FULL PAPER



Selective vapor-phase oxidation of o-xylene to phthalic anhydride over Co-Mn/H₃PW₁₂O₄₀@TiO₂ using molecular oxygen as a green oxidant

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to phthalic The oxidation of o-xylene anhydride over Co-Mn/ $H_{3}PW_{12}O_{40}$ $\otimes TiO_{2}$ was investigated. The experimental results demonstrated that the prepared catalyst effectively catalyzed the oxidation of o-xylene to phthalic anhydride. Also, the synergistic effect between three metals plays vital roles in this reaction. From a green chemistry point of view, this method is environmentally friendly due to carrying out the oxidation in a fixed-bed reactor under solvent-free condition and using molecular oxygen as a green and cheap oxidizing agent. The resulting solid catalysts were characterized by FT-IR, XRD, XPS, ICP-OES, FESEM, TEM, EDX, DR-UV spectroscopy, BET and thermogravimetric analysis. The oxidation of o-xylene yields four products: otolualdehyde, phthaldialdehyde, phthalide and finally phthalic anhydride as the main product. The reaction conditions for oxidation of o-xylene were optimized by varying the temperature, weight hourly space velocity and oxygen flow rate (contact time). The optimum weight percentage of phosphotungstic acid (HPW) and Co/Mn for phthalic anhydride production were 15 wt % and 2 wt%, respectively. The best Co/Mn ratio was found to be 10/1. Oxygen flow rate was very important on the phthalic anhydride formation. The optimum conditions for oxidation of o-xylene were T = 370 °C, WHSV = 0.5 h⁻¹ and oxygen flow rate = 10 mL min^{-1} . Under optimized conditions, a maximum of 88.2% conversion and 75.5% selectivity to phthalic anhydride was achieved with the fresh catalyst. Moreover, reusability of the catalyst was studied and catalytic activity remained unchanged after at least five cycles.

KEYWORDS

o-Xylene, phosphotungstic acid, phthalic anhydride, TiO_2 , vapor-phase oxidation

1 | INTRODUCTION

Selective oxidation, specially using heterogeneous vaporphase oxidation processes, plays a vital role in chemical industry.^[1] Particularly, the catalytic oxidation of *o*-xylene to phthalic anhydride is a process of great industrial and commercial importance. With increasing global consumption of about 4,000,000 t year⁻¹ in recent decades, phthalic anhydride is listed as one of the most important chemical intermediates in chemical industry.^[2] Phthalic anhydride has been commercially manufactured by BASF since 1872 by developing the naphthalene oxidation process.^[3] The primary use of phthalic anhydride as a chemical intermediate is in the production of plastics from vinyl 2 of 13 WILEY Organometallic-Chemistry

chloride. Phthalate esters, which function as plasticizers, are derived from phthalic anhydride. Major use of phthalic anhydride has been in the production of polyester resins and alkyl resins used in paints and lacquers, certain dyes (anthraquinone, phthalein, rhodamine, phthalocyanine, fluorescein and xanthene dyes), insect repellents, and urethane polyester polyols.^[1]

Limitations on the use of naphthalene (high price, low availability and low purity) led the research toward the discovery of cheaper processes and alternative raw materials, such as *o*-xylene, which is nowadays available in adequate quantities from cracking plants and refineries. On the other hand, *o*-xylene has several advantages compared to naphthalene such as lower price, easier transportation, high excess and availability, high purity of products and long catalyst lifetime.^[3,4]

In the last few decades, the liquid-phase oxidation of *o*-xylene and *p*-xylene has been done in acetic acid,^[5,6] but because acetic acid at high temperatures is very corrosive, scientists pay more attention to vapor-phase oxidation of *o*-xylene. This process not only increases the phthalic anhydride yield but also saves raw materials and decreases emission of CO_x gases, which occurs as the main by-product in this type of reaction.^[2] Lack of solvent in vapor-phase oxidation reactions has promoted it to an environmentally friendly process. From the standpoint of environmental friendliness, much attention has been paid to the development of metal catalysts for the selective oxidation using molecular oxygen as a green oxidizing agent in vapor-phase.^[1,4]

Recently, considerable efforts have been devoted to the design of catalysts based on transition metal oxides, like CoO_x and MnO_x which exhibit catalytic activity for oxidation reactions as both a homo and heterogeneous catalyst because of their oxidation-reduction properties and ability to demonstrate several valences $(Co^{2+}, Co^{3+};$ Mn^{2+} , Mn^{3+} , Mn^{4+} , Mn^{7+}) with easy electron transfer between these states.^[7] The most efficient cobalt oxide for oxidation reaction is Co₃O₄ with a spinel structure, but at high temperatures the active phase Co_3O_4 transforms into the less active CoO, leading to a decrease in activity of the catalyst.^[8] To solve this problem, some promoters such as Br⁻ have been used to increase stability of the cobalt oxide catalyst. For example, the oxidation of *m*-xylene in liquid-phase, over the Co-Mn and Br ion as promoter of nanoparticles immobilized on activated carbon was investigated.^[9] Also in our previous work, the Co-Mn-Br nanoparticles immobilized on modified bentonite was used for oxidation of p-xylene in liquidphase.^[6] Unfortunately, bromide ion corrodes the expensive reactors and also forms methyl bromide which must be sequestered because it can deplete the ozone layer.^[9] In this work, we have attempted to develop other Co-Mn catalytic systems without bromide ion for oxidation of *o*-xylene. Furthermore, using heteropolyacids (HPAs) in this catalytic system was the most effective approach.

