Diphenyl carbonate is a versatile chemical intermediate as well as the main raw material for the cleaner production of polycarbonate (PC) [1]. The main synthetic methods of DPC are phosgene method, transesterification method and oxidative carbonylation method. Phosgene method gradually dies out due to serious environmental pollution problems [2]. The transesterification reaction of DPC by phenol and DMC is limited by the thermodynamic conditions, the equilibrium constant of which is small leading to the lower catalytic efficiency [3]. The most attractive method is oxidative carbonylation of phenol using monoxide and oxygen in one-step [4], in which H₂O is the sole by-product and the use of highly toxic and corrosive phosgene can be avoided. Compared to homogeneous catalysts, the heterogeneous catalysts are easy to be separated [5]. Thus, it is essential to decrease the intraparticle diffusion resistance and improve catalytic activity of heterogeneous catalysts in oxidative carbonylation of phenol to DPC.

The formula of the Keggin-type heteropolyacids (HPAs) is H₈⁻ₓ[XM₁₂O₄₀], where X refers to the heteroatom (most frequently P⁵⁺ or Si⁴⁺), x refers to its oxidation state, and M means the addenda atom (usually W⁶⁺ or Mo⁶⁺). The Keggin-type HPA is a promising acid catalyst as well as a nice oxidation/reduction catalyst and a good bifunctional catalyst (acid catalyst and oxidation/reduction catalyst) [6] for its adjustment of architecture [7], oxidation state, and M means the addenda atom (usually W⁶⁺ or Mo⁶⁺). The Keggin-type HPA is a promising acid catalyst as well as a nice oxidation/reduction catalyst and a good bifunctional catalyst (acid catalyst and oxidation/reduction catalyst) [6] for its adjustment of architecture [7], oxidation state, and M means the addenda atom (usually W⁶⁺ or Mo⁶⁺). The Keggin-type HPA is a promising acid catalyst as well as a nice oxidation/reduction catalyst and a good bifunctional catalyst (acid catalyst and oxidation/reduction catalyst) [6] for its adjustment of architecture [7], oxidation state, and M means the addenda atom (usually W⁶⁺ or Mo⁶⁺). The Keggin-type HPA is a promising acid catalyst as well as a nice oxidation/reduction catalyst and a good bifunctional catalyst (acid catalyst and oxidation/reduction catalyst) [6] for its adjustment of architecture [7], oxidation state, and M means the addenda atom (usually W⁶⁺ or Mo⁶⁺). The Keggin-type HPA is a promising acid catalyst as well as a nice oxidation/reduction catalyst and a good bifunctional catalyst (acid catalyst and oxidation/reduction catalyst) [6] for its adjustment of architecture [7], oxidation state, and M means the addenda atom (usually W⁶⁺ or Mo⁶⁺). The Keggin-type HPA is a promising acid catalyst as well as a nice oxidation/reduction catalyst and a good bifunctional catalyst (acid catalyst and oxidation/reduction catalyst) [6] for its adjustment of architecture [7], oxidation state, and M means the addenda atom (usually W⁶⁺ or Mo⁶⁺).
ging the proton with metal, converting into salts or dispersing them on suitable support [9]. The activity of HPAs in oxidation can be improved by partial substitution of redox metal ions in the Keggin structure [10]. Vanadium incorporated molybdophosphoric acid (HAMPV) catalysts show unique catalytic features in oxidation due to the bifunctional character—the good redox nature of vanadium and the oxidation/acidic character of the molybdophosphoric acid [11]. Authors have investigated V-incorporated molybdophosphoric acid catalysts through the way of replacing 1–3 Mo atoms with the corresponding number of V atoms [12,13]. The acidity, redox and thermal stability of the HAMPV catalysts are influenced by the degree of V substitution [14]. It is helpful to increase the surface area by loading modified HPAs on support. It is always advantageous to use supports such as Nb_2O_5, TiO_2, SiO_2 and Al_2O_3, all of which are capable of releasing oxygen by the mobility of lattice oxygen and form oxygen vacancies [15]. Acidified and modified cross-linked kaolin with the porous structural [16] has been widely applied for industrial catalysts [17] and carriers [18] owing to its acidity and high surface area itself.

