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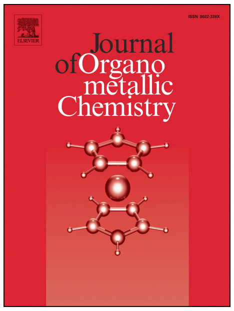

Effect of metal oxide composite method on catalytic oxidation performance and adsorption oxygen of aerogel supported Pd catalysts in oxidative carbonylation of phenol

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Effect of metal oxide composite method on catalytic oxidation performance and adsorption oxygen of aerogel supported Pd catalysts in oxidative carbonylation of phenol

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Abstract:

A series of metal manganese-cerium silicon composite aerogel supported Pd catalysts were prepared by the in-situ method, the precipitation method and the impregnation method. The catalysts were applied to synthesize diphenyl carbonate (DPC) by oxidative carbonylation. The effects of different preparation methods and composite metal oxide contents on catalytic activities were studied. The prepared catalysts were characterized by XRD, FTIR, BET, TEM, H_2-TPR and XPS. The results showed that the metal composite method had a great influence on the catalyst particle size and specific surface area; the low temperature oxidation performance and surface oxygen species content of the catalysts prepared by different methods were different. The catalyst prepared by the impregnation method has a large specific surface area and particle size, good low-temperature oxidation performance and more surface adsorption oxygen, which helps to improve the multi-step electron transfer efficiency, to promote the regeneration of the active component Pd^{2+} and to increase catalytic activity.

Key words: diphenyl carbonate, aerogel, oxidative carbonylation, oxygen species, supported palladium catalyst

1. Introduction

Diphenyl carbonate (DPC) is an important intermediate for the preparation of polycarbonate (PC), which is the second largest engineering thermal plastic. The main methods of its preparation are phosgene, transesterification and oxidative carbonylation method [**1,2**], among which the oxidative carbonylation method is to synthesize DPC directly with CO, O_2 and phenol in the presence of catalyst. Because of its simple process, cheap raw materials, only a single by-product H_2O, and a high atom utilization, this method is a green environmental protection method with bright prospect in industrial application [**3**]. The catalysts for the synthesis of DPC by the oxidative carbonylation are divided into two main types: homogeneous complex catalysts and heterogeneous supported catalysts. The former has a big disadvantage-its product is very hard to separate. As a consequence of good performance of easy product separation, the heterogeneous catalytic oxidation method becomes the most active research direction of synthesizing DPC by carbonylation [**4,5**]. After more than a decade of active research and development, a variety of supported catalysts have been attempted such as the activated carbon, molecular sieves, polymers, carbon nanotubes [**6-9**] and so on. Unfortunately, the active component Pd is very easy to aggregate, and Pd^{2+} is very poor to be recycled, which led to the low yield of DPC. This kind of research has been confronted with a bottleneck, with no industrialized report.

Metal silicon composite aerogel has many excellent carrier properties of aerogel such as low density, high specific surface area, high porosity, 3D network structure and so on [**10-12**]. Silicon aerogel with a mesoporous structure limits the grain size of the metal oxide, and its high specific surface area promotes the active ingredient and the metal cocatalyst to be highly dispersed on the carrier, thereby providing more catalytic active sites; electron transfer between metal and silicon-based aerogels, ie metal-carrier strong interaction (SMSI effect), can regenerate high-valence metals and improve the oxidation capacity of metal cocatalyst; in addition, silicon aerogels have chemical stability and thermal stability, so it is destined to have a good application prospect in the oxidative carbonylation of phenol to DPC. The preparation process of metal / silicon-based composite aerogel is simple, the reaction raw materials is easy to get and the reaction process is easy to control. At present, the mature preparation methods include in-situ method, precipitation method and impregnation method [**13,**

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14].

