

Phosphotungstic Acid Supported on Magnetic Mesoporous Tantalum Pentoxide Microspheres: Efficient Heterogeneous Catalysts for Acetalization of Benzaldehyde with Ethylene Glycol

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Abstract

In this study, magnetically-recoverable core–shell catalysts with different amount of $H_3PW_{12}O_{40}$ loading [Fe₃O₄@C@ mTa₂O₅-NH₂-PW₁₂ (w%)] were prepared by the application of phosphotungstic acid supported on amino group functionalized magnetic core–shell mesoporous tantalum pentoxide microspheres. The prepared samples were characterized by FT-IR, N₂-adsorption–desorption isotherms, TEM, SEM, Pyridine-IR analysis, XRD and magnetism. Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ samples present both Brönsted and Lewis acidity, large BET surface area and high magnetization. The catalytic activity was evaluated by the acetalization of different aldehydes with diols, and the results show that Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ (14.47%) catalyst exhibits the highest catalytic activity for acetalization of aldehydes with glycols with 94.5% conversion of benzaldehyde and 99% selectivity to benzaldehyde glycol acetal at 80 °C. The catalytic activity of the catalyst for acetalization is related to its total acidity and Brönsted–Lewis acid synergy. The catalyst Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ can be easily recovered and reused for at least 5 times without obvious decrease of catalytic activity.

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Graphic Abstract



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1 Introduction

The acetalization of aldehydes with diols is a widely used method in organic chemistry [1]. Acetals are commonly used as solvents, intermediates or final products due to their unique properties required in practical industrial productions [2, 3]. Moreover, acetals are excellent protection groups for carbonyl groups during multi-step organic synthesis [4]. The currently used catalysts for the acetalization include Lewis or Brönsted acids, such as hydrochloric acid, sulfuric acid, acidic polymers [5], metal catalysts [6], MOFs [7, 8], and solid acids [9]. However, most of the those catalysts suffer from some disadvantages to a certain extent, such as difficulty of catalyst recovery, low activity, low selectivity, harsh conditions, unavoidable equipment corrosion and environmental problems [10]. Therefore, it is imperative to develop reusable, efficient and environmental-benign catalysts for the production of acetals.

Heteropoly acids (HPAs), especially 12-tungstophosphoric acid (HPW), which has the super strong Brönsted acidity, have been used as solid-acid catalysts for esterification, hydration, alkylation and hydrolysis [11, 12]. However, most of HPAs have high solubility in polar medium, resulting in the difficulty of catalyst recovery. Therefore, immobilizing HPAs onto different supports with high surface area, such as silica [13], titania [14], zeolites [15], polymers [16], and active carbons [17], is an effective approach for successful applications in heterogeneous catalysis. Meanwhile, the type of support and the extent of loading can greatly affect the acidity and catalytic activity of the supported HPAs. For example, combining HPAs with acidic supports, like Lewis metal, the ionic liquid and MOF, the composite materials would possess both Brönsted and Lewis acid centers, and the total acidity and Brönsted/Lewis acid site ratio could also be adjusted, therefore further affecting the catalytic activity [18–21].

It is well known that the process of the acetalization can be effectively promoted by the synergistic effect of Brönsted (B) and Lewis (L) acids in a catalyst system [22–24]. For example, Ni ion-exchanged tungstophosphoric acid-based ionic liquid catalyst (Ni[MIMPSH] $PW_{12}O_{40}$, MIMPS = methylimidazolium propyl sulfobetaine) was revealed to be very effective in the acetalization of aldehydes with glycols, affording 94.6% of acetal yield [25]. SnO₂-based solid acids catalyst (SO₄^{2–}/SnO₂) showed high reactivity and selectivity in the acetalization of glycerol with acetone, furfural and its derivatives [26].

As acidic metal oxides, Ta₂O₅ was applied to the acid catalysis due to its Lewis acidity. For example, heterogeneous catalyst $Ta_2O_5 + Pt/SiO_2$ was reported to be an excellent acid catalyst on the conversion of 5-hydroxymethylfurfural to 3-hydroxymethylcyclopentanone [27]. Xu et al. prepared mesoporous heteropolyacids-tantalum pentoxide hybrid catalyst (H₃PW₁₂O₄₀/Ta₂O₅), which showed an excellent catalytic performance in esterification and transesterification under mild conditions [28]. Inspired by these facts, it is rational to prepare Brönsted/ Lewis acid bifunctional composite catalysts by pairing Ta₂O₅ with HPW such that the catalyst simultaneously contains Brönsted acid site from HPW and Lewis acid site from Ta_2O_5 in the composite structure. The prepared catalysts might be very effective for the acetalization of aldehydes with glycols. Although the HPAs-based composites have higher acid catalytic activity, the separation process is usually regarded as time-consuming and energyintensive, and stably immobilizing HPAs onto supports is still challenging.

In recent years, magnetic nanoparticles (MNPs) have been used as a kind of catalyst support because the magnetic separation is fast, simple and environmentally friendly [29]. The surface of MNPs was usually coated with SiO₂, ZrO₂, polymer or other materials to form magnetic core–shell nanoparticles, and further used as a support for HPAs. Various HPAs-based MNPs have been prepared and applied to acid catalysis [30–35]. The catalytic activity and stability of these HPAs-based magnetic composite materials depend mainly on the type of supports, the extent of loading, and the interaction modes between supports and HPAs.

In this work, for the first time, we successfully fabricated the amino group functionalized mesoporous tantalum pentoxide magnetic core-shell microspheres, which were further used as the support for immobilizing $H_3PW_{12}O_{40}$. Magnetic core-shell mesoporous tantalum pentoxide microspheres have high pore volume and large surface area, $H_3PW_{12}O_{40}$ was firmly fixed on the surfaces of mesoporous tantalum pentoxide through more amino groups and hydroxyl groups exposed on shell of tantalum pentoxide. A series of magnetically-recoverable core-shell catalysts with different amount of HPW loading [Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ (w%)] were synthesized. By changing the amount of HPW immobilized, the site ratio of Brönsted and Lewis acidity could be adjusted, and the relationship between the acidity of the catalysts and catalytic activity in the acetalization of benzaldehyde with ethylene glycol was investigated. A possible mechanism for the Brönsted/Lewis acid-catalyzed acetalization of aldehyde with diols was proposed. In addition, the reusability of the catalyst was also studied.