Some research groups focus on Pd/Mn system because the potentials of MnO_2/Mn^{2+} pair are between the potentials of Pd^{2+}/Pd and O_2 + H^+/H_2O pairs. Therefore, Mn^{4+} of MnO_2 can oxidize Pd to form Pd^{2+} and Mn^{2+}, then the latter one could be reoxidized by O_2 to Mn^{4+}. Manganese oxide has been studied for the first time as co-catalyst and support by Min [19], which made it easy for the metallic parts of the catalytic system to separate. But the yield of DPC was only 10.7% [19]. Xiaojun prepared palladium supported on Pb-cation-doped manganese oxide octahedral molecular sieves as heterogeneous catalysts and the yield of DPC increased to 18.1% [20]. The spinel ferrite MnFe_2O_4 has been prepared by Zhang in the sol-gel method as a catalyst support applied in oxidative carbonylation of phenol to diphenyl carbonate. It cannot be reused although the single pass yield of DPC reached 33.12% and TOF was 70.56 mol DPC (mol Pd·h)^{-1} [21].

In this work, heteropoly salts (MPAs) loaded on the modified kaolin as a co-catalyst is applied in the synthesis of diphenyl carbonate by oxidative carboxylation of phenol. In addition, the influence of V replacing Mo in heteropoly salts on the catalytic activity in the reaction is also studied.

**EXPERIMENTAL**

**The preparation of the Keggin-type heteropoly salt**

Keggin-type molybdophosphoric acid, molybdo phosphoric salt and vanadium-incorporated molybd phosphoric salt have been successfully synthesized based on the synthesis procedure reported previously [22].

**Synthesis of H_4PMo_{11}VO_{40}**

1.56 g Na_2HPO_4·12H_2O (0.01 mol) was dissolved in 50 ml deionized water. 26.64 g NaMoO_4·2H_2O (0.11 mol) was dissolved in 60 ml deionized water. Then the two solutions were mixed together and heated with stirring until it boiled to reflux for about 30 min and 1.53 g NaN_3·2H_2O (0.01 mol) was added into it. Then the mixture was heated with reflux at 110 °C for 30 min. The pH was adjusted to 2 with sulfuric acid in a mole ratio of 1:1 until it turned to scarlet. It was cooled down to room temperature and transferred into a 500 ml tap funnel. 50 ml diethyl ether was added and shaken until the solution was divided into two layers. Then 1:1 sulfuric acid (about 30 ml) was dropped and shaken until red granular objects sank into the solution. When the solution was divided into three layers, the upper was diethyl ether, the middle was aqueous solution, the lower reddish-brown oil was ether compounds of heteropolyacids and ether, which was taken for vacuum drying to obtain brown-red powder - H_4PMo_{11}VO_{40} (HAMPV).

The preparation of HAMPV_3 and HAMPV_5 was the same as the way above with the different mixing ratios.

**Synthesis of the Keggin-type heteropoly salt**

1g desiccative HAMPV prepared above was dissolved in 5 ml deionized water. 0.1392 g Mn(NO_3)_2·4H_2O was dissolved in 5 ml deionized water. The two solutions were mixed, stirred for 30 min at a magnetic stirrer and placed in a vacuum oven, dried at 70 °C for 6 h. The mixture was cooled down to the room temperature, transferred to a small mug and calcined at 200 °C for 4 h in a muffle furnace. It was cooled down to the room temperature to obtain a powder—MnAMPV.

CuCl_2·2H_2O, Co(NO_3)_2·6H_2O, Pb(NO_3)_2, Ce(NO_3)_3·6H_2O or FeCl_3·6H_2O took the place of Mn(NO_3)_2·4H_2O to prepare different heteropoly salts.