It is well known that heteropolyacids (HPAs) have been largely employed as solid-acid catalysts in homogeneous and heterogeneous reactions due to their unique structural and chemical properties.^[9] Moreover, the high acidity, redox properties and pseudo-liquid behavior of these compounds make them attractive catalysts for a large number of reactions. Phosphotungstic acid (H₃PW₁₂O₄₀, HPW) is the strongest HPA among the Keggin series and is a well-established catalyst for selective oxidation reactions and acid catalyzed reactions.^[10] Although HPAs in their acidic form or transition metal ion substituted forms are versatile compounds, their main disadvantages being high solubility in polar solvents and low surface area ($<10 \text{ m}^2/\text{g}$). Therefore, in a homogeneous reaction the isolation of the products and the reuse of the catalyst after reaction become difficult.^[10] Several studies were published on the heterogenization and immobilization of HPAs on various supports and their use in catalysis as green catalysts.^[11–13] Accordingly, this is an attractive strategy to improve the ease of separation, increasing surface area, and catalyst reusability. Since physically adsorbed HPW on the support surface can leach out easily, encapsulation of these catalysts onto the porous material might be the most effective approach.

In the present study and in continuation of our works on stabilization of heterogeneous catalysts, we have synthesized and characterized a composite of Co-Mn/HPW encapsulated into a mesoporous anatase TiO_2 network, and used as a heterogeneous catalyst for catalyzing the vapor-phase oxidation reaction of *o*-xylene to phthalic anhydride in a fixed-bed reactor. The synergistic effects between three metals have been considered as the main reason responsible for the high catalytic performance of the prepared catalysts.

2 | EXPERIMENTAL

2.1 | Materials and Instruments

All materials were used for synthesis of the catalysts and oxidation reaction obtained commercially without further purification: cobalt (II) acetate tetrahydrate, manganese (II) acetate tetrahydrate, phosphotungstic acid hydrate (H₃PW₁₂O₄₀.xH₂O) and polyvinylpyrrolidone were purchased from Merck Company. Titanium (IV) isopropoxide (Ti [OCH (CH₃)₂]₄, 97%) purchased from Sigma Aldrich Company. The *o*-xylene used in the present investigation was obtained from Titrachem Company. Molecular oxygen (99.99%) was obtained from Argon Company. All reactions were monitored by gas chromatography (Agilent GC-14C, column RTX-50 equipped with a flame ionization detector and a PEG-20 M capillary column, 30 m \times 0.25 mm \times 0.25 mm. Temperature program was carried out as: initial temperature = 70 °C, 0 min; final temperature = 280 °C, 1 min; with two ramps heating rate = 20 and 10 °C/min, temperature of injector = 260 °C, temperature of detector = 280 °C). Also, all products were identified by GC-Mass (Agilent 5975C gas chromatograph coupled with a mass spectrometer).

2.2 | Characterization Techniques

The catalysts were characterized by FT-IR, DR-UV, ICP-OES, FESEM-EDX, TEM, XPS, XRD, TGA and N2 adsorption-desorption techniques. Infrared spectra were recorded in the range of 4000-400 cm⁻¹on a Jasco 680plus FT-IR spectrophotometer using potassium bromide (KBr) pellets. Diffuse reflectance spectra were recorded in the range of 200-900 nm with a Jasco V-670 UV-vis. FESEM images were obtained using the TESCAN Mira-3, 15 kV instrument and transmission electron microscopy (TEM) were registered on a Philips CM120 transmission electron microscope with accelerator voltage of 100 kV. Thermogravimetric analysis (TGA) was done under an argon atmosphere at heating rate of 10 °C/ min on BAHR-STA/TGA-503. The weight percentage of cobalt, manganese and tungsten in the catalysts were obtained by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on Varian Vista-PRO CCD Simultaneous ICP-OES Inductive gekoppeltes. Nitrogen adsorption-desorption isotherms were measured with a PHS-1020 (PHS China) at 77 K. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method and pore size distribution was derived from the adsorption branches of the isotherms using the distribution Barrett-Joyner-Halenda (dBJH) method. X-ray diffraction (XRD) measurements were carried out using a Philips powder diffractometer type PW 1373 goniometer (Cu K_{α} = 1.5406 Å, Philips X'pert), over an angular range from 5° to 50°, and finally X-ray photoelectron spectroscopy (XPS) were recorded with a Kratos XSAM 800 (Al Kα, 1486.6 eV).

2.3 | Catalyst preparation

For the synthesis of the Co-Mn/ $H_3PW_{12}O_{40}$ @TiO₂, titanium (IV) isopropoxide was used as the precursor of TiO₂. In the first step, 1 g polyvinylpyrrolidone (PVP) was dissolved in 100 ml deionized water under magnetic stirring at room temperature. Then, phosphotungstic acid (0.75 g, 0.0002 mol), cobalt (II) acetate tetrahydrate (0.0909 g, 0.00036 mol) and manganese (II) acetate tetrahydrate (0.00909 g, 0.000037 mol) were added to the solution. The resulting solution was sonicated for 30 min. Then, titanium (IV) isopropoxide (4.278 g, 0.015 mol) was added dropwise during 5 hr with continuous stirring. Finally, the resulting precipitate was dried at room temperature and then calcined at 450 $^{\circ}$ C in air for 3 hr.