2 Result and Discussion

2.1 Synthesis and Characterization of Fe₃O₄@C@ mTa₂O₅-NH₂-PW₁₂ Catalyst

The Fe₃O₄ magnetic microspheres (ca. 300 nm) were synthesized via the solvothermal method. Afterwards, Fe₃O₄@C microspheres were prepared through hydrothermal reaction of glucose on Fe₃O₄ microspheres. The Fe₃O₄@C microspheres coated with a thin mesoporous tantalum pentoxide layer, Fe₃O₄@C@mTa₂O₅, could be obtained through a surfactant-templating sol-gel approach by the treatment of Fe₃O₄@C with tantalum ethoxide using cetyltrimethylammonium bromide as template agent of mesopores in ethanol-water solution. In order to obtain $Fe_3O_4@C@mTa_2O_5-NH_2$, the as-prepared $Fe_3O_4@C@$ mTa₂O₅ microspheres were covalently modified with amino groups via reacting with aminopropyltriethoxysilane. As previous reports, amino groups functionalized silica may combined with HPAs to construct a stable catalyst in two ways:one is the electrostatic interaction of protonated amino groups with Keggin anions and the interaction of the protonated hydroxyl groups of the silica surface with Keggin anions; another is the exchange reaction of the protonated hydroxyl groups of the silica surface with external oxygen atoms of the Keggin anions [36, 37]. Similarly, amino groups and hydroxyl groups on shell of tantalum pentoxide may also provide suitable sites interacting with HPAs ions to construct a stable catalyst Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂. The different amounts of HPW were immobilized on Fe₃O₄@C@mTa₂O₅-NH₂ magnetic microspheres in order to check which one has the highest catalytic activity. The determined $H_3PW_{12}O_{40}$ loading is ca. 8.51, 14.47, 21.20, 23.41% according to the ICP result. The following results indicated that $Fe_{3}O_{4}@C@mTa_{2}O_{5}-NH_{2}-PW_{12}$ (14.47%) has the highest catalytic efficiency. The schematic preparation process of H₃PW₁₂O₄₀ grafted Fe₃O₄@C@mTa₂O₅-NH₂ magnetic mesoporous microspheres is shown in Scheme 1. To obtain more information about the structural characteristics, the as-synthesized catalyst was studied through FT-IR, SEM, TEM, XRD, N₂-adsorption-desorption isotherms, magnetism, EDX analysis, potentiometric titration and pyridine-IR analysis.

The FT-IR spectra of Fe_3O_4 , $Fe_3O_4@C@mTa_2O_5$, $Fe_3O_4@C@mTa_2O_5$ -NH₂, $Fe_3O_4@C@mTa_2O_5$ -NH₂-PW₁₂(14.47%) and $H_3PW_{12}O_{40}$ are presented in Fig. 1. For Fe_3O_4 , the peak at 584 cm⁻¹ assigns to Fe–O stretching vibration (Fig. 1a). In addition, the broad and intense bands around 3400 cm⁻¹ and 1640 cm⁻¹ are assignable to O–H stretching vibration and H–O–H bending vibration of water at the surface of Fe_3O_4 , respectively. After

 $\label{eq:scheme1} \begin{array}{l} \mbox{Scheme1} & \mbox{Scheme1} & \mbox{schematic illustration of} \\ \mbox{Fe}_{3}O_{4}@C@mTa_{2}O_{5}\mbox{-}NH_{2}\mbox{-}PW_{12} \\ \mbox{catalyst} \end{array}$



Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂



Fig. 1 The FT-IR spectral pattern of various materials: (a) Fe_3O_4 , (b) $Fe_3O_4@C@mTa_2O_5$, (c) $Fe_3O_4@C@mTa_2O_5$ -NH₂, (d) $Fe_3O_4@C@mTa_2O_5$ -NH₂-PW₁₂(14.47%), and (e) $H_3PW_{12}O_{40}$

coating with mesoporous Ta_2O_5 shell, there appears a wide broad peak at 633 cm⁻¹ (Fig. 1b), which was attributed to the superimposition of the characteristic absorption band of Ta–O vibration appeared at 660 cm⁻¹ and Fe–O stretching vibration appeared at 584 cm⁻¹. When the surface was further treated with 3-aminopropyltriethoxysilane, another two new bands appear at 1517 and 1225 cm⁻¹, the peak at 1225 cm⁻¹ is originated from the C–N stretching vibration, a new weak peak at 1517 cm⁻¹ and the peak at 1630 cm⁻¹ are ascribed to $-NH_3^+$ bending vibration. Besides, the peaks at 3430 cm⁻¹ and 1630 cm⁻¹ are strengthened due to N–H stretching vibration and N–H bending vibration, which coincide with O–H stretching



Fig. 2 SEM images of a Fe_3O_4 , b $Fe_3O_4@C$, c $Fe_3O_4@C@mTa_2O_5$, d $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%)

vibration and H–O–H symmetrical bending vibration. All of these verified the amino-functionalization of the Ta₂O₅ shell (Fig. 1c). Concurrently, for the HPAs immobilized samples, the four bands appeared at 1083 cm⁻¹ ν_{as} (P–O), 984 cm⁻¹ ν_{as} (W=O), 892 cm⁻¹ ν_{as} (W–O_b–W) and 804 cm⁻¹ ν_{as} (W–O_c–W) (Fig. 1d) could be attributed to characteristic peaks of H₃PW₁₂O₄₀ (Fig. 1d). The peak intensity of different amount of HPW immobilized catalysts increases with the HPW amount (Fig. S1). The FT-IR spectra indicated that the surface of the Fe₃O₄ magnetic microspheres have been successfully coated and functionalized, and further immobilized with H₃PW₁₂O₄₀.