Surface modification of Pb catalysts with rare earth oxides to improve the oxidation activity and to enhance catalytic performance is one of the hotspots [**15-18]**. Among them, the most important rare earth in industrial catalysis is a composite oxide of Ce. Its special catalytic performance is manifested in the following three aspects: 1. The ionic radius of rare earth is large, with a high charge, and easy to form a stable new crystal structure; 2. The ionic radius of rare earth is large, with high coordination, and between different coordination structures, the conversion energy barrier is so low, that it is suitable for catalytic reaction; 3. Cerium is easy to convert between +3 valence state and +4 valence state, and it is easy to form flowing oxygen vacancies in the structure, so it has better oxygen storage performance and transmission capacity on surface, and can produce a synergistic effect with the metal interface [**19]**, which will contribute to the multistep electron transfer process of the oxidative carbonylation. Based on the above three reasons, the metal Ce is inevitably a good promoter in the carbonylation catalytic oxidation process. According to the theory of redox potential, the metal oxides, which can play an intermediate role in the redox chain of the oxidative carbonylation, generally have an oxidation-reduction potential between the following two states, that is, a high-valent cation can oxidize Pd^0 to form an active component Pd^{2+}, and the reduced state, low-valent ions are rapidly oxidized by oxygen to high-valent ions. While the redox potential of MnO_2/Mn^{2+} (1.224 V) just lies between Pd^{2+}/Pd^0 (0.99 V) and O_2/H_2O (1.23 V). Theoretically, Mn oxides can implement the redox cycle regeneration of the catalytic active component Pd^{2+}. Therefore, the composite oxide of Ce-Mn is a promising cocatalyst for oxidative carbonylation of phenol to DPC.

In this paper, Ce-Mn oxide silicon-based composite aerogel supported Pd catalysts were prepared with the low-energy atmospheric pressure drying technology and the catalytic carrier reconstruction technology, which fully utilized the synergistic promotion of the cocatalyst, Ce-Mn oxide and the carrier, silicon-based aerogel. It investigated the different effects of in-situ, precipitation and impregnation methods on the synthesis of DPC by oxidative carbonylation of phenol.

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2. Experiment

2.1. Preparation of catalysts

2.1.1. In-situ method

According to the sum of the mass of Ce and Mn (in which the molar ratio was 1:1) and the mass of silica (calculated as the source of silicon in ethyl orthosilicate) , that is 10% , 20% , 40% and 60% respectively, manganese nitrate ($Mn(NO_3)_2$) and cerous nitrate ($Ce(NO_3)_3$) were dissolved in ethanol, and added stepwise to the precursor of silica-based aerogel (the final molar ratio of ethanol, TEOS , deionized water, N, N-dimethylformamide was 3:1:6:0.8), and adjusted to the pH of 3 with nitric acid solution. And then it was stirred at 50 ℃ for 6 h, poured into a petri dish, and kept at room temperature to form alcoholic gel. After 12 h aging, at 40 ℃, the mixture was soaked for 24 h respectively with a mixture of ethanol, and a mixture of TEOS and ethanol (volume ratio of 1:1). Then the gel was washed with ethanol twice, and dried at 40 ℃ for 12 h, and at 70 ℃ for 48 h. Finally it was calcined in a muffle furnace at 500 ℃ for 4 h to get a metal silicon aerogel carrier.

$PdCl_2$ was selected as the active Pd source, and the Pd loading was 1% of the carrier. The accurately required $PdCl_2$ was added a certain volume of deionized water to, and then its pH value was adjusted with hydrochloric acid until $PdCl_2$ was completely dissolved in the mixture to form a brown solution. Next the above metal silicon based aerogel carriers separately were added to the solution and stirred for 30 min until the mixture was evenly mixed. And then the pH value of the mixture was adjusted to 9-10 with 1 mol/L NaOH solution, was continued to be stirred for 30 min after the carriers were filtered off, washed with deionized water for 3 times, dried in an oven at 110 ℃ for 12 h, and finally the catalysts were prepared by calcination at 300 ℃ for 3 h in a muffle furnace. They were recorded as S-10, S-20, S-40, S-60 respectively.

2.1.2. Precipitation method

In the pure silicon aerogel powder sample (labeled as SA) prepared in the same manner as above, a mixed solution of $Mn(NO_3)_2$ and $Ce(NO_3)_3$ was added, and the NaOH solution was slowly added as a precipitant to until it precipitated completely,

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which was filtered and dried at 90 ℃ for 12 h. Finally it was calcined at 500 ℃ for 4 h to obtain different catalyst carriers, and then Pd was loaded by the above method to obtain catalysts. The catalysts obtained by adjusting the mass ratio of metal and SA were also labeled as C-10, C-20, C-40 , C-60.

2.1.3. Impregnation method

The pure silicon aerogel powder samples, which were prepared in the same manner, were added a mixed solution of cerium nitrate and manganese nitrate dropwise, stirred for 20 min, aged for 24 h, dried at 110 ℃ for 12 h, and finally calcined at 500 ℃ for 4 h to obtain different carriers. And then Pd was loaded by the above method to obtain catalysts. The catalysts obtained by adjusting the mass ratio of metal to SA were also labeled as I-10, I-20, I-40 and I-60 respectively.