2.3.1 | o-Xylene oxidation procedure and apparatus

The vapor-phase tests were performed using approximately 0.44 g of the catalyst (mesh of 20-40) mixed with 1.0 g inert quartz beads in grain size (2-4 mm) to achieve better heat transfer in a fixed-bed vertical down flow tubular reactor (length: 36 cm; diameter: 1 cm). The Pyrex reactor was inserted in an electric oven controlled by a thermocouple and operating at atmospheric pressure. With this arrangement, the reaction temperature could be controlled with a precision of 1 °C. The feed (o-xylene) was introduced by an infusion pump, GENIE, Kent Scientific Corporation, and oxygen as the carrier gas, regulated by a mass-flow meter. The catalyst was previously activated in situ for 4 h at 250 °C under a 10 ml min⁻¹ O₂ flow. In each experiment, the products were collected by condensing them in a trap containing salt-ice, and analyzed off-line using an Agilent gas chromatograph, equipped with a PEG-20 M capillary column and a FID detector, and all products were identified by GC-Mass. After the reaction, the reactor was cooled to room temperature and on the basis of consumed oxylene, the mass balances were calculated from the weights of the reaction mixture after the reaction; in each reaction there was between 10-20% weight lost because of decomposition of the main product and intermediates.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of the catalyst

3.1.1 | FT-IR analysis

FT-IR spectra of mesoporous HPW@TiO₂, Co-Mn@TiO₂, Co-Mn/HPW@TiO₂ and reused catalyst after 5th run are shown in Figure 1. There are four characteristic peaks in the range of 1100 cm⁻¹ to 800 cm⁻¹ that may be ascribed to HPW Keggin structure. The band at 1079 cm⁻¹ was attributed to the stretching frequency of P–O in the central PO₄ tetrahedron. The peak at 982 cm⁻¹ was assigned to the terminal bonds for W=O_d in the exterior WO₆ octahedron. Bands at 891 cm⁻¹ and 804 cm⁻¹ were attributed to the W–O_b–W and W–O_c–W



FIGURE 1 FT-IR spectra of (a) HPW@TiO₂, (b) Co-Mn@TiO₂ (c) Co-Mn/HPW@TiO₂ and (d) reused Co-Mn/HPW@TiO₂ after 5^{th} run

bridges, respectively.^[12] For HPW@TiO₂ and Co-Mn/ HPW@TiO₂ catalysts (Figures 1a, 1c and 1d) these peaks are located at 805, 889, 974 and 1079 cm^{-1} , so that the red shift observed in the peak corresponding to W=O_d bond probably suggests the existence of hydrogen bonds between oxygen of the W=O_d bond in the Keggin oxoanion and the ≡Ti-OH groups of titania network.^[14,15] The IR spectrum of the sample without HPW shows none of these characteristic peaks (Figure 1 b). In Figure 1d, one could see that the primary Keggin structure of the HPW has not been destroyed and remains intact in the TiO₂ network after oxidation reaction. Furthermore, the FT-IR spectra indicate a broad band around 660 and 570 cm⁻¹ that can be ascribed to Co-O vibrations in the cobalt oxide lattice^[16] which are overlapped with Mn–O stretching at 613 and 509 cm⁻¹ and Ti-O stretching at 550 cm⁻¹.^[15,17] However, because of the low quantities of Co and Mn in these catalysts these bands were not seen clearly as distinct peaks.^[16] Also, the bands at around 1630 and 3400 cm^{-1} can be assigned to the deformation modes of OH bonds in TiO₂ and adsorbed H₂O.^[18]

A possible mechanism for the formation of welldispersed HPW and Co and Mn in the mesoporous TiO_2 matrix is directly related to the preparation method used here for preventing aggregation of the HPW crystallites but such matrix was not able to stop leaching of the HPW from the matrix. Although during the hydrolysis of titanium (IV) isopropoxide in the presence of $H_3PW_{12}O_{40}$, the Keggin units were entrapped by the titania network, the surface hydroxyl groups of Ti (\equiv Ti–OH) form hydrogen-bonding with the HPW which results in composites such as (\equiv TiOH₂⁺) ($H_2PW_{12}O_{40}^-$) (see Figure S1 at supporting information).^[19] In such composites, hydrogen bondings such as $W=O_t \dots HO-Ti$, $W-O_c \dots$ HO–Ti, and $W-O_e \dots HO-Ti$ also formed between the oxygen atoms of Keggin ion and the \equiv Ti–OH groups of titania network.^[14]

3.1.2 | XRD studies

According to reference pattern in Figure 2a, the broad diffraction peaks appearing in Figure 2b-d at $2\theta = 25.2^{\circ}$ (101), 37.9° (103) and 48.3° (200) just could be related to deformed anatase structure and the reason for peak broadening is conceivably due to the HPW, cobalt oxide, and manganese oxide in the TiO₂ matrix which prevented formation a uniform anatase crystalline TiO₂.^[14] No diffraction peaks could be assigned to HPW, cobalt oxide, and manganese oxide which means that these components form too small crystallites or are well dispersed in the mesoporous anatase TiO₂ framework rather than existing as aggregates in the matrix.^[20-22] In authorization of this comment, results obtained from EDX and elemental mapping analysis (Figure 6d inset) indicate high dispersion of HPW and other components over the TiO₂ network, which could explain why XRD of the catalysts did not show any crystalline phases related to the phosphotungstic acid and others.^[17,18,23]