The morphology of the as-synthesized catalysts was characterized by SEM and TEM. Figure 2 shows SEM images of Fe₃O₄, Fe₃O₄@C, Fe₃O₄@C@mTa₂O₅ and Fe₃O₄@C@



Fig. 3 TEM images of a Fe_3O_4 , b $Fe_3O_4@C$, c $Fe_3O_4@C@mTa_2O_5$, d $Fe_3O_4@C@mTa_2O_5$ -NH₂-PW₁₂ (14.47%)

mTa₂O₅-NH₂-PW₁₂ (14.47%) microspheres, respectively, indicating that the products are all well dispersed with nearspherical morphology. Figure 3 shows typical TEM images of Fe₃O₄, Fe₃O₄@C, Fe₃O₄@C@mTa₂O₅ and Fe₃O₄@C@ mTa₂O₅-NH₂-PW₁₂ (14.47%) microspheres, proving that the coating process is layer-by-layer and uniform, Fe₃O₄@C@ mTa₂O₅-NH₂-PW₁₂ microspheres possess a sandwichlike core-shell structure. As shown in Figs. 2a and 3a, the obtained Fe₃O₄ microspheres are uniform with a mean size of ~300 nm. After coated with a thin carbon layer (ca.10 nm), the obtained Fe₃O₄@C microspheres show smoother surface than Fe_3O_4 microspheres and become a little larger (Figs. 2b and 3b). After the surfactant-assembly sol-gel process, a uniform mesoporous Ta2O5 shell (ca.30 nm) was coated on Fe₃O₄@C microspheres, the obtained microspheres show rougher surface (Figs. 2c and 3c). After immobilized HPW onto $Fe_3O_4@C@mTa_2O_5$, the morphology was well kept (Figs. 2d and 3d). The energy dispersive X-ray spectroscopy (EDX) of the Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ (14.47%) microspheres exhibit the characteristic peaks of Fe, O, C, Ta, N, P and W (Fig. S2), suggesting that the Fe₃O₄ cores are successfully coated by mesoporous Ta₂O₅ shell and further immobilized $H_3PW_{12}O_{40}$. The average diameters of Fe₃O₄, Fe₃O₄@C, Fe₃O₄@C@mTa₂O₅ and Fe₃O₄@C@ mTa₂O₅-NH₂-PW₁₂ (14.47%) microspheres represented in Fig. S3 are ca. 304.45, 314.08, 376.26 and 382.07 nm, respectively (close to the size measured by TEM), which provide additional evidence for the successful coating.

It is worth noting that the ratio of ethanol/water (v/v) is an important factor for the preparation of the core–shell



Fig. 4 SEM images of $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ using different ethanol/water ratio(ν/ν): **a** 10:1, **b** 5:1, **c** 1:1, and **d**1:5

 $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ microspheres. The ratio of ethanol/water (v/v) affects the hydrolysis rate of tantalum ethanol and further affects the morphology of the Ta₂O₅ shell. As the water content in the ethanol/water mixture increases, the hydrolysis rate of tantalum ethanol will become faster. It has been confirmed by the TEM images of Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ obtained using different ratio of ethanol/water (v/v) (Fig. 4). When the ethanol/water ratio (v/v) is 10:1, almost no Ta₂O₅ shell was observed, the morphology is similar to Fe₃O₄@C (Figs. 2b and 4a). When the ethanol/water ratio (v/v) is 5:1, the Ta₂O₅ shell composed of dense Ta₂O₅ nanoparticles was formed (Fig. 4b). However, with the increase of the water content in the ethanol/ water mixture, the ratio of ethanol/water (v/v) achieved 1:1. the Ta₂O₅ shell is looser and there are small particles on the surface of the magnetic microspheres, which may be easy to fall off and aggregate, probably resulting in a decrease in catalytic activity when the catalyst is recycled (Fig. 4c, d). Therefore, it is concluded that adjusting the ratio of ethanol/water and optimizing the appropriate ratios of ethanol/ water (v/v) are beneficial to construct stable Fe₃O₄@C@ mTa₂O₅-NH₂-PW₁₂ microspheres, and the optimum ratios of ethanol/water (v/v) is 5:1.

Wide-angle XRD patterns of Fe_3O_4 , $Fe_3O_4@C@mTa_2O_5$, $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%) and $H_3PW_{12}O_{40}$ are shown in Fig. 5A. The diffraction peaks of the obtained Fe_3O_4 microspheres agree with the standard Fe_3O_4 (JCPDS card No. 19-0629). For the wide-angle XRD patterns of $Fe_3O_4@C@mTa_2O_5$ and $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%) (Fig. 5A—b, c), the characteristic diffraction peaks of Fe_3O_4 are weakened than the original Fe_3O_4 because of the carbon and mesoporous Ta_2O_5 shell; Meanwhile, two typical broad band peaks are observed in the range of $2\theta = 15^\circ$ -40° and 45° -65°, which originated from amorphous Ta_2O_5 [28]. The pattern of $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%) is



Fig. 5 Typical Wide-angle (A) and Low-angle (B) PXRD patterns of (a) Fe_3O_4 , (b) $Fe_3O_4@C@mTa_2O_5$, (c) $Fe_3O_4@C@mTa_2O_5$ -NH₂-PW₁₂ (14.47%), (d) $H_3PW_{12}O_{40}$

similar to that of $Fe_3O_4@C@mTa_2O_5$ and no diffraction peaks corresponding to $H_3PW_{12}O_{40}$ are observed in as-prepared catalysts because of high dispersion of the HPW on $Fe_3O_4@C@mTa_2O_5$ (Fig. 5A—c).