2.2. Characterization

In this study, the X-ray diffractometer (Model 50-A, SHIMADZU, Japan) was used to analyze the structural characteristics and related phase parameters of the samples. Fourier transform infrared spectroscopy (NEXU-470, Nicolet Corporation, U.S.) was used to analyze the composition of the samples. The specific surface areas of the test samples were measured by a specific surface area & pore analyzer (Model NOVA2000e, Quantachrome, USA). With a transmission electron microscopy mirror (a JEM-2010 the FEF type, Japan JEOL Co.) surface morphology and structure of the samples were analyzed. With an automatic chemisorption analyzer (2920 FEF, USA Micromeritics Corporation) the surface activities and the contents of the oxygen species of the samples were analyzed. With an X-ray photoelectron spectrometer (VG of Multilab 2000, Thermal Electron Corporation, U.S.), the material chemical compositions, valence states of the elements and oxygen species from the surface of the samples were analyzed.

2.3. Activity evaluation

Accurately 50 g of phenol, 1 g of catalyst, 2 g of 4A molecular sieve, and 1 g of tetrabutylammonium bromide were added into a 250 ml high-pressure batch reactor. O_2 and CO were separately introduced into the reactor until a total reaction pressure of 5 MPa (wherein the oxygen volume fraction was about 7%). The reaction

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temperature was controlled at 70 ℃, and the stirring speed was maintained at 600 r/min. After 4 h reaction, the reaction liquid was filtered. The reaction liquid was analyzed by a GC-2014 gas chromatograph (SHIMADZU, Japan) to determine the selectivity and yield.

3. Results and discussion

3.1. Characterization of the catalysts

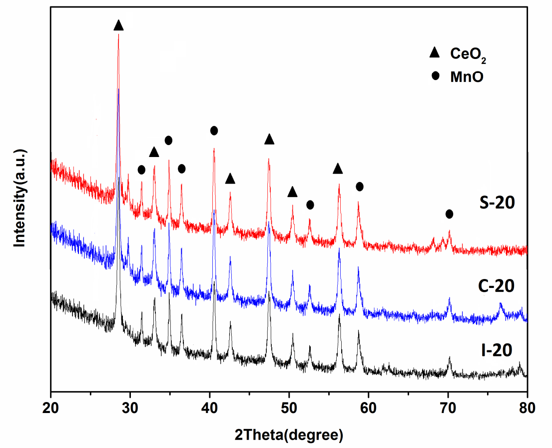

Fig. 1. XRD pattern of silicon-based composite aerogel supported Pd catalyst

The XRD pattern of the catalysts prepared by the three methods is shown in Fig. 1. Clear diffraction peaks appear respectively at 36.5°, 41.2°, and 58.7° of the three XRD curves, which matches the MnO standard spectra (JCPDS 07-0230) in the PDF card library. So it describes that the samples have a metal oxide with aggregated phase MnO. At 28.60°, 47.64°, 56.48°, etc. there are also clear diffraction peaks, and it matches CeO_2 standard spectra (JCPDS 34-0394) in the PDF card library, so it describes that the samples have a metal oxide, CeO_2. Therefore, the silicon-based aerogel supported Pd catalysts are actually compounded with a cerium-manganese composite metal oxide.

Fig 2 shows the FTIR spectra of the composite aerogel supported Pd catalysts (S-20, C-20, I-20) prepared by the three methods. The absorption peaks at 1100 cm^{-1} and 800 cm^{-1} of the three kinds of samples respectively correspond to the asymmetric stretching vibration and symmetric stretching vibration of Si-O-Si. It is indicated that the main components of the three catalysts are amorphous SiO_2. And S-20 (Fig 2. (a)) has obvious finger-like peaks from 500 cm^{-1} to 700 cm^{-1}, which are caused by structures of -O-Mn-O- and -O-Ce-O-. At 3480 cm^{-1} and 940 cm^{-1} absorption peaks appearing, are attributed to the vibration absorption peaks of Si-OH, which describes that the surface of carriers contains more Si-OH. Therefore cerium manganese oxide and the active component Pd are dispersed well in the gel carriers, helping to increase the active sites so as to enhance catalytic performance.