**Pretreatment of kaolin carrier**

The kaolin was purified by immersing in deionized water and stirred at room temperature for 6 h. It was filtrated, dried at 110 °C, ground and calcined at 300 °C for 2 h, after which it was immersed in 20 wt. %
H₂SO₄, activated at 100 °C for 4 h. The solution was cooled down to room temperature, washed with deionized water, filtrated to neutral state and finally dried at 120 °C for 8 h. The modified kaolin was prepared for later use.

**The supported of heteropoly salt**

0.3 g MnAMPV was dissolved into 80 ml solution mixed with anhydrous ethanol and distilled water in volume ratio 1:1. 1 g modified kaolin was added into the mixed solution above and stirred in hot reflux for 8 h. Then it was dried at 100 °C for 6 h, calcined in the muffle furnace at 300 °C for 3 h and cooled down to the room temperature to prepare 30 wt.% MnAMPV/MK co-catalyst. 10 wt.% MnAMPV/MK and 20 wt.% MnAMPV/MK could be obtained by changing the ratio of MnAMPV and MK.

**Supporting the PdCl₂**

The active component PdCl₂ was loaded on the support by coprecipitation method. PdCl₂ was dissolved into 50 ml distilled water with hydrochloric acid of proper volume completely. 5 g support was dipped into the PdCl₂ solution in order to have a palladium loading of 1 wt.%. The NaOH solution as a precipitant was then added into the solution to keep pH value at 9-10 with stirring. Filtrated, dried and finally calcined it at 300 °C for 3 h to obtain the catalysts.

**Characterization**

The phase identification and crystalline structure analysis were characterized by the X-ray diffractometer (XRD, D8 Advance, Germany) operating at 40 kV and 40 mA using CuKα radiation and Ni filter. The scanning rate is 4°·min⁻¹ in the 2θ range 5-80°. BET surface area measurement was done by applying the Quantachrome Instruments Nova2000e. The chemical shift and valence of element on surface were studied by X-ray photoelectron spectra (XPS) in a Perkin-Elmer PHI 1600 ESCA system with MgKα X-ray radiation (1253.6 eV, 250 W). Temperature-programmed reduction (H₂-TPR) experiments were performed in a quartz reactor using a thermal conductivity detector (TCD) as detector on Micromeritics AutoChem2920 (USA) instrument.

**Catalytic activity test**

DPC synthesis by oxidative carbonylation of phenol was carried out in a stainless steel autoclave of ca. 250 ml of capacity provided with a magnetic stirrer. Typical reaction conditions were as follows: \( t = 65 °C, p = 5 \text{ MPa}, \text{CO}_2/\text{O}_2 = 93/7 \text{ mole ratio}, \) phenol, 20 g, 1.0 g catalyst (Pd/carer = 1/100 mass ratio), tetrabutylammonium bromide (TBAB) 1 g, 4Å molecular sieve as drying agent, reaction time 8 h. Then the autoclave was pressurized with the mixture of carbon monoxide and oxygen, and the reaction autoclave was cooled down to room temperature and vented in the end.

The reaction products were identified and quantified by gas chromatography with a flame ionization detector (FID, GC4000A of EAST&WEST Analytical Instruments made in China).

**RESULTS AND DISCUSSION**

**Catalyst characterization**

**XRD and BET characterization**

The heteropolyanion of the Keggin-type absorption peaks generally appear at 8.28, 8.90, 9.10, 27.9 and 28.9°, which are basically identical with the characteristic peaks of MnAMPV (Figure 1). Therefore, the prepared heteropoly salt belongs to Keggin-type heteropoly compound. From the XRD pattern of MK, it is known that the absorption peak of MK is consist with the characteristic peak of the kaolin at around 26.3°. The absorption peak of heteropolyanion is gradually enhanced with the increase of heteropoly salt loading, the intensity of which is weaker than pure molybdovanadophosphoric heteropoly salt. It indicates that molybdovanadophosphoric heteropoly salt has good dispersion on the carriers instead of aggregation. The characteristic peak of Pd is hard to be found for its content of merely 1%.
Comparison of the surface areas and pore volumes of MnAMPV, Pd/10%MnAMPV/MK, Pd/20%MnAMPV/MK, Pd/30%MnAMPV/MK and MK (Table 1) indicates that surface area and pore volume of MnAMPV supported on MK are larger than that of pure MnAMPV. Surface area and pore volume of the catalysts decrease with the increase of MnAMPV loading on MK (10-30 wt.%). For instance, Pd/10%MnAMPV/MK has the surface area of 45 m$^2$/g and the total pore volume of 0.23 cm$^3$/g. The surface area of Pd/30%MnAMPV/MK decreases to 27 m$^2$/g, the total pore volume reduces to 0.15 cm$^3$/g. The surface area and the total pore volume of the pure MnAMPV are only 8 m$^2$/g and 0.04 cm$^3$/g, respectively. The decrease of surface areas attributed to the subsequent filling of support pores by active component.