Figure 5B shows the Low-angle XRD patterns of $Fe_3O_4@C@mTa_2O_5$ and $Fe_3O_4@C@mTa_2O_5$ -NH₂-PW₁₂ (14.47%). In these two curves, a broader reflection peak (100) indicates the formation of mesoporous structure [28]. Compared to $Fe_3O_4@C@mTa_2O_5$, the peak of $Fe_3O_4@C@mTa_2O_5$ -NH₂-PW₁₂ (14.47%) becomes broader and the diffraction intensity decreases simultaneously. The reason for this phenomenon is that HPW was filled in the pores and scattered X-rays [38]. This results in increased phase

cancellation between X-rays scattered from the walls and the pore regions, and therefore reduces the intensities of XRD peaks [39].

The surface area and porous structure of $Fe_3O_4@C$, $Fe_3O_4@C@mTa_2O_5$ and $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%) were examined by N₂ adsorption measurement. Figure 6 shows the N₂ adsorption–desorption isotherms. It was found that the pore size of $Fe_3O_4@C$ is uneven, and the average pore diameter is mainly at 1.4 nm, the BET surface area is calculated to be $10.1 \text{ m}^2 \text{ g}^{-1}$. Compared to $Fe_3O_4@C$, the other two samples show type-IV curves, indicating their mesoporous structure. After coating with mesoporous Ta_2O_5 shell, the average pore size and BET surface area



Fig. 6 Nitrogen adsorption–desorption isotherms (a) and pore size distribution curves (b) of Fe₃O₄@C, Fe₃O₄@C@mTa₂O₅ and Fe₃O₄@C@mTa₂O₅ and Fe₃O₄@C@mTa₂O₅ NH₂-PW₁₂ (14.47%)



Fig.7 Magnetization curves of the samples measured at 300 K: a Fe₃O₄, b Fe₃O₄@C, c Fe₃O₄@C@mTa₂O₅, d Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ (14.47%)

of $Fe_3O_4@C@mTa_2O_5$ increase rapidly to 3.9 nm and 92.6 m² g⁻¹, respectively. The average pore size and BET surface area of $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%) decrease to 3.2 nm and 78.5 m² g⁻¹, respectively. The most likely reason is that HPW was dispersed and deposited on the surface of $Fe_3O_4@C@mTa_2O_5$, decreasing the pore diameter and thus diminishing the surface area.

Figure 7 shows the magnetization curves of the asprepared Fe₃O₄, Fe₃O₄@C, Fe₃O₄@C@mTa₂O₅ and $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%) microspheres. The magnetization saturation values of Fe₃O₄, Fe₃O₄@C, Fe₃O₄@C@mTa₂O₅ and Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ (14.47%) are 80.8, 49.3, 40.8 and 29.7 emu g⁻¹, respectively. The saturation magnetization values of Fe₃O₄@C, Fe₃O₄@C@mTa₂O₅ and Fe₃O₄@C@mTa₂O₅-NH- $H_3PW_{12}O_{40}$ (14.47%) significantly decrease than that of Fe_3O_4 core due to the existence of non-magnetite C, Ta_2O_5 shell and HPW. However, compared to some reported magnetic nanoparticle catalysts, the value of 29.7 emu g^{-1} is still higher [30, 32]. From the partial enlargement of the magnetization curves of the as-prepared samples, it can be found that there are hysteresis loops in the curves (Fig. S4), but the coercive force of as-prepared samples are much lower than that of the magnetic Fe_3O_4 bulk material (115–150 O_e). These results indicate that the as-prepared samples have good magnetic properties. The Fe₃O₄@C@mTa₂O₅-NH₂- PW_{12} (14.47%) microspheres can be easily enriched with the aid of a permanent magnet (Fig. 7, inset).

For the acid-catalyzed reaction, the acid types, concentration and strength of acid sites are the key factors which can determine the catalytic performance of the catalyst. The total acidity of $Fe_3O_4@C@mTa_2O_5$ and $Fe_3O_4@C@mTa_2O_5$ mTa₂O₅-NH₂-PW₁₂ was measured through potentiometric

titration with *n*-butylamine in acetonitrile (0.05 mol L^{-1}). Based on the total acidity displayed in Table S1, it can be seen that the acid-site density of different amount of HPAs immobilized catalysts increases gradually with increasing the contents of HPW owing to the fact that HPW has strong Brönsted acid capacity.

The different types of acid sites of Fe₃O₄@C@mTa₂O₅ and various Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ samples were determined by Pyridine-FTIR spectra (Fig. 8). The peaks at 1450 cm^{-1} and 1611 cm^{-1} correspond to the Lewis acid (L) sites, which is attributed to pyridine coordinatively bonded to the unsaturated surface Ta^{5+} . The peak at 1540 cm⁻¹ correlates with pyridinium ions formed by protonation of the Brönsted acid (B) sites. The characteristic peak of the coexistence of B and L sites can be observed at 1490 cm^{-1} [40]. The peak at 1540 cm⁻¹ was not observed on Fe₃O₄@C@ mTa₂O₅, but observed on Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂. Therefore, the immobilization of HPW on Fe₃O₄@C@ mTa₂O₅ introduced strong B sites at the catalyst surface, these B sites are attributed to the protons of HPW. The peak at 1490 cm⁻¹ confirms that Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ possesses both B and L sites. On the basis of the peak intensities, it can be inferred that both of B sites and the co-existence of B and L sites increase in the following order: Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂(8.51%)<Fe₃O₄@C@ mTa₂O₅-NH₂-PW₁₂(14.47%)<Fe₃O₄@C@mTa₂O₅-NH₂- $PW_{12}(21.20\%) < Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}(23.41\%),$ which indicates that the acid intensity of as-prepared catalyst is associated with the amount of H₃PW₁₂O₄₀ immobilized. Thus, it can be inferred that changing the amount of H₃PW₁₂O₄₀ immobilized can control the Brönsted/Lewis acid site ratio for Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂.