FIGURE 2 XRD patterns of (a) reference pattern of anatase TiO₂, (b) HPW@TiO₂, (c) Co-Mn@TiO₂, (d) Co-Mn/HPW@TiO₂ and (e) commercial HPW

3.1.3 | TGA studies

The thermal behavior of HPW@TiO₂, Co-Mn@TiO₂ and Co-Mn/HPW@TiO2 were investigated by TGA analysis. As shown in Figures 3a and 3c, there are two main weight losses in TGA curves of the HPW@TiO2 and Co-Mn/HPW@TiO2 catalysts. The first mass loss of 1.8 and 2.6% (between 30 °C and 160 °C) may be due to removal of surface adsorbed water from these catalysts, respectively. The HPW@TiO₂ and Co-Mn/HPW@TiO₂ catalysts were stable in the range of about 160-500 °C, where they show a second weight loss (1.07 and 1.7%) after 500 °C which could be attributed to the decomposition of the heteropolyacid and more condensation of the metal oxides in the composites. In the Co-Mn@TiO₂ the total weight loss (2.7 wt%) could be due to elimination of adsorbed water and different types of condensations that might occur in the metal oxides.^[7]

3.1.4 | DR-UV studies

As illustrated in Figure 4, the DR-UV spectrum of the HPW@TiO₂ sample has shown two absorption bands near 245 and 315 nm with a well-defined absorption edge at 390 nm. These features agree very well with typical anatase TiO₂ spectrum reported elsewhere,^[23] and were related to $O^{2-} \rightarrow Ti^{4+}$ charge transfer transitions. The peaks at 260 nm and 310 nm were the typical absorption bands of HPW anion.^[24] The absorption band at 260 nm could be attributed to the ligand to metal charge transfer from O^{2-} ion to a W⁶⁺ ion where leads to the following process:

$$[W^{6+}-O^{2-}-W^{6+}] \rightarrow [W^{5+}-O^{-}-W^{6+}]$$

The produced excited state, i.e. $[W^{5+}-O^{-}-W^{6+}]$ has a strong oxidation ability for oxidation of the xylene.^[25] In addition to this, there is an absorption band at 310 nm which is also characteristic of $H_3PW_{12}O_{40}$.^[26] The broadening of the absorption bands could be due to the



FIGURE 3 TG curves of (a) HPW@TiO₂, (b) Co-Mn@TiO₂ and (c) Co-Mn/HPW@TiO₂



FIGURE 4 DR-UV spectra of (a) HPW@TiO₂, (b) Co-Mn@TiO₂ and (c) Co-Mn/HPW@TiO₂

introduction of phosphotungstic acid in TiO₂ framework and changing the coordination environment of TiO₂.^[14]

The UV-Vis spectrum of the catalyst containing cobalt and manganese is displayed in Figure 4b. The absorption bands around 215, 420 and 720 nm were observed for cobalt oxide. The band at around 215 nm can be assigned to the oxygen to metal charge transfer from $O^{2-} \rightarrow Co^{3+}$. The characteristic bands related to the d-d transition of ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ of Co³⁺ ions in octahedral coordination and ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(P)$ of Co²⁺ ions in tetrahedral coordination in the complex of Co₃O₄ $(\equiv Co^{2+}(Co^{3+})_2O_4)$ spinel were shown at around 400 and 700 nm, respectively, indicating Co₃O₄ should be the dominant phase for cobalt oxide encapsulated in TiO₂ network with most oxidative property.^[7,27] Moreover, the manganese oxide displayed an intense band at about 260-286 nm caused by the oxygen to metal charge transition in Mn_3O_4 ($\equiv Mn^{2+}(Mn^{3+})_2O_4$) complex. The weak shoulders at around 370 and 470 nm could be assigned to d–d transitions of the ${}^5B_{1g} \rightarrow \, {}^5B_{2g}$ and $\, {}^5B_{1g} \rightarrow \, {}^5E_g$ of Mn^{3+} in Mn_2O_3 , and the weak peak at around 640 nm corresponded to $^6A_{1g}$ \rightarrow $^4T_{2g}$ transition of Mn^{2+} in MnO.^[7,28] Therefore, a mixture of manganese oxides (Mn³⁺ and Mn²⁺) was dispersed in the calcined Co-Mn@TiO₂ catalyst.

3.1.5 | XPS studies

X-ray photoelectron spectroscopy (XPS) is a powerful technique used to investigate the chemical properties of the species in HPW@TiO₂, Co-Mn@TiO₂, Co-Mn/HPW@TiO₂ and the reused Co-Mn/HPW@TiO₂ after 5th run. As shown in Figure 5, the studied XPS detailed regions were Ti 2p, W 4d, Co 2p, Mn 2p and O 1 s. The XPS of Ti 2p levels for the all samples are presented in Figure 5a which show the doublet arising from spin-orbit splitting Ti $2p_{3/2}$ and Ti $2p_{1/2}$. The analysis of the Ti $2p_{3/2}$ level (more intense signal) shows the binding energy value at 458.7 eV that is typical of Ti^{4+[29]} whereas, in



FIGURE 5 XPS patterns of (a) Ti 2p, (b) W 4d, (c) Co 2p and (d) Mn 2p; For all samples: (I) HPW@TiO₂, (II) Co-Mn@TiO₂ (III) Co-Mn/HPW@TiO₂ and (IV) reused Co-Mn/HPW@TiO₂ after 5th run

the reused Co-Mn/HPW@TiO₂ catalyst after 5th run, it shifted to 459.1 eV. The XPS spectrum in Figure 5b shows the most intense W $4d_{5/2}$ component of the W 4d doublet at a binding energy of 247.5 eV which confirms the oxidation state of +6 (W⁶⁺) for tungsten in the catalysts.