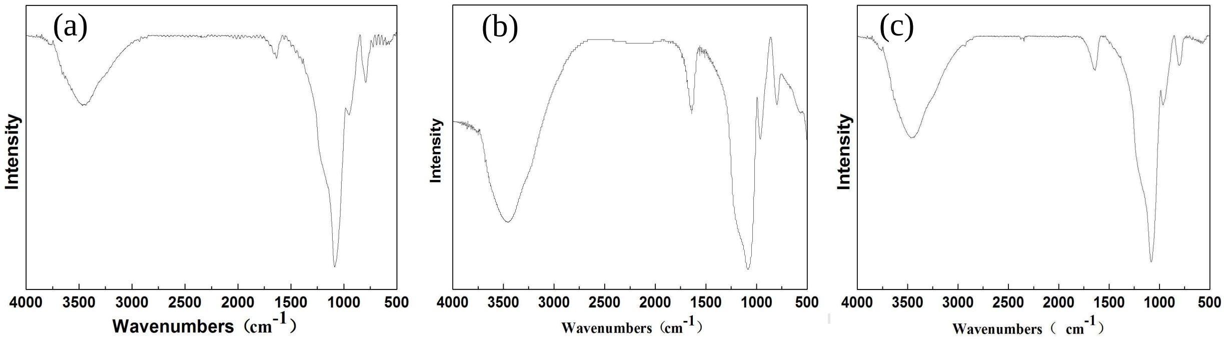

Fig. 2. FTIR spectrum of silicon-based composite aerogel supported Pd catalysts: (a) S-20, (b) C-20 , (c) I-20.

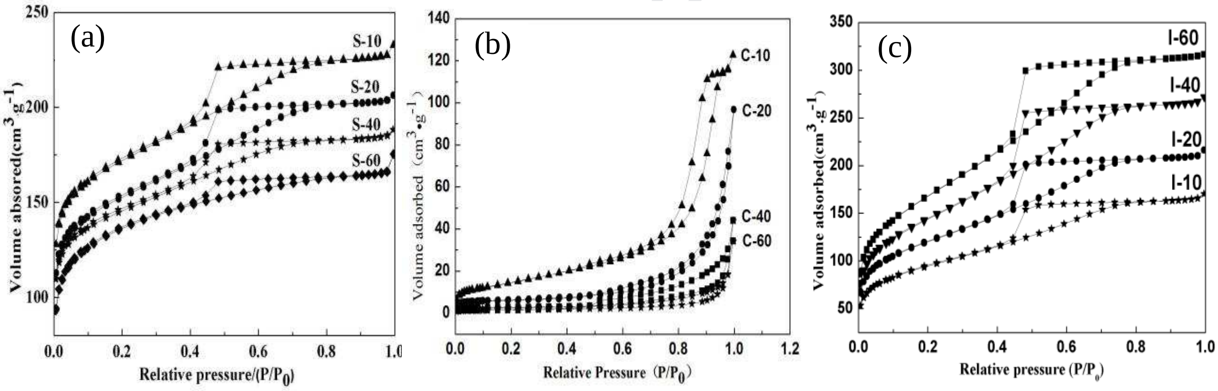

Fig. 3. Nitrogen adsorption-desorption isotherm of silicon-based composite aerogel supported Pd catalysts: (a) in-situ method, (b) precipitation method, (c) impregnation method.

The adsorption desorption curves of all catalysts prepared by in-situ method, precipitation method and impregnation method are shown in Fig. 3. Based on the contrast of the three figures, according to the IUPAC isotherm classification of gas adsorption, the adsorption desorption curves of catalysts prepared by in-situ and impregnation methods (Fig. 3(a) and (c)) belong to Type IV. There are some stairs at a relative pressure between 0.4 and 0.8, because capillary condensation causes Type H2 hysteresis loop, whose shape indicates that the aerogel has a structure with ink bottle pores and is a microporous material with a small pore structure. The adsorption desorption curves of catalysts C-10, C-20, C-40 and C-60 prepared by the precipitation method, belong to Type II, which indicates that there are no significant adsorption desorption hysteresis loops at relatively low pressures, showing its irregularly macroporous structure.

Table 1. Specific surface area, pore size, pore volume of silicon-based composite aerogel supported Pd catalysts.