2.2 Catalysis of Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂

The catalytic activity was evaluated by the acetalization of benzaldehyde (BzH) with ethylene glycol (EG). A series of controlled experiments were carried out to investigate the catalytic active components of catalysts, as shown in Table 1. It is clear that only 42-51% of benzaldehyde is converted to benzaldehyde ethylene glycol acetal (BEGA) without catalyst or using Fe₃O₄ as catalyst (entries 1 and 2). Fe₃O₄@C@mTa₂O₅, which presents predominantly Lewis acidity, afforded 68% conversion of benzaldehyde (entry 3). These indicate that Lewis acidity facilitates the acetalization of BzH with EG. When H₃PW₁₂O₄₀ was taken as homogeneous catalyst, which possesses Brönsted acidity, we can obtain 81.5% conversion and 99% selectivity (entry 4). This suggests that Brönsted acidity is essential for acetalization of BzH with EG. The catalytic activity of physical mixture of H₃PW₁₂O₄₀ and Fe₃O₄@C@mTa₂O₅ is close to that of H₃PW₁₂O₄₀ (entry 9). Notably, Fe₃O₄@C@ mTa2O5-NH2-PW12 samples show superior catalytic performances, exhibiting 85.3-94.5% conversion in comparison with that of $H_3PW_{12}O_{40}$ catalyst (entries 5–8). This can be explained from the following two aspects: one is that Brönsted and Lewis acid sites are co-existing in $Fe_3O_4@C@$ mTa₂O₅-NH₂-PW₁₂, the Brönsted–Lewis acid synergy is a key factor in improving catalytic efficiency; another is that the composite catalysts have a larger surface area, enough pore distribution, which allows the substrate molecules to contact with more active sites and promotes the reaction. In general, Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ catalysts show better catalytic activity than HPW.

It is noteworthy that the B/L site ratio of the catalyst also play an important role on catalytic activity [41]. The incorporation of Brönsted and Lewis acidity is favorable for the acetalization of BzH with EG, and the conversion of benzaldehyde was found to reach a maximum at a moderate B/L site ratio [25]. In order to clearly demonstrate the relationship between B/L site ratio and catalytic activity in the acetalization, magnetic mesoporous tantalum pentoxide microspheres with different amounts of HPW immobilizing, $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12} (w\%) (w=8.51,$ 14.47, 21.20 and 23.41), were prepared. Among them, the $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%) catalyst exhibited the highest activity and the best catalytic performance with 94.5% conversion and 99% selectivity. However, the total acidity and the B/L site ratio of the $Fe_3O_4@C@$ mTa₂O₅-NH₂-PW₁₂ catalysts followed the asending order: $Fe_{3}O_{4}@C@mTa_{2}O_{5}-NH_{2}-PW_{12}$ (8.51%) < $Fe_{3}O_{4}@C@$ $mTa_{2}O_{5}-NH_{2}-PW_{12}$ (14.47%) < Fe₃O₄@C@mTa₂O₅-NH₂- PW_{12} (21.20%) < Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ (23.41%) (Table S1, Fig. 8). Thus, an appropriate ratio of Brönsted and Lewis acidity is preferred for acetalization. This is well in agreement with the reported literature [25]. In other word, the acetalization of BzH with EG invokes a Brönsted-Lewis acid synergy effect.

A reasonable reaction pathway for acetalization of aldehydes with diols over the $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ composite catalyst is presented in Scheme 2. The catalytic process involving co-participation of Brönsted and Lewis acid is summerized as follows: the Lewis metal center (Ta^{5+}) is prone to combine with the oxygen atom (which possessed strong electronegativity) in the carbonyl groups to induce interactions between the carbon atom in the carbonyl group and the oxygen in the alcohol hydroxyl group. The coupling of Brönsted acidic H⁺ with the oxygen atom in the carbonyl group tends to reduce the negative charge, which facilitates the release of Ta^{5+} . The intermediate formed by coupling between carbocation and oxygen in the alcohol hydroxyl group release proton (H⁺) to obtain the final product.

To verify the scope and limitation of the catalyst, taking $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%) as catalyst, the acetalization of different aldehydes with diols were investigated. As displayed in Table 2, $Fe_3O_4@C@$ $mTa_2O_5-NH_2-PW_{12}$ (14.47%) catalyst exhibited a high catalytic activity in most acetalization reactions conducted, indicating general applicability of the catalyst.

Table 1Acetalization ofbenzaldehyde with ethyleneglycol catalyzed by differentsamples

Entry	Catalyst	Conversion (%)	Selectivity (%)	
1	_	42.6	98	
2	Fe ₃ O ₄	51.4	98	
3	Fe ₃ O ₄ @C@mTa ₂ O ₅	68.4	98	
4	^[a] H ₃ PW ₁₂ O ₄₀	81.5	99	
5	Fe ₃ O ₄ @C@mTa ₂ O ₅ -NH ₂ -PW ₁₂ (8.51%)	85.3	99	
6	Fe ₃ O ₄ @C@mTa ₂ O ₅ -NH ₂ -PW ₁₂ (14.47%)	94.5	99	
7	Fe ₃ O ₄ @C@mTa ₂ O ₅ -NH ₂ -PW ₁₂ (21.20%)	92.6	99	
8	Fe ₃ O ₄ @C@mTa ₂ O ₅ -NH ₂ -PW ₁₂ (23.41%)	86.7	98	
9	$^{[b]}Fe_{3}O_{4}@C@mTa_{2}O_{5}-NH_{2}+H_{3}PW_{12}O_{40}$	83.7	98	

Reaction condition: benzaldehyde 0.1 mol, glycol 0.15 mol, cyclohexane 12.0 mL, catalyst 0.42 g, 80 °C for 2 h. [a] the mass of catalyst 0.06 g, [b] 0.36 g Fe₃O₄@C@mTa₂O₅ mixed with 0.06 g H₃PW₁₂O₄₀

Scheme 2 Reaction mechanism for acetalization of aldehydes with diols over the $Fe_3O_4@C@$ mTa₂O₅-NH₂-PW₁₂ catalyst (14.47%)

