13). The existence of the heteroatoms could cause the dispersion of the original Ru dense arrangement, leading to a larger distance between two adjacent Ru atoms. Thus, the presence of more Ru atoms in the unit area led to higher chemisorption energy of the intermediates on the surface of Ru (101). For instance, the chemisorption energies of **1a** and **2a** ($E_{ad} > 4$ eV) were much higher than those of the other three surfaces (Figs. 3(a–h)). Another change in the geometric structure may be due to the adsorption behavior of the molecular structure. The calculation results showed that, in

the hydrogenation reaction, the weakly adsorbed 1,2,3,4-tetrahydroquinoline (C₉H₁₁N) on the Ru₂P (112) surface was closer to flat than the Ru (101) surface (Figs. 3(a–d)). This is more conducive to the hydrogenation reaction. In the dehydrogenation reaction, the inclined adsorption of quinoline (C₉H₇N) on the Ru₂P (112) surface was also more beneficial to the reaction. Meanwhile, the change in the chemisorption energy was caused not only by the geometric properties but also by the electronic configurations of the Ru-based catalyst. The average charge distribution of Ru was carefully examined through Bader charge analysis (Fig. S14), which showed that Ru was regulated from a zero-charged state to a positively charged state by the different heteroatoms, thus achieving electron transfer from Ru to the heteroatoms. It is worth noting that various types of heteroatoms had different abilities to localize the electrons from Ru, which is consistent with the results of XPS (Fig. 2(a) and Fig. S(4)). For instance, O atoms localized more electrons on average than other heteroatoms (S, P) from Ru atoms with a value of 1.17|e|, followed by the S atom with a value of 0.32|e|. In particular, it was surprising to observe that only tiny electrons were transferred from the Ru to the P atom with a value of 0.03|e| (Fig. S14), which further confirmed the Ru 3p XPS result (Fig. S4). The Bader charge analysis of the desorption products for the hydrogenation and dehydrogenation processes is displayed in Figs. 3(a–h). More electrons were localized on **2a** (0.35|e|) and **1a** (0.77|e|) for Ru (101), leading to a poor desorption ability for both hydrogenation and dehydrogenation reactions. Along with heteroatoms (S, O, P) and Ru forming a new crystal plane structure, the electrons in the intermediates were greatly reduced, leading to a better desorption ability. In particular, a striking feature was revealed on Ru₂P (112), where the least electrons were localized on **2a** (0.01|e|) and **1a** (0.33|e|) compared with those on the other three surfaces. This explains the origin of the high desorption ability of Ru₂P (112) for both hydrogenation and dehydrogenation.

To further understand the high performance of the bifunctional catalyst Ru₂P (112), both hydrogenation and dehydro-

Fig. 3. (a–d) Charge density difference of the product of hydrogenation (**2a**) on Ru(101), RuS₂(200), RuO₂(110), and Ru₂P(112), respectively, and (e–h) Charge density difference of the product of dehydrogenation (**1a**) on Ru(101), RuS₂(200), RuO₂(110), and Ru₂P(112), respectively.

Fig. 4. (a) 2-D activity heat map displaying the hydrogenation reaction conversion rate of various catalysts as a function of the desorption energy and rate-determining step barrier of **2a**. Hydrogenation conditions: 0.5 mmol quinoline, 15 mg Ru₂P/AC catalyst, H₂ (5 bar), EtOH 2 mL at 60 °C for 2 h. (b) 2-D activity heat map displaying the dehydrogenation reaction conversion rate of various catalysts as a function of the rate-determining step barrier and desorption energy of **1a**. Dehydrogenation conditions: 0.25 mmol tetrahydroquinoline, 20 mg Ru₂P/AC catalyst, N₂ (1 bar), 3 mL mesitylene at 145 °C for 10 h.

genation reactions were calculated. The corresponding energy data and reaction structures are displayed in Tables S6–S13 and Figs. S15–S22. A 2-D activity heat map was used to describe the catalytic activity as a function of the rate-determining step barrier and product desorption energy (Figs. 4(a,b)). For the hydrogenation process, the rate-determining step barrier concept was used to determine the important elementary steps. The calculated values are displayed in Fig. 5. The optimized catalyst (Ru₂P) for hydrogenation on the top of the volcano surface exhibited the highest desorption ability together with lowest rate-determining step barrier. The activity of Ru (101) was limited by the poor desorption ability of the intermediate, although the rate-determining step barrier was low. RuS₂ (200) and RuO₂ (110) displayed a higher rate-determining step barrier ($E_a > 1.45$ eV) and lower desorption ability ($E_{ad} < -2.3$ eV) than that Ru₂P (112), which also inhibited the performance of the hydrogenation process. Similarly, the highest dehydrogenation performance of Ru₂P (112) was attributed to the lowest rate-determining barrier ($E_a = 0.75$ eV) and high desorption ability ($E_{ad} = -2.35$ eV). It should be noted that the desorption ability of RuS₂ (200) ($E_{ad} = -2.33$ eV) and RuO₂ (110) ($E_{ad} = -2.50$ eV) were close to that of Ru₂P (112). Thus, the primary difference of activity derived from the higher rate-determining barrier of RuS₂ (200) ($E_a = 1.77$ eV) and RuO₂ (110) ($E_a = 1.11$ eV). Ru had a moderate rate-determining step barrier (1.24 eV) but the poorest desorption ability ($E_{ad} = -4.26$ eV), which highly restricted the activity. These results indicated that Ru₂P (112) allowed the achievement a balance between reaction and de-