Entry	Sample	BET / ($m^2 \cdot g^{-1}$)	Pore size / (nm)	Pore volume / ($cm^3 \cdot g^{-1}$)
1	S-10	492	2.78	0.35
2	S-20	420	2.56	0.31
3	S-40	371	2.38	0.26
4	S-60	316	2.25	0.23
5	C-10	61.8	14.64	0.89
6	C-20	59.6	25.25	0.86
7	C-40	36.4	37.38	0.90
8	C-60	19.6	51.47	0.96
9	I-10	589	3.32	0.49
10	I-20	509	3.30	0.42
11	I-40	431	3.29	0.33
12	I-60	339	3.31	0.26

As Table 1 shows the comparison of specific surface areas, pore sizes and pore volumes of the catalysts prepared by the in-situ method, impregnation method and precipitation method, in general, the specific surface areas of the catalysts are reduced with the loading increasing of the cerium manganese oxide, when the catalysts are prepared by the same method. When catalysts are prepared by the in-situ method, due to the greater presence of strong capillary forces when being dried, a part of the metal in the solvent substitution process is to be lost. The bigger metal loading, the more capillary forces, the stronger drying stress, the more easily leading to syneresis and some tunnels collapse or disappearance, and the smaller specific surface areas, apertures and pore volu remessulted in. In the precipitation preparation, the required solution of NaOH is added as a precipitating agent, with increasing the mass content

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of cerium and manganese, the hydroxide of cerium manganese precipitates and is absorbed onto the carriers. The more absorption, the more hydroxide of cerium manganese precipitating on the carriers' channels and surface, the larger amount of metal particles agglomerating to form metal clusters and blocking the pores, resulting in a decrease in specific surface areas and pore volumes of the carriers. When most of pore blockage, metal clusters deposit into larger holes, forming an stacking irregular macroporous structure (with the same result as the adsorption desorption curve). So the specific surface area of catalysts prepared by precipitation method, is much smaller than that by other preparation methods. The specific surface area of C-60 is only 19.6 $m^2 \cdot g^{-1}$, while the pore size is much larger, about 51.47 nm. At this time, a large amount of the cocatalyst of cerium manganese oxide is agglomerated, but the dispersion is the most uneven, and the active sites are the least. When prepared by the impregnation method, the structural stability of the silicon aerogel network becomes better with the increasing of metal loading, the average pore size does not change substantially, and the specific surface area and pore volume decrease due to more and more metal entering the aerogel channel. As Table 1 shows, the specific surface area of catalysts prepared by impregnation method, is the largest. The complex carriers have a more complete pore structure, with narrow pore size distribution.

Fig. 4 is the TEM photographs of three silicon composite aerogel support Pd catalysts with the same mass fraction of metal as 20%, which are produced by different methods. Since the loading of Pd is less than 1%, the metal particles observed on the photograph are basically cerium manganese oxide. The picture comparison shows that the catalysts of C-20 (Fig.4 (c), (d)) synthesized by precipitation method has the most uneven dispersion of cerium manganese oxide particles, and even small metal particles are almost non-existent. They are basically large metal clusters, serious agglomeration formation, as shown in the portion indicated by the yellow arrow (Fig. 4(a) and (b)). The large-area agglomeration of the cocatalyst, cerium manganese oxide, is detrimental to the multi-step electron transfer in the catalytic oxidation process, resulting in low regeneration efficiency of the active component Pd^{2+}.

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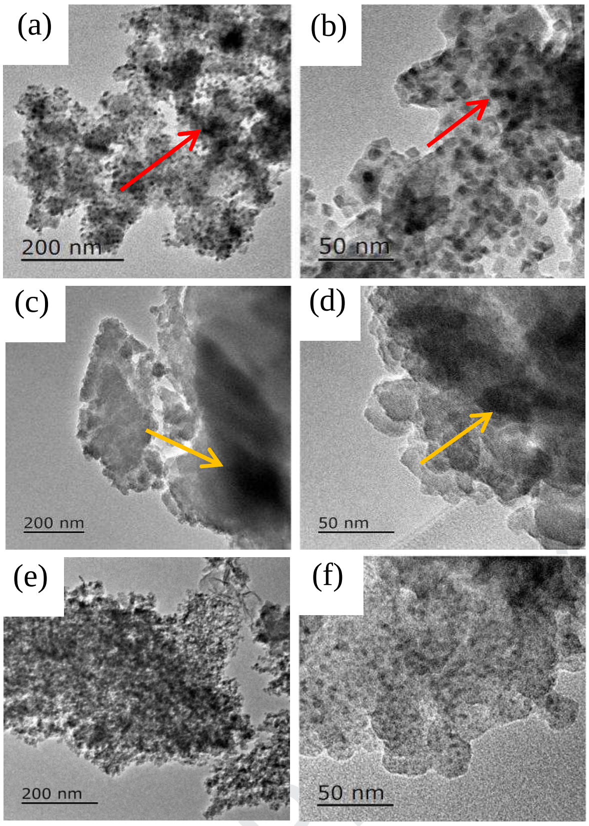

Fig. 4. TEM photographs of the catalysts: (a), (b) S-20; (c), (d) C-20; (e), (f) I-20.