Table 2 Acetalization of various aldehydes with diols, catalyzed by Fe₃O₄@C@ mTa₂O₅-NH₂-PW₁₂ (14.47%)



Ta⁵⁺: represent Lewis acid;

H⁺: represent Brönsted acid

Entry	Aldehyde Diol		Conversion (%)	Selectivity (%)	
1	Benzaldehyde	Ethylene glycol	94.5	99	
2		Propylene glycol 91.2		98	
3		Butylene glycol	89.5	98	
4		Pentylene glycol	82.6	98	
5	p-Tolualdehyde	Ethylene glycol	94.2	99	
6		Propylene glycol	90.7	99	
7		Butylene glycol	84.6	98	
8		Pentylene glycol	82.5	98	

Reaction condition: aldehydes 0.1 mol, glycol 0.15 mol, cyclohexane 12.0 mL, catalyst 4 wt%, 80 °C for 2 h $\,$

Supposing the acetalization occurs mainly in the pores of the $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%) catalyst, the conversion of the aldehyde decreases along with the length of carbon chain in the diols increases, probably because of steric hindrance for the reaction. Thus, diols with short carbon chains can easily enter into the pores of $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%) and catalytically react with aldehyde, and the products can also easily diffuse through the pore canal of Fe₃O₄@C@mTa₂O₅-NH₂- PW_{12} (14.47%) to leave out the catalyst. As the size of either reactant or product increases, the steric hindrance would be essential for the acetalization, leading to the lower yields from Entries 1 to 4 and from Entries 5 to 8 in Table 2 [7]. In contrast, the non-porous $Fe_3O_4@C@$ Ta₂O₅-NH₂-PW₁₂ (14.82%) catalyst exhibited a low catalytic activity in the acetalization reactions of benzaldehyde with different diols (Table S2). Moreover, the conversion of the benzaldehyde to different diols is very close. These results confirm that the mesoporous structure of $Fe_{3}O_{4}@C@mTa_{2}O_{5}-NH_{2}-PW_{12}$ (14.47%) can promote the acetalization reaction, probably due to the occurrence of the reaction in pores.

We also compared catalytic performance of Fe₃O₄@C@ mTa2O5-NH2-PW12 (14.47%) with some reported heteropolyacid composite catalysts in the acetalization of benzaldehyde with ethylene glycol. As shown in Table 3, the catalytic activity of Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ (14.47%) is superior to Cs-VImPS-PW and H₄[SiW₁₂O₄₀]/SiO₂ (entries 4 and 5). Although the catalytic activity of Ni[MIMPSH] $PW_{12}O_{40}$ or HPW@MIL-100(Fe) is a little higher than that of $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%) (entries 2 and 3), the reaction conditions of Ni[MIMPSH]PW₁₂O₄₀ is environmental-unfriendly as the reaction temperature is much higher, and their separation efficiency is lower than $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%), which can be quickly magnetically separated. Moreover, the TOF (min^{-1}) of Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ (14.47%) catalyst is 12.1, indicating that the as-prepared catalyst has high catalytic activity. Therefore, in terms of performance and reaction conditions, although the catalytic activity of $Fe_3O_4@C@$

Table 3 Comparison of different heteropolyacid catalysts in acetalization of benzaldehyde with ethylene glycol

Entry	Catalyst	Benzaldehyde (mmol)	ethylene -glycol (mmol)	Cyclohexane (mL)	Temp. (°C)	Time (h)	Conversion (%)	Ref.
1	Fe ₃ O ₄ @C@ mTa ₂ O ₅ -NH ₂ -PW ₁₂ (14.47 wt%)	100	150	12	80	2	94.5	This work
2	Ni[MIMPSH]PW ₁₂ O ₄₀	100	150	12	110	2	95.8	[25]
3	HPW@MIL-100(Fe)	70	126	10	80	2	98.1	[42]
4	H ₄ [SiW ₁₂ O ₄₀]/SiO ₂	1	1.5	0	60	6	73	[10]
5	Cs-VImPS-PW	10	15	5	80	2	94.1	[43]

 mTa_2O_5 -NH₂-PW₁₂ (14.47%) is not the highest, Fe₃O₄@C@ mTa_2O_5 -NH₂-PW₁₂ (14.47%) could still serve as a more promising catalyst candidate for the acetal formation.

2.3 Effects of Reaction Parameters

The synthesized $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%) was applied to acetalization reaction of benzaldehyde and

ethylene glycol, acetal was detected as the final product (Fig. 9). In the acetalization, water is inevitably formed. Cyclohexane was used as the water-carrying agent to improve the acetal yield by seperating water from the reaction mixture at 80 °C. As shown in Fig. 9, the amount of catalyst and cyclohexane, EG to BzH molar ratio, and reaction time can significantly change the yield of acetal. The highest yield (94.5%) was obtained under the following





Fig.9 The effect of different a molar ratio of EG/BzH, b reaction time, c catalyst amount, and d cyclohexane amount on acetal yield. While changing each experimental variable, the other parameters

were kept constant: molar ratio of EG/BzH=1.5:1, catalyst 4 wt%, cyclohexane 12.0 mL, 80 °C for 2 h

reaction conditions: a EG/BzH molar ratio of 1.5:1, the reaction time of 2 h, 4 wt% catalyst loading, and 12 mL cyclohexane. Thereafter, with further increasing the EG/BzH ratio and the reaction time, the increase in yield is negligible. Further increase in the cyclohexane amount results in significant decrease of benzaldehyde conversion, which is ascribed to the dilution effect by excessive cyclohexane. Further increasing the catalyst amount beyond 4 wt% cannot promote the reaction and lead to a slight decrease of the conversion, the most likely reason is the mass transfer hindrance caused by the low dispersity of the excess catalyst in the reactant mixture.