Fig. 5. (a) Energy profiles of C₉H₁₁N hydrogenation; (b) Energy profiles of C₉H₁₁N dehydrogenation in the presence of Ru₂P (112), Ru (101), RuS₂ (200), and RuO₂ (110).

Fig. 6. Reusability test of the catalyst: (a) reusability test for the hydrogenation by the Ru₂P/AC catalyst over 8 cycles at 60 °C for 5 h under H₂ (5 bar); (b) reusability test for the hydrogenation by comparative catalysts over 5 cycles: Ru/AC was used at 80 °C for 5 h under H₂ (10 bar), while RuS₂/AC was used at 80 °C for 12 h under H₂ (10 bar); (c) reusability test for the dehydrogenation by the Ru₂P/AC catalyst over 8 cycles at 145 °C for 24 h under N₂ (1 bar); (d) reusability test for the dehydrogenation by the Ru/AC and RuS₂/AC catalysts over 5 cycles at 145 °C for 24 h under N₂ (1 bar).

sorption, leading to high performance in both hydrogenation and dehydrogenation processes.

3.4. Catalytic stability

By taking into account what discussed above, Ru₂P/AC also displayed an obvious advantage in reusability compared with other catalytic systems (Fig. 6). In terms of stability, the activity of Ru₂P/AC was not significantly reduced after 8 cycles of reuse in both the hydrogenation and dehydrogenation reactions (Fig. 6(a), (c)), which suggested a potential advantage in practical applications. As illustrated in Fig. 6(b), the hydrogenation conversion gradually decreased with the reaction cycles for Ru/AC and RuS₂/AC at elevated reaction temperatures and longer reaction times. Gratifyingly, Ru₂P/AC showed excellent conversion and selectivity in the dehydrogenation reaction even after eight runs, as shown in Fig. 3(c). According to the results of the DFT calculations and catalytic activity performance, the stability of the catalyst was also greatly influenced by the reaction barrier and desorption ability. During the hydrogenation process, it was likely that the catalyst reusability was inversely proportional to the desorption ability of 1,2,3,4-tetrahydroquinoline. The Ru catalyst showed the fastest catalytic activity attenuation in the recycling experiment, followed by RuS₂. In contrast, Ru₂P, which displayed the highest desorption ability and lowest rate-determining step barrier, exhibited the best reuse performance in the hydrogenation of quinoline. For the dehydrogenation reaction, the Ru catalyst with the worst desorption ability exhibited a negligible catalytic activity. Other catalysts displayed a similar desorption ability and reaction barrier (Fig. 4(b)), therefore their reuse performance in the dehydrogenation process was relatively better than that in the quinoline hydrogenation process. Only after the

Table 2Ru₂P/AC catalyzed hydrogenation and dehydrogenation of various quinolines.

$ \begin{array}{ccc} \text{R}_1-\text{C}_6\text{H}_3-\text{N}=\text{C}-\text{R}_2 & \xrightleftharpoons[\text{Dehydrogenation}]{\text{Hydrogenation}} & \text{R}_1-\text{C}_6\text{H}_4-\text{N}-\text{CH}_2-\text{R}_2 \\ \text{A} & & \text{B} \end{array} $						
Entry	Substrate (A)	Substrate (B) ^a	Hydrogenation ^b		Dehydrogenation ^c	
			Conversion (%)	Selectivity ^d (%)	Conversion (%)	Selectivity ^e (%)
1			98.7	>99.9	98.0	>99.9
2			99.1	>99.9	99.9	92.5
3			99.5	>99.9	99.9	86.8
4			99.4	>99.9	99.9	93.4
5			98.9 ^f	>99.9	99.9	95.8
6			99.2	>99.9	99.9	98.0
7			99.6	>99.9	99.9	89.9
8			99.2	>99.9	99.9	87.6
9			99.5 ^g	>99.9	99.0	89.4