The spectrum in Figure 5c exhibits an intense doublet due to the two spin-orbit components for Co 2p3/2 (780.8 eV) and Co $2p_{1/2}$ (795.5 eV). From the spin-orbital splitting value of the 2p level one could measure the oxidation of the metal in the catalyst; the spin-orbit splitting for Co₃O₄ is 15 eV, while it is 16 eV for CoO.^[16] In the prepared catalyst in this work the spin-orbit splitting of 14.7 eV is consistent with the Co_3O_4 .^[16,30,31] Clearly, Co 2p is detected, and quantified in the Co-Mn@TiO2 and Co-Mn/HPW@TiO2 samples. On the contrary, in the reused Co-Mn/HPW@TiO2 catalyst after five consecutive runs, its presence is 'suspected' but cannot be quantified and it is probably duo to leaching of some of the cobalt after five recycles which coincides with the result of ICP studies (see section ICP Studies). Furthermore, Mn was not detected by XPS after an accumulation of 50 sweeps suggesting that the Mn surface concentration is lower than the detection limit of the XPS analysis (Figure 5d) and this result is consistent with the conclusion obtained from the XRD analysis.

Finally, we must mention that the analysis of the O 1 s core levels (see Figure S2) reveals a peak at 530.2 eV assigned to oxygen bound to metallic ions (mainly Ti^{4+}) except in reused Co-Mn/HPW@TiO₂ after 5th run where the region is dominated by higher binding energy components (531.5 eV) corresponding to organic oxygen (bound to carbon) and commonly to OH from hydroxyl ions.^[29]

3.1.6 | FESEM, EDX and elemental mapping studies

The FESEM images of the HPW@TiO₂, Co-Mn@TiO₂ and Co-Mn/HPW@TiO2 samples in magnification of 500 nm are shown in Figure 6, and in other magnifications are demonstrated in Figures S3 and S4. As seen, they have approximately similar surface morphology and roughness. All of the samples are narrowly distributed and approximately having a uniform particle size. These results indicate that the encapsulation method developed in this work is highly efficient on increasing the surface to volume ratio of the catalyst. To demonstrate the presence of HPW, Co and Mn oxides in the catalyst, elemental analysis was done using EDX and the characteristic peaks were identified (Figure 6d). Clearly, the analysis shows the presence of Ti, Co, Mn, P, W, and O in the Co-Mn/HPW@TiO₂ catalyst. However, the XRD patterns do not show any peaks related to cobalt oxide, manganese oxide and phosphotungstic



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FIGURE 6 FESEM images of (a) HPW@TiO₂, (b) Co-Mn@TiO₂ and (c)Co-Mn/HPW@TiO₂ at magnification of 500 nm, (d) EDX and elemental mapping images (inset) of Co-Mn-HPW@TiO2 catalyst

acid particles. Therefore, one might conclude that HPW, cobalt oxide and manganese oxide are uniformly dispersed in the anatase matrix. According to the elemental mapping analysis (Figure 6d inset), all of the elements have been discovered with a homogeneous and uniform distribution in the Co-Mn/HPW@TiO₂ catalyst.

3.1.7 **TEM studies**

TEM images show the presence of overall and uniform nanoparticles in the as-prepared catalysts in different magnifications (20, 60 and 100 nm) in Figure 7a-i. The images also show that most of the nanoparticles have spherical shape which are coherent together. We could judge that the mesoporous structure is obtained by the agglomeration of mono-dispersed TiO₂ particles; the particles dispersion is obvious on the TiO₂ matrix. This dispersion of particles is due to the use of PVP in preparation of the catalyst and by burning PVP during calcination of the catalyst at 450 °C, leads to a uniform dispersion of HPW, manganese and cobalt oxides in the anatase TiO₂ matrix. The average sizes of most

particles in the HPW@TiO₂, Co-Mn@TiO₂ and Co-Mn/ HPW@TiO₂ catalysts were found to be around 4, 7 and 5 nm in diameter, respectively (Size distribution histogram was shown in Figure S5).

3.1.8 | N₂ adsorption-desorption isotherms studies

The specific surface area is an important representative of a catalyst. The specific surface area, pore diameter and pore volume of the catalysts were determined by BET and dBJH methods. The specific surface area of the HPW@TiO2, Co-Mn@TiO2 and Co-Mn/HPW@TiO2 catalysts were 109, 122 and 90 m^2/g , respectively (Table 1). The porosities of these catalysts were investigated by nitrogen adsorption-desorption techniques. According to IUPAC definition the nitrogen adsorption-desorption isotherms show type IV behavior for all samples with steep hysteresis loop at high relative pressure, which is typical for mesoporous materials (Figure 8a-c). As demonstrated in Table 1, pore diameter (~2.6 nm) and pore 8 of 13 WILEY Organometallic Chemistry



FIGURE 7 TEM images of (a-c) HPW@TiO₂, (d-f) Co-Mn@TiO₂ and (g-i) Co-Mn/HPW@TiO₂ at magnification of 100, 60 and 20 nm

TABLE 1 Textural properties of the prepared catalysts

Entry	Catalyst	S_{BET} (m ² /g)	V _{pore} (cm ³ /g)	D _{pore} (nm)
1	HPW@TiO ₂	109	0.199	2.6
2	Co-Mn@TiO ₂	122	0.359	2.6
3	Co-Mn/HPW@TiO ₂	90	0.194	2.6



FIGURE 8 N₂ adsorption-desorption isotherms of (a) HPW@TiO₂, (b) Co-Mn@TiO₂ and (c) Co-Mn/HPW@TiO₂ and dBJH-Plots pore size distribution of these samples (inset)

volume ($\sim 0.1-0.3 \text{ cm}^3/\text{g}$) of the catalysts were calculated using the dBJH method (Figure 8a-c, inset).