**XPS characterization**

XPS spectra shows more information on the structure of different catalysts (Figure 2a). Pd/20%MnAMPV/MK, Pd/20%MnAMPV$_3$/MK, Pd/20%MnAMPV$_5$/MK are selected as target samples for the optimum result of activity test. It is observed that no change in binding energy of Pd species. The Pd 3d binding energies at 337.5 and 343.0 eV corresponding to the Pd$^{2+}$ are almost the same in catalysts at varying quantities of V.

**Table 1. BET surface areas and pore volumes of different samples**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m$^2$/g)</th>
<th>Total pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnAMPV</td>
<td>8</td>
<td>0.04</td>
</tr>
<tr>
<td>Pd/10%MnAMPV/MK</td>
<td>35</td>
<td>0.23</td>
</tr>
<tr>
<td>Pd/20%MnAMPV/MK</td>
<td>28</td>
<td>0.20</td>
</tr>
<tr>
<td>Pd/30%MnAMPV/MK</td>
<td>23</td>
<td>0.15</td>
</tr>
<tr>
<td>MK</td>
<td>39</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The strong interaction between the active component and the carrier of the supported catalyst, the SMSI effect, leads to the transfer of electrons between them resulting in the binding energy shift. If the active component transfer electrons to the carrier, the binding energy will increased, and vice versa red-

![Figure 2. XPS spectra of Pd3d, Mn2p and O1s of: a) Pd/20%MnAMPV/MK, b) Pd/20%MnAMPV$_3$/MK and c) Pd/20%MnAMPV$_5$/MK.](image)
duced. XPS spectrum of Mn2p (Figure 2b) shows that the binding energies of V-incorporated catalysts are increasing with the rise of the V number. Pd/20%MnAMPVx/MK is about 0.4 eV higher than that of Pd/20%MnAMPV/MK catalysts. This small shift suggests the decrease of Mn atoms electronic densities owing to the transferring of electrons from active component to carrier makes the high-valence Mn species increase. Mn2+ transforms to Mn3+ in five atoms of V-incorporated catalysts. It is known that the lattice is strained when the tunnels Mo5+ is exchanged with smaller radius ions. As a result, it is confirmed that the lattice strain and the increase of Mn3+ sites is owing to the substitution of Mo5+ (0.139 nm) with relatively smaller ionic radius of V5+ (0.134 nm) [23]. Since Mn3+ is more easily oxidized than Mn2+, the increase of Mn3+ is beneficial to the supplement of reduced Mn4+ in redox cycle and leads to the increasing activities of five atoms of V incorporated catalysts.

Figure 2c, O1s, shows the corresponding XPS spectra of oxygen species and Table 2 indicates that the proportion of different oxygen species originates from fitted O1s spectrum, which refers to the XPS results obtained by Peluso [24]. Mn3+ sites could form a weak Mn-O bond, which makes active oxygen species come into being in the lattice [24]. Two photoemission peaks correspond to two distinct oxygen species. The high binding energy (about 531.3 eV) indicates strongly adsorbed molecular oxygen, and the line with low binding energy (about 529.5 eV) indicates the crystal lattice oxygen (O2–) [24]. With the rise of V number in catalysts, the lattice oxygen content decreases, which originates amounts of oxygen vacancies and the adsorption of oxygen increases in the crystal phase. Therefore, the catalysis with five V might possess good low-temperature oxidation performance.