Compared with the precipitation method, the cerium manganese oxide grains in the catalysts C-20 and I-20, prepared by the in-situ method and impregnation method, are evenly dispersed relatively, with similar sizes of particles. The cerium manganese oxide is embedded in the three-dimensional network structure of silicon-based aerogel in the form of small particles. However, in the S-20 catalysts there is a small amount of metal agglomeration, as shown in the Fig. 4(a) and (b) with a red arrow indicating. And the particle size is significantly larger than the metal oxide particles in I-20. These large particles and a small amount of agglomeration may block the silicon-based aerogel pores, so that the specific surface areas and pore volumes decrease (consistent with the BET results), which is detrimental to the dispersion of the cocatalysts, resulting in a decrease in the active sites. In contrast, in the catalyst I-20 prepared by the impregnation method, the grain sizes of cerium manganese oxide particles are smaller, so that it has the most uniform dispersion on the surface of the carrier channel, and the most active sites.

3.2. Activity test of catalysts

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Table 2. DPC yield of catalysts prepared by the methods of in-situ, precipitation and impregnation.

Entry	Sample	Yield of DPC (%)	Selectivity (%)	TOF (mol DPC/mol Pd h^{-1})
1	S-10	10.37	95.17	73.09
2	S-20	15.31	96.21	107.90
3	S-40	8.63	92.25	60.82
4	S-60	6.26	90.19	44.12
5	C-10	3.31	89.21	23.33
6	C-20	2.10	87.25	14.80
7	C-40	1.23	90.19	8.67
8	C-60	0.83	89.27	5.85
9	I-10	16.28	96.31	114.74
10	I-20	21.58[a]	97.27	152.09
11		13.02[b]	92.87	91.76
12		10.28[c]	86.33	72.45
13	I-40	15.63	93.25	110.16
14	I-60	12.74	90.29	89.79

[a] 1st run; [b] 2nd run; [c] 3rd run

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All the catalysts prepared by in-situ method, precipitation method and impregnation method were applied to synthesize DPC by oxidative carbonylation of phenol. The results of the activity evaluation are shown in Table 2. In the synthesis of DPC by oxidative carbonylation of phenol, the production of one molecule of DPC is accompanied by the reduction of one molecule of Pd^{2+} to Pd^0. The cerium manganese oxide acts as a metal cocatalyst to participate in the multi-step electron transfer process in the oxidative carbonylation, promoting the conversion of Pd^0 to Pd^{2+}. The synergistic effect of bimetallic cerium manganese enhances the redox of the catalyst. Comparing the activity evaluation data in Table 2, generally speaking, the activity of the catalyst prepared by the impregnation method, is the highest, and the single yield of I-20 reaches 21.58%. This is mainly due to the fact that the pore structure of the silicon-based aerogel in the catalyst prepared by the impregnation method remains

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intact and has a larger specific surface area. The particle size of the cocatalyst of cerium manganese oxide is small, highly dispersed on the carriers, and the surface of the catalyst is relatively highly capable of good oxygen storage and surface oxygen transfer, helping to improve multi-step electron transfer efficiency, so the catalyst has the most active sites. While the catalyst prepared by the precipitation method is almost inactive, the highest yield of C-10 is only 3.31%. The main reason is that a large amount of agglomerated cerium manganese metal oxide particles in the catalyst prepared by the precipitation method blocks the pores of the aerogel network, and the dispersion of the cocatalyst is extremely uneven, resulting in the extremely small specific surface area of the carriers and few active sites of the catalyst, which hinder the multi-steps electron transfer process. In addition, the loading of the metal oxide also affects the activity of the catalyst, even when the preparation method is the same. For example, I-10, I-20, I-40 and I-60 prepared by the same impregnation method, have different DPC yields, that is 16.28%, 21.58%, 15.63%, 12.74% respectively. The main reason is that when the composite of cerium manganese oxide cocatalyst just started, the active sites increased with the increase of its loading, which helped to promote the multi-step electron transfer process and improved the regeneration efficiency of the active component Pd^{2+}. However, when the loading amount increases to a certain degree, the cerium manganese metal oxide crystal grains gradually grow up, and the poly groups gather and block the pores, which causes the specific surface areas and pores volume of the carriers to decrease, so the active sites are instead reduced. It is not conducive to the reactants' adsorption on the surface and desorption of the product in the catalyst, so the activity of the catalyst is reduced (this is consistent with the BET results).