3.1.9 | ICP studies

To determine the contents of W, Co and Mn in the Co-Mn/HPW@TiO₂ catalyst before and after five consecutive runs, ICP-OES technique was applied and the data of analysis were shown in Table 2. As observed, the fresh catalyst had W (2.67 w%), Co (0.917 w%) and Mn (0.099 w%), which perfectly agrees with the theoretical calculations (Co/Mn ratio is 10/1). From the ICP data, we could judge that the catalyst has lost 1.793 wt% of HPW,

TABLE 2 ICP analysis results of fresh and reused Co-Mn/HPW@TiO₂ catalyst

Entry	Catalyst	Co (wt %)	Mn (wt %)	W (wt %)
1	Co-Mn/HPW@TiO ₂ (Fresh)	0.917	0.099	2.67
2	Co-Mn/HPW@TiO ₂ (After 5 runs)	0.698	0.069	0.877

0.219 wt% cobalt and 0.03 wt% manganese after 5 runs. These results indicate that the activity of this catalyst remained at a satisfactory state after at least five cycles.

3.2 | Catalytic performance

3.2.1 | Effect of temperature

The reaction temperature has a great impact on both conversion and selectivity. As shown in Table 3 the effect of temperature on this reaction was studied by changing the temperature from 300 °C to 450 °C while the other parameters remained unchanged. The conversion and selectivity of phthalic anhydride increased when the temperature reached to 370 °C. Beyond this temperature the efficiency of Co-Mn/HPW@TiO₂ slightly decreased due

TABLE 3 Effect of temperature on the oxidation of o-xylene

to the instability of the heteropoly acid at high temperatures which shows itself in the selectivity of the main product; therefore, at 370 °C this catalyst exhibited a high conversion and selectivity.

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3.2.2 | Effect of WHSV

Weight hourly space velocity (WHSV) plays an important role in this type of reactions. The influence of feed rate of the reactant (*o*-xylene) over Co-Mn/HPW@TiO₂ catalyst was studied by using 2 ml *o*-xylene at 370 °C. Hence, the amount of catalyst in each run was determined by the selected WHSV defined as follows:

WHSV =
$$\frac{\text{"Mass flow of } o-\text{xylene } (g/h)\text{"}}{(\text{"Weight of catalyst used } (g"))}$$

			Selectivity (%)				
Entry	Temperature (°C)	Conversion (%)	СНО	СНО			
1	300	0.2	88.7	11.2	0	0	
2	330	22.4	10.3	44	28	17.5	
3	350	64.6	7.6	20.6	22.9	48.8	
4	370	88.2	2.1	4.2	18.1	75.5	
5	390	56.1	4.2	18.8	24.5	52.3	
6	410	54.2	8.2	19.1	27.3	45.1	
7	430	51.2	7.3	15.4	29.4	43.0	
8	450	36.4	66.1	14.4	16	3.4	

Reaction conditions: o-xylene: 2 ml, WHSV: 0.5 h⁻¹, O₂ flow rate: 10 ml min⁻¹, amount of catalyst: 0.44 g selected catalyst (Co-Mn/HPW@TiO₂).

TABLE 4 Effect of WHSV on the oxidation of o-xylene

			Selectivity (%)				
Entry	WHSV (h ⁻¹)	Conversion (%)	СНО	СНО			
1	0.25	78.3	5.5	10.7	23.3	60.3	
2	0.5	88.2	2.1	4.2	18.1	75.5	
3	1	38.1	8	26.4	22.7	42.8	
4	1.5	22.5	12	29.3	22.7	35.7	

Reaction conditions: o-xylene: 2 ml, temperature: 370 °C, O₂ flow rate: 10 ml min⁻¹, amount of catalyst: 0.44 g selected catalyst (Co-Mn/HPW@TiO₂)

TABLE 5 Effect of O₂ flow rate on the oxidation of *o*-xylene

			Selectivity (%)			
Entry	O_2 flow rate (ml min ⁻¹)	Conversion (%)	СНО	СНО		
1	5	41.6	6.1	37.3	25.4	31
2	10	88.2	2.1	4.2	18.1	75.5
3	20	20.6	8.4	44.2	28.4	18.8

Reaction conditions: o-xylene: 2 ml, temperature: 370 °C, WHSV: 0.5 h⁻¹, amount of catalyst: 0.44 g of the selected catalyst (Co-Mn/HPW@TiO₂).