**TPR characterization**

For the oxidation cycle regeneration efficiency of the active Pd source is the important factor in the catalytic reaction, the oxides supporters must be activated in a reducing atmosphere. To study this activation process, the reducibility of 20%MnAMPVx/MK systems is tested by temperature-programmed reduction and the reduction profiles are displayed in Figure 3. It is observed that the TPR flows from the diverse vanadium containing samples. There is a main reduction peak within the range of 650-750 °C of all the samples. The reduction peaks during 650-750 °C may result from the reduction of free metal oxides produced by the decomposition of the Keggin anion decomposing above 540 °C [25]. The reduction peaks below 500 °C may originate from the reduction of vanadium in the primary structure of the Keggin ion. The increasing reduction peak with enhancement in vanadium content especially in Pd/20%MnAMPVx/MK illustrates the vanadium expulsion from main structure. In the case of Pd/20%MnAMPVx/MK, the intact vanadium that containing the Keggin ion has reduced at around 650 °C. The expulsion of vanadium is expected for the catalysts with more vanadium atoms as resulting metal oxides being reduced at high temperatures. On the other hand, the V-incorporated catalyst possesses the low reduction temperature, which corresponds to the results of XPS. On the other hand, the lattice oxygen in its primary or secondary structure of the catalyst with V is more reactive than one with no V. These might be two reasons for high activity of the catalyst with V compared to catalyst without V.

**Efficiency of oxidative carbonylation with various catalysts**

Under high pressure of a closed system, the Keggin type heteropolyacids, heteropoly salts and the modified kaolin supported heteropoly salts have been investigated as the redox co-catalysts for the oxidative carbonylation of phenol to DPC in the absence of oxygen...
of solvent. The results are shown in Table 3. Pd/HAMP catalyst is hardly active for the oxidative carbonylation of phenol to DPC, although the yield of DPC reaches only 0.58% based on phenol with a TON of 7 after 8 h (entry 1). Pd/HAMPV has higher activity than Pd/HAMP. The activity can be improved to 2.30% with a TON of 29 (entry 2). This result shows that HAMP is inactive as the co-catalyst. In other words, V-incorporated catalyst can improve the reaction activity. All of the Pd/MPAs catalysts are more active than Pd/HPAs. The main reason is that the cation substitutes HPAs as a counter ion [26,27].

There are two kinds of counter ion, one has a large ionic radius with stability [28], who can make the dispersion of the active center, keep the active phase and improve the stability of the catalyst as well as the integrity (it includes surface area, porosity, and framework flexibility). Another is the multivalent metal with the use of improving the activity of catalyst in oxidation-reduction by charge transfer of atom with redox electron pair and heteropolyanion [29]. However, Pd/MnAMPV is more active than the others among Pd/MPAs catalysts, whose yield can be improved to 12.02% with a TON of 144 (entry 3). There are two reasons. On the one hand, the Mn atoms with suitable ionic radius can disperse active center well and enhance the catalyst stability. On the other hand, Mn is the multivalent metal and its electron transfers to the atom of heteropolyanion so as to improve the activity of the catalyst.

Under the same condition, the yield of the unmodified kaolin is lower (entry 9). It is necessary to modify the kaolin since the alkalinity of Al2O3 in the kaolin is stronger enough to neutralize acid parts of heteropoly acid to affect the yield of carbonylation reaction. In this experiment, the kaolin will be modified by immersion in 20% H2SO4 and then activating treatment under 100 °C. Besides, the modified kaolin may release oxygen attributed to the mobility of lattice oxygen and the formation of the oxygen vacancies [20]. It is beneficial for the conversion of Pd to active Pd2+ and the increase of the DPC yield. It is showed that the DPC yields changed with the different loading of MnAMPV. When the loading of MnAMPV is 20 wt.%, the DPC yield is up to 17.88%, it indicates the best catalytic activity. The reasons for high activity and selectivity of Pd/20%MnAMPV/MK catalyst can be explained based on the observation made from characterization results. The catalysts show well-dispersed MnAMPV at 20 wt.% and beyond that crystalline nature of AMPV is observed. The high activity is due to well-dispersed Keggin ion in MK.