The regeneration of I-20 catalyst was done and they were used in the carbonylation reaction with the fresh mixture. The yield decreased to about 13.02% in the second run and 10.28% in the third run. But the selectivity remained little changed, i.e., 92.87 to 86.33%. The main results are that the active component Pd is very easy to aggregate and Pd^{2+} is very poor to be recycled.

3.3. Reasons for catalyst synergy

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Studies have shown that the redox ability of the cocatalyst and the surface oxygen species play a crucial role in the redox regeneration of the active component Pd^{2+} [**8**], so we studied the redox abilities of the catalysts prepared by different methods, via H_2-TPR profiles and O_2-TPD profiles (Fig. 5), compared the XPS spectrum (Fig. 7) to study the surface oxygen species of the catalysts, and explored the reasons for the difference of catalytic activity.

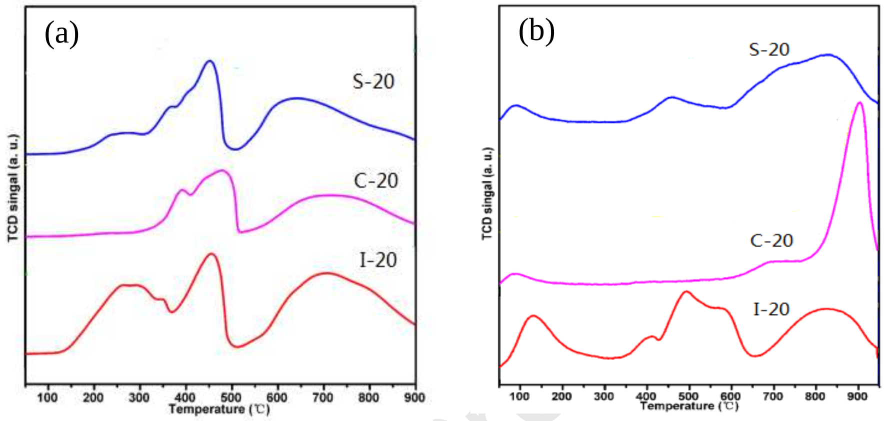

Fig. 5. H_2-TPR (a) and O_2-TPD (b) of the silicon-based composite aerogel supported Pd catalysts.

Fig. 5(a) is a H_2-TPR spectrum of a silicon-based composite aerogel supported Pd catalysts obtained by different preparation methods. It can be seen from the graph that the curves of reduction processes of the three catalysts show approximate peak shapes, mainly including the reduction of two reduction processes, $MnO_2 \rightarrow MnO$ and $CeO_2 \rightarrow Ce_2O_3$. At low temperatures, 150-250 ℃ is mainly caused by $Mn^{4+} \rightarrow Mn^{3+}$ reduction process [**8**]; 250-400℃ is mainly caused by $Mn^{3+} \rightarrow Mn^{2}$ reduction process. At high temperatures, above 500℃ is mainly caused by the reduction of CeO_2 in the bulk phase ($Ce^{4+} \rightarrow Ce^{3+}$) [**20**]. In the temperature-programmed reduction process, the initial reduction temperature indicates the level of surface activity of the sample and the strength of structural stability. Comparing the three curves, it is found that the initial reduction temperatures of the silicon-based composite aerogel supported Pd catalysts obtained by different preparation methods are different. The initial reduction temperatures of the catalyst I-20 prepared by the impregnation method, is the lowest (150 ℃), and the initial reduction temperature of the catalyst C-20 prepared by the precipitation method is the highest (the first H_2 reduction peak almost disappears). It indicates that the average manganese valence in I-20 is