TABLE 6 Effect of HPW and Co-Mn load

			Selectivity (%)			
Entry	Catalyst	Conversion (%)	Сно	СНО		
1	Co-Mn (1%)/HPW (15%)@TiO ₂	30.3	10.8	23.5	28.6	36.9
2	Co-Mn (2%)/HPW (15%)@TiO ₂	88.2	2.1	4.2	18.1	75.5
3	Co-Mn (4%)/HPW (15%)@TiO ₂	66.7	3.1	11.3	24.2	61.3
4	Co-Mn (2%)/HPW (10%)@TiO ₂	36.4	9	22.4	33.1	35.3
5	Co-Mn (2%)/HPW (25%)@TiO ₂	58.7	3.5	14.7	28.7	53
6	Co-Mn (2%)/HPW (15%)@TiO ₂ *	51	9.3	25.4	24.3	41
7	HPW (15%)@TiO ₂	43.3	8.8	28.1	29	34
8	Co-Mn (2%)@TiO ₂	48.1	9.5	31.7	26.7	32
9	Blank	0	-	-	-	-

Reaction conditions: *o*-xylene: 2 ml, temperature: 370 °C, WHSV: $0.5 h^{-1}$, O_2 flow rate: 10 ml min⁻¹, amount of catalyst: 0.44 g, Co/Mn ratio: 10/1 in all samples, *the catalyst was prepared in the absence of PVP.

While the catalyst weight was kept at 0.44 g, the contact time was varied by changing the feed rate, for example, 125, 250, 500 and 1000 μ l/h (i.e. 0.25–1.5 h⁻¹). On the basis of the experimental data, 0.5 h⁻¹ was chosen as selected WHSV for the oxidation reaction (Table 4). In addition, the conversion and selectivity decreased by increasing of WHSV from 0.5 to 1.5 h⁻¹. According to definition of WHSV, mass flow has a reverse relation with weight of the catalyst, therefore increasing the mass flow rate has a direct relation with decreasing the weight of catalyst and decreasing the oxidative sites which is consistent with the results presented in Table 4.

3.2.3 | Effect of oxygen flow rate

The effect of oxygen flow rate on the *o*-xylene conversion was studied and it was measured with gas flow meter (i.e., ml/min). According to the experimental results shown in Table 5, the conversion decreased with an increase of oxygen flow rate, because the oxygen passes quickly through the catalyst in a fixed-bed down flow

quartz tubular reactor and the catalyst do not have enough time to oxidize *o*-xylene. So, the optimum oxygen flow rate for this oxidation reaction is 10 ml min⁻¹ and lower than this flow rate, oxidation reaction faces to lack



FIGURE 9 Reusability of the Co-Mn/HPW@TiO₂ catalyst over oxidation of *o*-xylene to phthalic anhydride

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of the oxidizing agent which has led to decrease in conversion.

3.2.4 | Effect of HPW and Co/Mn load

The efficiency of the Co-Mn/HPW@TiO₂ catalyst can be improved by optimizing the HPW and manganese and cobalt oxides loads. Our experience^[6] had shown that the Co/Mn ratio could influence the catalytic activity of the catalyst in oxidation of *o*-xylene. Therefore, in this study we decided to start with the ratio of Co/Mn = 10/ 1, and optimize the loading of HPW and Co-Mn oxides. The Co-Mn/HPW@TiO₂ catalyst with different HPW, cobalt, and manganese oxides loads were compared for the *o*-xylene oxidation at 370 °C, WHSV = 0.5 h⁻¹, O₂ flow rate = 10 ml min⁻¹. Table 6 shows the *o*-xylene oxidation for five catalysts. The change of HPW and cobalt and manganese oxides affected on conversion and selectivity. The maximum *o*-xylene conversion and phthalic anhydride selectivity appeared on the catalyst with

 TABLE 7
 Catalytic activities of Co-Mn/HPW@TiO2 and some previously reported catalysts in the o-xylene oxidation

Entry	Catalyst	Temperature (°C)	Conversion (%)	Phthalic anhydride selectivity (%)	Ref.
1	V ₂ O ₅ /TiO ₂ ^a	380-400	100	70-75	[32]
2	V-Mn-MCM-41 ^b	300	60-70	80–90	[1]
3	V-Mo-MCM-41 ^c	350	90.2	87.3	[33]
4	AgMoVO ₆ ^d	387	42	34	[2]
5	V ₂ O ₅ -P ₂ O ₅ /TiO ₂ ^e	460	99.8	72.3	[34]
6	$V_2O_5/TiO_2\text{-}ZrO_2 \ ^{\rm f}$	435	76	57	[35]
7	V/ZrO2 ^g	410	99.2	35.2	[36]
8	Sb/ZrO ₂ ^g	440	13.2	0.9	[36]
9	Sb-V/ZrO ₂ ^g	400	96.2	43.5	[36]
10	V_2O_5/ZrO_2^{h}	450	100	50-60	[37]
11	Vanadium-PTG ⁱ	280	100	50	[38]
12	Pd/Al ₂ O ₃ ^j	160	100	-	[39]
13	Pd/Co ₃ O ₄ ^k	249	90	-	[40]
14	Mn-CeO _x ¹	240	100	-	[41]
15	α -MnO ₂ ^m	220	100	-	[42]
16	Au-Pd/3DOM Mn ₂ O ₃ ⁿ	250	90	-	[43]
17	HPW@TiO2°	370	43.3	34	This work
18	Co-Mn@TiO2 ^o	370	48.1	32	This work
19	Co-Mn/HPW@TiO2°	370	88.2	75.5	This work

Reaction conditions:

^ao-xylene: 0.54 mol%, amount of catalyst: 0.5 g.

^bamount of catalyst: 0.3 g, WHSV: 0.5 h^{-1} , air flow rate: 0.02 mol h^{-1} , V/Mn ratio = 50:50.