As the Pd/20%MnAMPV catalyst shows the best activity, this loading is optimum. Catalysts with V atoms in place of one, three and five Mo atoms in the primary structure of the Keggin ion are prepared by keeping the MnAMPV content as 20 wt.% on the modified kaolin. The results show that the activity is enhanced with the increase of the number of vanadium atoms and the maximum activity is obtained (entry 14) for the catalyst with five vanadium atoms in the Keggin structure. The catalysts without any V, i.e., Pd/HAMP show slight activity. The obvious increase of activities is due to V replacing Mo in the primary structure of molybdophosphoric acid and the redox property of vanadium. The V atom substituting Mo

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield of DPC, %</th>
<th>Selectivity of DPC, %</th>
<th>TON, mol DPC/mol Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd/HAMP</td>
<td>0.58</td>
<td>96.82</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Pd/HAMPV</td>
<td>2.30</td>
<td>97.21</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>Pd/MnAMPV</td>
<td>12.02</td>
<td>99.14</td>
<td>144</td>
</tr>
<tr>
<td>4</td>
<td>Pd/CuAMPV</td>
<td>3.41</td>
<td>98.01</td>
<td>41</td>
</tr>
<tr>
<td>5</td>
<td>Pd/CoAMPV</td>
<td>2.28</td>
<td>97.28</td>
<td>28</td>
</tr>
<tr>
<td>6</td>
<td>Pd/PbAMPV</td>
<td>4.66</td>
<td>99.04</td>
<td>56</td>
</tr>
<tr>
<td>7</td>
<td>Pd/FeAMPV</td>
<td>6.81</td>
<td>98.87</td>
<td>82</td>
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<tr>
<td>8</td>
<td>Pd/CeAMPV</td>
<td>4.16</td>
<td>96.56</td>
<td>50</td>
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<tr>
<td>9</td>
<td>Pd/10%MnAMPV/K</td>
<td>3.23</td>
<td>97.21</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>Pd/10%MnAMPV/MK</td>
<td>13.74</td>
<td>98.88</td>
<td>170</td>
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<tr>
<td>11</td>
<td>Pd/20%MnAMPV/MK</td>
<td>17.88</td>
<td>99.22</td>
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<tr>
<td>12</td>
<td>Pd/30%MnAMPV/MK</td>
<td>14.15</td>
<td>98.72</td>
<td>176</td>
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<tr>
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<td>19.27</td>
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<td>Pd/20%MnAMPV5/MK</td>
<td>24.68a</td>
<td>99.13</td>
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<td>15</td>
<td>Pd/20%MnAMPV/MK</td>
<td>15.90b</td>
<td>98.16</td>
<td>191</td>
</tr>
<tr>
<td>16</td>
<td>Pd/20%MnAMPV5/MK</td>
<td>10.81c</td>
<td>98.02</td>
<td>130</td>
</tr>
</tbody>
</table>

\*1st run; \*2nd run; \*3rd run
atom is beneficial for the conversion of Pd to active Pd$^{2+}$ [30]. In the reaction, the V atoms occupy the position of the cross-linked cation on the proton position, or are extruded from the Keggin structure, forming an independent structure [31]. That should be V$^{5+}$, and under the influence of oxygen, the oxidation and the reduction state of V is easy to the mutual conversion. Meanwhile, compared to the redox potential of H$_3$PMo$_{12}$O$_{40}$ 0.52 V [32], the redox potential of H$_4$PMo$_{11}$VO$_{40}$ increases to 0.65 V [31], so the ability of Pd oxidation to Pd$^{2+}$ is enhanced, which accelerated the catalytic cycle and increased the yield of DPC.