^a Substrate B was prepared by hydrogenation of substrate A; ^b Hydrogenation conditions unless otherwise mentioned: 0.5 mmol substrate A, 15 mg Ru₂P/AC catalyst, H₂ (5 bar), 2 mL EtOH at 60 °C for 5 h; ^c Dehydrogenation conditions unless otherwise mentioned: 0.25 mmol substrate B, 20 mg Ru₂P/AC catalyst, N₂ (1 bar), 3 mL mesitylene at 145 °C for 24 h; ^d Sel. of the hydrogenation product determined by GC-MS; ^e Sel. of the dehydrogenation product determined by GC-MS; ^f 10 h; ^g 0.25 mmol substrate A, 20 mg Ru₂P/AC catalyst, H₂ (10 bar), 80 °C for 40 h. (Corresponding NMR characterization can be found in the SI).

fourth run, RuO₂ showed an obvious decrease in catalytic activity. Meanwhile, the desorption also played a crucial role in catalytic performance. Furthermore, the catalyst was analyzed by TEM after its 8 recycles, and the results clearly demonstrated that the particle size and relatively clear lattice fringes of Ru₂P remained unchanged, which indicated excellent stability and recyclability (Fig. S23). In contrast, almost all Ru NPs in Ru/AC were surrounded by a bubble structure (Fig. S24), which implied that quinoline and tetrahydroquinoline might be concentrated around the catalyst and could not be dispersed in accordance to the strong adsorption energy observed by the DFT calculations. Only a trace amount of Ru was leached into the solvent, as demonstrated by ICP-MS (Table S1), which was also responsible for the good reusability of the as-prepared Ru₂P/AC catalyst.

3.5. Scope

As Ru₂P/AC showed an excellent catalytic hydrogenation and dehydrogenation performance, the general scope of Ru₂P/AC was further investigated in the reversible transformation of *N*-heteroarenes with different substituent groups (Table 2 and Table S14). Hydrogenation and dehydrogenation reactions of quinolines with methyl substituents either on the benzene or heteroaromatic ring proceeded smoothly (Table 2, entries 2 and 3). The presence of electron-withdrawing (F, Cl) and electron-donating (CH₃O, OH) functional groups on the

benzene ring did not affect the activity of the catalyst (Table 2, entries 4–7). The most challenging substrate containing an ester group smoothly underwent hydrogenation. Interestingly, only the pyridine ring was hydrogenated, while the C=O bond was retained (Table 2, entries 8). The reason may be that the ester group was located on the benzene ring away from the catalyst surface, which was difficult to hydrogenate. Ru₂P/AC could also efficiently catalyze the hydrogenation of isoquinoline as well as the reversible reaction.

In particular, 2,2'-biquinoxaline was formed upon hydrogenation of quinoxaline in the presence of Ru₂P/AC, except for the product 1,2,3,4-tetrahydro-quinoxaline (Table 3). This out-

Table 3Hydrogenation of quinoxaline: molecular coupling experiments^a.

$ \begin{array}{ccc} \text{Quinoxaline} & \xrightarrow[\text{H}_2]{60\text{ }^\circ\text{C}} & \text{1,2,3,4-tetrahydro-quinoxaline} + \text{2,2'-biquinoxaline} \\ \text{3a} & & \text{4a} \quad \quad \quad \text{5a} \end{array} $					
Entry	H ₂ pressure (bar)	Time (h)	Conversion (%)	Selectivity ^b (%)	
				4a	5a
1	—	12	0	—	—
2	5	5	12.4	6.5	3.7
3	10	5	16.3	9.1	6.1
4	10	10	16.7	—	16.4
5	N ₂	12	0	—	—

^a Reaction conditions unless otherwise mentioned: 0.5 mmol substrate **3a**, 15 mg Ru₂P/AC catalyst, 2 mL EtOH at 60 °C; ^b Sel. of products **4a** and **5a**, as determined by GC-MS.

Graphical Abstract

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Geometric and electronic effects on the performance of a bifunctional Ru₂P catalyst in the hydrogenation and acceptorless dehydrogenation of *N*-heteroarenes

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The P element is the decisive factor! Ru₂P/AC allowed for efficient reversible transformations between unsaturated and saturated *N*-heterocycles. The P atom finely modified the geometric and electronic structures, leading to a balance between reaction and diffusion, and boosting the hydrogenation and dehydrogenation processes.

come may be attributed to the dehydrogenative dimerization of quinoxaline, which is the most straightforward and attractive route [49–53]. The tetrahydro-quinoxaline product (**4a**) was obtained in 9.1% yield under 10 bar H₂ atmosphere at 60 °C using the Ru₂P/AC catalyst, while **5a** was detected in 6.1% yield. When the pressure of H₂ was modified to 5 bar and the reaction time was extended to 10 h, only product **5a** was observed. This represents powerful evidence that Ru₂P/AC is an excellent bifunctional catalyst for the hydrogenation and dehydrogenation of *N*-heteroarenes.