The effect of reaction temperature on the conversion and selectivity of acetalization of benzaldehyde with ethylene glycol was also evaluated. As the reaction temperature increases from 70 to 110 °C, the conversion of benzaldehyde increased from 75.6 to 98.9%. High temperature facilitates to the further acetalization of benzaldehyde. Compared to 70 °C, the conversion of benzaldehyde at 80 °C increased significantly. Further increasing the reaction temperature from 80 to 110 °C, the increase in conversion is slight. Therefore, considering the performance and cost, the best reaction temperature is 80 °C (Fig. S5).

The stability and reusability of Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ was evaluated through five catalytic recycles. The Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ catalyst could be easily recycled by a permanent magnet after the reaction. Then, the recovered catalysts were washed with acetone for three times and dried under vacuum and reused for the next run. It was found that the catalytic efficiency for the acetalization of benzaldehyde with ethylene glycol of the recovered catalysts is almost not changed (Fig. 10). After five cycles, the recovered catalyst was characterized by FT-IR spectra (Fig. S6). The FT-IR spectrum of the fresh catalyst is quite similar to that of the reused catalyst, indicating that Keggin polyanions are still retained in the recovered catalyst. To confirm that the catalytic action of $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ is truly heterogeneous, ICP was used for determining the content of W in the catalytic mixture after removing magnetically the heterogeneous catalyst. The ICP results revealed that there is almost no W in the mixture, which means that $H_3PW_{12}O_{40}$ is not leached during the reaction. Meanwhile, changes of acidity of the recovered catalyst are negligible (entry 6 in Table S1).

For comparison, $Fe_3O_4@C@mTa_2O_5$ immobilized with $H_3PW_{12}O_{40}$ were synthesized, denoted as $Fe_3O_4@C@mTa_2O_5$ -PW₁₂ (15.12%), the preparation process was shown in Support Information. Under the same reaction conditions, the $Fe_3O_4@C@mTa_2O_5$ -PW₁₂ (15.12%) catalyst exhibited 94.3% conversion for the acetalization of benzaldehyde with ethylene glycol, which is close to that of $Fe_3O_4@C@mTa_2O_5$ -NH₂-PW₁₂ (14.47%). The reusability of the $Fe_3O_4@C@mTa_2O_5$ -PW₁₂ (15.12%) catalyst was also



Fig. 10 Reusability of $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ (14.47%) in the acetalization of benzaldehyde with ethylene glycol. Reaction condition: benzaldehyde 0.1 mol, ethylene glycol 0.15 mol, cyclohexane 12.0 mL, catalyst 0.42 g, 80 °C for 2 h

carried out. After three cycles, the conversion of benzaldehyde decreased from 94.3 to 81.2% due to leaching of HPW active species. FT-IR spectra showed that the absorption of HPW declined after three cycles (Fig. S7). These results clearly show that the Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ catalyst is stable and the electrostatic interaction of protonated amino groups with Keggin anions plays an important role in constructing the stable catalyst.

3 Conclusions

In this study, we have successfully synthesized phosphotungstic acid supported on amino-functionalized magnetic core-shell mesoporous tantalum pentoxide microspheres with a facile procedure. The magnetically recoverable catalyst possesses large BET surface area, high stability, strong Brönsted and Lewis acidity, and present high efficient catalytic activity for acetalization of different aldehydes and diols. The results show that the Brönsted/Lewis acid site ratio of the catalyst play an important role on catalytic activity, and Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ (14.47%) with a moderate Brönsted/Lewis acid site ratio exhibits the highest catalytic activity with 94.5% conversion of benzaldehyde and 99% selectivity to benzaldehyde glycol acetal. Additionally, the as-prepared catalyst could be easily recycled by magnetic separation and reused at least 5 cycles without significant loss of its catalytic activity. To our knowledge, this is the first report that H₃PW₁₂O₄₀ anchored to amino-functionalized Fe₃O₄@C@mTa₂O₅ microspheres and used for acetalization of aldehydes with diols. As-prepared

multifunctionalized hybrid catalysts are considered as promising candidates for other acid catalyzed reactions.

4 Experimental

4.1 Materials and Chemicals

 $H_3PW_{12}O_{40}$ was purchased from Aladdin Chemistry Co., Ltd.;Ferric chloride (FeCl₃·6H₂O), sodium acetate anhydrous (NaAc), polyethylene glycol, glucose, cetyltrimethylammonium bromide (CTAB) were supplied by Tianjin Kemiou Chemical Reagent Co., Ltd.; Tantalum ethoxide (99%) was purchased from Sigma Aldrich; (3-aminopropyl) triethoxysilane (APTES, 98%), cyclohexane, benzaldehyde (99%), 3-methylbenzaldehyde (99%), cyclohexanone(99%), ethylene glycol (99%), 1,3-propanediol (99%), 1,4-butanediol (99%), 1,5-pentadiol (98%) were obtained from Adamas. All chemicals were directly used without any further purification.

4.2 Catalyst Preparation

4.2.1 Preparation of Fe₃O₄

Fe₃O₄ magnetic microspheres (ca.300 nm) were synthesized through the solvothermal reaction [44]. FeCl₃·6H₂O (2.0 g), polyethylene glycol (1.5 g) were added into ethylene glycol (60 mL) under vigorous magnetic stirring. After completely dissolved, NaAc (5.4 g) was added to the above solution. Subsequently, the mixture was stirred for 1 h and sealed in a teflonlined stainless-steel autoclave (100 mL capacity). Through hydrothermal treatment at 200 °Cfor 8 h, the black products were obtained. Finally, the precipitate was washed with ethanol and deionized water and dried under vacuum at 50 °C for 8 h.