^camount of catalyst: 0.2 g, feed flow rate ratio: 0.016 cc, o-xylene: 200 cc, oxygen gas per minute, contact time (W/F₀): 24.41 h, Si/(V + Mo) ratio = 46.

^dfeed composition = o-xylene: 1 vol %, O₂: 20 vol%, H₂O: 5 vol %, GHSV: 3000 h⁻¹.

eamount of catalyst: 2100 g, V2O5 (5.9 wt%), P2O5 (0.25 wt%), and TiO2 (93.8 wt.%), flow rate: 4.5 Nm3 h^-1.

^famount of catalyst: 0.3–0.5 g, feed flow rate: 1.0–2.0 ml h^{-1} , O₂ flow rate: 80–90 ml min⁻¹.

^gamount of catalyst: 0.06 g, (W/F) was 42 g.s.L⁻¹, The molar concentrations of o-xylene and oxygen in the feed were 0.8 and 20.8% respectively (78.4% nitrogen).

^hTemperature: 310, 330, 350, 370, 390 and 410 °C and different WHSV: 1500, 2000 and 2500 h⁻¹, initial concentration of o-xylene - C_{xylene} = 42 g/nm³.

ⁱPorous titania glass (PTG) has been loaded with vanadia.

 $^{j}o\mbox{-xylene:}$ 100 ppm, flow rate: 100 ml min $^{-1}$ (20 vol% $O_{2}\mbox{:}80$ vol% $N_{2}\mbox{)},$ GHSV: 50,000 $h^{-1}\mbox{.}$

^kamount of catalyst: 0.1 g, *o*-xylene: 150 ppm, flow rate: 100 ml min⁻¹(20 vol% O_2 :80 vol% N_2), GHSV: 60,000 h⁻¹.

¹amount of catalyst: 0.25 g, o-xylene: 700 ppm, flow rate: 50 ml min⁻¹(20 vol% O_2 :80 vol% N_2), GHSV: 8,000 h⁻¹.

 $^{\rm m}o$ -xylene: 700 ppm, flow rate: 50 ml min $^{-1}$ (20 vol% $\rm O_2$:80 vol% $\rm N_2$), GHSV: 8,000 $\rm h^{-1}.$

ⁿamount of catalyst: 0.05 g, o-xylene: 1000 ppm, flow rate: 16.6 to 166.0 ml min⁻¹ (20 vol% O_2 :80 vol% N_2), GHSV: 9,100–191,000 h⁻¹.

°o-xylene: 2 ml, amount of catalyst: 0.44 g, temperature: 370 °C, WHSV: 0.5 h⁻¹, O₂ flow rate: 10 ml min⁻¹.

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15 wt% HPW, and 2 wt% cobalt and manganese oxides. Beyond this load the conversion and selectivity decreased probably because of aggregation of the effective catalysts. It should be mentioned that when the optimized catalyst was prepared in the absence of PVP in solution the conversion decreased appreciably (Table 6, entry 6); naturally one would expect that PVP causes more dispersion of the catalyst components in the TiO₂ matrix. In addition, it should be mentioned that Co-Mn/HPW@TiO₂ catalyst was very superior to the HPW@TiO₂ and Co-Mn@TiO₂ catalysts due to the synergistic effects between cobalt, manganese, and tungsten (Table 6, entries 2, 7 and 8). The support without HPW, cobalt and manganese oxides showed no activity.

3.2.5 | Reusability of the catalyst

The stability of the Co-Mn/HPW@TiO₂ catalyst was studied in the oxidation of o-xylene by applying the catalyst in consecutive runs. By separating the catalyst after each run, it was washed with ethyl acetate and dried in an oven for 1 h at 80 °C. Then, the recovered catalyst was charged into the reactor, and preheated at 250 °C for 4 h in a flow of oxygen (10 ml min⁻¹) at atmospheric pressure. According to the results shown in Figure 9, both conversion and selectivity remained at a satisfactory level after five runs. As mentioned in *section ICP studies*, the catalyst after five consecutive runs lost a percentage of its components and in this respect the activity of the catalyst decreased slightly. These results indicate that the catalyst is reusable, stable and has strong oxidation ability even after five runs.

The data in Table 7, compare the results obtained over Co-Mn/HPW@TiO₂ catalyst and other catalytic systems such as V_2O_5/TiO_2 ,^[32] V-Mn-MCM-41,^[1] V-Mo-MCM-41,^[33] V_2O_5/TiO_2 -ZrO₂,^[35] Pd/Al₂O₃,^[39] Sb-V/ZrO₂,^[36] and V_2O_5/ZrO_2 ,^[37] which have been reported for vaporphase oxidation of *o*-xylene to phthalic anhydride in a fixed-bed reactor. Clearly, the catalyst used in the present study might be one of the best catalysts for producing phthalic anhydride.

4 | CONCLUSION

The following conclusions can be highlighted: (1) the Co-Mn/HPW@TiO₂ catalyst was found to be the most efficient catalyst among the investigated catalysts for oxidation of *o*-xylene to phthalic anhydride. (2) The presence of PVP in aqueous solution when preparing the catalyst lead to higher activity for the oxidation reaction. (3) The loading of HPW, cobalt and manganese oxides play an important role in the conversion and selectivity of the

main product. (4) The conversion of *o*-xylene to phthalic anhydride increased by enhancing the temperature, and the highest selectivity to main product was obtained at a reaction temperature of 370 $^{\circ}$ C. (5) The catalyst was reasonably active even after five consecutive runs.

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