Recyclability of the catalysts

The regeneration of the catalysts was done by filtration after 8 h reaction, washing with conductivity water for several times followed by drying at 80°C in an air oven and they were used in the oxidative carboxylation reactions with a fresh reaction mixture. As a typical example, the catalyst Pd/20%MnAMPV$^5$/MK showing (Table 3) yield of 24.68% in the first run decreased to about 15.90% (entry 15) in the second run and 10.81% (entry 16) in the third run, respectively. The TON also decreased with subsequent reuse. This decrease in catalytic activity was attributed to the leaching of HPA (of about 3-5%) and the loss of Pd ion from the support into the liquid phase during the catalytic reactions, which was confirmed by the well-known ascorbic acid test [33]. A hot filtration technique promoted the percolate of catalyst into the reaction mixture in process of the reaction too. Under optimized reaction conditions for 8 h, we used fresh Pd/20%MnAMPV$^5$/MK catalyst. After 8 h, the filtration separated the catalyst, then stirring the hot filtrate for 2 h under the same reaction conditions. It can be observed that in defect of the catalyst the conversion was increased about 3%. What is more, it indicated the presence of some amount of HPA and Pd ion in the reaction mixture. The catalyst was washed after filtration to remove all the adsorbed reactants and products, while some of the adsorbed reactants and products species still remained, which might cause the blockage of active sites and a decrease in catalytic activity. Therefore, the activity would reduce when we reused the catalyst. Yet, the selectivity remained little changed, i.e., 98.16 to 98.02%.

Multistep electron transfers catalytic cycle

The results in Table 2 show that there is a synergistic effect existing between vanadium incorporated molybdophosphoric salts loaded on MK for the regeneration of the Pd(II) species. A possible mechanism of the multistep electron transfer is proposed in Figure 4. The Pd(II) species would be reduced to Pd during the DPC formation from two molecules of phenol and one molecule of CO. The Pd would be reoxidized by Mn(IV) to form Pd(II) and Mn(II), and in turn Mn(II) would be reoxidized to Mn(IV) by HPA.

CONCLUSION

Vanadium incorporated molybdophosphoric salt supported on modified kaolin acts as efficient stable solid acid co-catalysts for synthesis of diphenyl carbonate by oxidative carboxylation with phenol. The high catalytic activity is attributed to the increase of surface area, the presence of the counter ion, the well-dispersed Keggin ion and Brønsted acid sites of the co-catalysts. Selectivity of all the carboxylation reactions is nearly 100% while the highest yield of DPC is 24.68% with a TON of 306 for the Pd/20%MnAMPV$^5$/MK catalyst in the absence of solvents. The catalyst can be regenerated and reused for several times. A new, more active and reusable heterogeneous catalyst for oxidative carboxylation of phenol to diphenyl carbonate is proposed in the research, which may be suitable for industrial experiments in the future.

Acknowledgement

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Analysis and Measurement, Huazhong Normal University for the XRD analyses.

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PRIMENA FOSFOMOLIBDATA SA INKORPORIRANIM VANADIJUMOM NANETIM NA MODIFIKOVANOM KAOLINU U SINTEZI DIFENIL-KARBONATA OKSIDATIVNOM KARBONILACIJOM FENOLA

Molibdofosforna kiselina Kegginovog tipa, njena so i molibdofosforna so sa inkorporiranim vanadijumom koja je naneta na modifikovani kaolin (MK) kotišćeni i su kao redoks katalizatori za oksidativnu karbonilaciju fenola do difenil karbonata (DPC) u odsustvu rastvarača. MnAMPV5 (jedna molibdofosforne soli sa inkorporiranim vanadijumom) koja je naneta na MK pokazala je najveću katalitičku aktivnost sa prinosom od 24,68% i molskim odnosom DPC/Pd od 306, dok je selektivnost skoro 100% u svim reakcijama karbonilacije. Katalizatori su okarakterisani tehnikama XRD, BET, XPS i H₂-TPR. Provera ponovne upotrebe pokazala je da su katalizatori stabilni i aktivni.

Ključne reči: vanadijum, molibdofosforna kiselina, oksidativna karbonilacija, kata-

lizator, difenil-karbonat.