4.2.2 Synthesis of Fe₃O₄@C Magnetic Microspheres

The Fe₃O₄@C magnetic microspheres were prepared through hydrothermal reaction of glucose on Fe₃O₄ magnetic microspheres [45]. Typically, Fe₃O₄ (0.1 g) microspheres were ultrasonicated for 15 min in 0.1 M HNO₃ aqueous solution (50 mL), then washed with deionized water. Thereafter, the treated Fe₃O₄ microspheres were redispersed in 0.5 M aqueous glucose solution (80 mL) by ultrasonication for 15 min. Finally, the mixture was transferred to autoclaves and heated at 180 °C for 4 h. The black products were collected and washed with deionized water and ethanol. After drying under vacuum at 80 °C for 4 h, the final sample was obtained (denoted as Fe₃O₄@C).

4.2.3 Synthesis of Fe₃O₄@C@mTa₂O₅ Magnetic Microspheres

The Fe₃O₄@C@mTa₂O₅ magnetic microspheres were synthesized through a sol-gel process with some modification [46, 47]. First, Fe₃O₄@C microspheres (0.15 g) were dispersed in the mixture (40 mL) containing of CTAB (0.64 g), deioned water and ethanol (v/v = 1/3) by ultrasonication for 15 min. Then, anhydrous ethanol (20 mL) containing of tantalum ethoxide (120 µL) was added into the mixed solution over a period of approximately 20 min under magnetic stirring. After stirred for 6 h, the products were magnetically separated and washed with ethanol and water. Next, the microspheres were redispersed in 80 mL of acetone and refluxed at 80 °C for 48 h to extract the template CTAB. After removal of CTAB templates, the mesoporous tantalum pentoxide magnetic microspheres were obtained (denoted as $Fe_3O_4@C@mTa_2O_5$). Finally, the catalyst was collected, washed with ethanol and dispersed in ethanol (40 mL). For comparison, non-porous tantalum pentoxide coated Fe₃O₄@C was also prepared according to the method similar to $Fe_3O_4@C@mTa_2O_5$, except that no template was added, the sample was denoted as $Fe_3O_4@C@Ta_2O_5$.

4.2.4 Synthesis of Fe₃O₄@C@mTa₂O₅-NH₂ Magnetic Microspheres

Amino-functionalized $Fe_3O_4@C@mTa_2O_5$ microspheres, designated as $Fe_3O_4@C@mTa_2O_5$ -NH₂, were synthesized as follows. First, 350 µL of APTES and 50 µL of NH₃·H₂O were added to $Fe_3O_4@C@mTa_2O_5$ ethanol solution. Then, the mixture was refluxed at 80 °C for 12 h. The obtained $Fe_3O_4@C@mTa_2O_5$ -NH₂ magnetic microspheres were washed with ethanol and air-dried.

4.2.5 Synthesis of Fe₃O₄@C@mTa₂O₅-NH₂-PW₁₂ Magnetic Microspheres

For the immobilization of $H_3PW_{12}O_{40}$ on $Fe_3O_4@C@$ mTa₂O₅-NH₂, 60 mL of methanol solution containing a certain amount of $H_3PW_{12}O_{40}$ (0.2–1.0 g) was added to a freshly activated $Fe_3O_4@C@mTa_2O_5$ -NH₂ (0.3 g) and the mixture was refluxed for 6 h. Subsequently, the products were gathered after being washed with deionized water and dried at 50 °C overnight. The actual amount of HPW in the catalyst was determined by ICP/AES. The obtained catalysts were denoted as $Fe_3O_4@C@mTa_2O_5$ -NH₂-PW₁₂ (w%) (w=8.51, 14.47, 21.20 and 23.41), respectively.

4.3 Catalyst Characterization

FT-IR spectra were recorded on a TENSOR 27 spectrometer. The XRD data were recorded by a Bruker D8 Advance diffractometer with Cu Ka radiation, operating at 40 kV and 40 mA. Morphologies were collected by scanning electron microscopy (SEM) images using ZEISS SIGMA 500 scanning microscope with an area energy dispersive X-ray spectrometer (EDS). Transmission electron microscope (TEM) images were collected on a GZF2.0 transmission electron microscope at an accelerating voltage of 200 kV. N₂ absorption-desorption experiment was carried out at 77 K on a Micromeritics TR2 Star3020 analyzer. The surface areas were calculated using the BET equation, and the pore size distributions were obtained using the BJH adsorption branch of the isotherms. Magnetic properties were determined on a Quantum Design MPMS SQUID magnetometer at room temperature. The content of W was determined by ICP/ AES on a VarioEL III elemental analyzer (German Ellman Elemental Analysis System Company).

4.4 Determination of the Acidity Content

The total acid content of as-synthesized catalysts was measured by potentiometric titration. In brief, the catalyst powder (50 mg) was added in acetonitrile (50 mL). After stirring for 2 h, the obtained suspension was titrated with a solution of *n*-butylamine in acetonitrile (0.05 mol L^{-1}) [31].

4.5 Characterization of Brönsted and Lewis Acidity

Brönsted and Lewis acidity of the prepared materials was determined by pyridine-FT-IR spectra. The as-prepared materials were exposed to pyridine vapour at 60 °C for 2 h in vacuum after drying at 100 °C for 2 h, the physisorbed pyridine was blown off with a N_2 flow. Finally, FT-IR spectra of adsorbed pyridine was recorded.

4.6 Acetalization Reaction

Acetalization reactions were performed in a three-necked flask equipped with a dean-stark apparatus. In a typical experiment, a mixture of 0.1 mol aldehyde, 0.15 mol ethylene glycol/1,3-propanediol/1,4-butanediol/1,5-pentadiol, 12 mL cyclohexane and 4 wt% of catalyst $Fe_3O_4@C@$ mTa₂O₅-NH₂-PW₁₂ (0.42 g) were stirred at 80 °C for 2 h. The reaction mixture was sampled periodically and analyzed with a HP SP-6890 gas chromatograph and identified via a gas chromatography-mass spectroscopy (GC–MS).

4.7 Recycling of the Catalyst

After reaction, the catalyst $Fe_3O_4@C@mTa_2O_5-NH_2-PW_{12}$ was recovered by magnetic separation, thoroughly washed with acetone and dried at 60 °C.

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