4. Conclusions

In this study, Ru₂P/AC was found to be a chemoselective and universally active catalyst for promoting reversible transformations between various substituted *N*-heterocycles under mild conditions. It could be reused 8 times consecutively with no signs of deactivation. DFT calculations revealed that the excellent performance of Ru₂P/AC could be ascribed to specifically synergistic geometric and electronic effects. The presence of P reduced the large Ru–Ru ensembles from 2.6 to 2.9 Å, causing a subtle electron transfer. The geometric and electronic effects of the microstructure changed the balance between reaction and desorption in the hydrogenation and acceptorless dehydrogenation reactions and further boosted the catalytic activity. The tuning of the active sites through the characteristics of the heteroatoms provided an effective and direct method to improve the catalytic performance, which can be extended to other catalytic reactions.

Conflict of interest

The authors declare no competing financial interests.

Electronic supporting information

Testing of reaction conditions for hydrogenation and acceptorless dehydrogenation; reaction energetics of each ele-

mentary step on different catalysts; energy profiles of reversible reaction on four systems and the calculated structures of reactant on related catalyst during the catalytic reaction. Supporting information is available in the online version of this article.

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双功能催化剂Ru₂P在N-杂环加氢和无受体脱氢反应中的几何效应和电子效应

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摘要: 饱和及不饱和N-杂环化合物是非常重要的药物中间体。由于它们在催化剂表面的吸附/脱附能力不同, 设计具有合适电子结构和几何结构的催化剂用于饱和与不饱和N-杂环化合物的可逆转化具有很大挑战性。目前, 负载型纳米金属催化剂通常被用于饱和N-杂环化合物的加氢反应或者不饱和杂环化合物的脱氢反应。然而反应过程中N-杂环化合物与纳米金属的强配位作用, 不仅影响其他反应底物与活性位点的接触, 而且导致催化剂的循环稳定性较差。在之前的研究中, 钌(Ru)催化剂被用于喹啉化合物的选择加氢反应, 但反应条件苛刻, 循环稳定性差, 不能实现杂环化合物的可逆转化。

本文在Ru纳米颗粒的晶格中引入杂原子, 诱导催化剂表现出不同的几何结构和电子性质, 从而调节反应势垒和底物在催化剂表面的脱附能力以优化反应性能。本文以活性炭(AC)为载体, 制备了Ru₂P, RuO₂, RuS₂和Ru四种负载型催化剂, 以喹啉和四氢喹啉为模型反应物, 考察其催化性能。研究发现, Ru₂P/AC可在温和条件下同时实现喹啉的加氢反应和四氢喹啉的无受体脱氢反应, 且催化剂经过8次循环使用后, 其转化率仍高达95%, 选择性达到99%, 远优于Ru/AC。

密度泛函理论计算结果表明, Ru₂P中的P原子使得两个相邻的Ru-Ru原子的间距从2.61 Å增加到2.9 Å。同时P对催化剂几何结构的变化使反应底物在催化剂表面的吸附行为发生改变, 即喹啉和四氢喹啉分子都更容易在Ru₂P的表面发生脱附, 从而有利于反应进行。通过差分电荷分析, P原子掺杂会将Ru从零价状态调整为缺电子状态。随着P原子掺杂到Ru金属中, 反应物表面的电荷大幅度下降, 提高了加氢反应和脱氢反应中产物的扩散能力。进一步计算反应路径结果表明, Ru₂P实现

了 N -杂环化合物可逆加氢/脱氢过程中反应与扩散之间的平衡,从而在加氢和脱氢反应中均表现出优异的催化性能.

通过浸渍、热解制备的 $\text{Ru}_2\text{P}/\text{AC}$ 对一系列 N -杂环化合物的加氢和脱氢反应均表现出优异的催化性能.这主要归因于 P 原子的掺入稀释了 Ru - Ru 团簇,引起的几何效应和电子效应的协同作用实现了 N -杂环化合物加氢/脱氢过程反应与扩散的平衡,从而提高了可逆反应的催化性能.本文通过原子掺杂调控催化活性的本征结构,从而优化出具有平衡反应和产物扩散的优异催化剂.该合成策略具有直接通用的特点,易于拓展到其它复杂的反应体系当中.

关键词: 磷化钌; 双功能催化剂; 反应机理; 几何和电子效应; 加氢; 无受体脱氢

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