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increased, that is, the Mn^{3+} and Mn^{2+} in the low-valent state are oxidized, while the Mn^{4+} in the high valence state is increased. The catalytic process is a multi-step electron transfer process, and the cerium-manganese composite oxide cocatalyst in this process plays a crucial role, with multi-step electron transfer schematically shown in Fig 6. The catalytic mechanism is as follows: when the active component Pd^{2+} reacts with phenol and CO to form DPC, it is reduced to Pd^0 by itself; then Mn^{4+} in the composite aerogel carrier, oxidizes the reduced Pd^0 to Pd^{2+}, to promote regeneration of the active ingredients, while itself is reduced to Mn^{2+}; Next Mn^{2+} can be oxidized by Ce^{4+} to Mn^{4+}, while Ce^{4+} is reduced to Ce^{3+}; Finally in an oxygen atmosphere, Ce^{3+} is further oxidized by O_2 to Ce^{4+}. The flexible transition between different valence states of Ce^{3+} and Ce^{4+}, makes it easy to form flowing oxygen vacancies while maintaining structural integrity, and has better ability to store oxygen and to transport oxygen on the surface [**19**], and can interface with metals generating synergies. Thus Mn^{4+} increased, can effectively promote the efficiency of multi-step electron transfer, so the surface activity of I-20 is the highest. Compared with TEM photographs, the main reason is that I-20 particles have a small average grain size and many surface defects, so they have good low-temperature catalytic oxidation activity in the catalytic oxidation process (this is consistent with the activity evaluation experiment results), so the impregnation method is good for preparation of silica-based composite aerogel supported Pd catalyst in the synthesis of DPC by oxidative carbonylation of phenol.

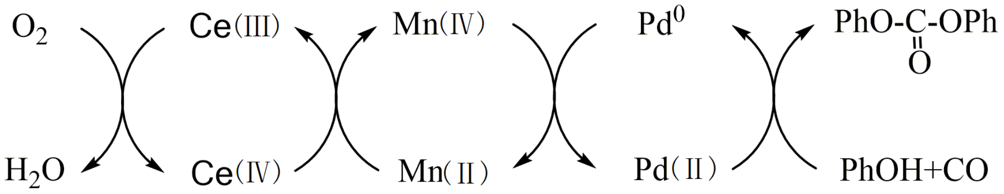

Fig. 6. multi-step electron transfer process.

The order of desorption of oxygen species on oxides is: oxygen molecule O_2→ oxygen molecule anion O_2^- → oxygen atom anion O^- → lattice oxygen O^{2-} [**21**]. Surface adsorbed species of O_2^- and O^-, belonging to the active oxygen on the catalyst surface (referred to as α oxygen), are more easily desorbed, while the lattice oxygen O_2^- (abbreviated as β oxygen) is difficultly desorbed and its desorption peak shape is asymmetry. Desorption peaks below 500 ℃ are generally classified as desorption of surface active adsorbed oxygen species (O_2^- and O^-) on the catalyst, and desorption peaks above 500 ℃ are assigned to desorption of lattice oxygen on the catalyst (O^{2-}) [**22**]. The desorption temperature and desorption strength of different oxygen species are closely related to the oxidation performance of the catalyst: the temperature of the desorption peak of the surface active adsorbed oxygen species and the size of the peak area represent the oxidation activity of the catalyst [**23**]. As shown in Fig. 5(b), in the range of less than 200 ℃, oxygen desorption peaks appeared in all three catalysts, but the start desorption temperature and the desorption peak area were different. Wherein the start desorption temperature of adsorbe oxygen species of catalyst I-20 prepared by impregnation method is the lowest, and its desorption peak area is the largest; while the desorption peaks of adsorbe oxygen species of catalysts C-20 hardly appeared. Therefore, it can be determined that the surface of the I-20 catalyst is rich in adsorbed oxygen species, while the surface oxygen species of the catalyst C-20 is the least. At the same time, the O_2-TPD curve of the catalyst I-20 has a large desorption peak at a temperature of 300-700 ℃, corresponding to the desorption peak of the mobile oxygen species [**24**]. And the desorption peak area of the S-20 in this range is small, while C-20 has almost no desorption peak in this range, indicating that the surface of the catalyst I-20 has abundant mobile oxygen species. The higher the content of mobile oxygen species in the carrier, the more oxygen vacancies which can be provided in the redox process to adsorb and transfer adsorbed oxygen species [**25**]. The surface of catalyst I-20 has more oxygen vacancies and stronger oxidation ability, can play an important role for the connection of the oxidation auxiliaries in the oxidation carbonylation of phenol, thus improving the catalyst catalytic activity. The oxygen desorption peak above 800 ℃ is attributed to the desorption peak of oxide decomposition. The O_2-TPD curve of C-20 indicates that the surface of the material has almost no adsorbed oxygen, and therein oxygen appears mainly in the form of lattice oxygen, so the catalyst has poor oxidation performance and low catalytic

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activity.

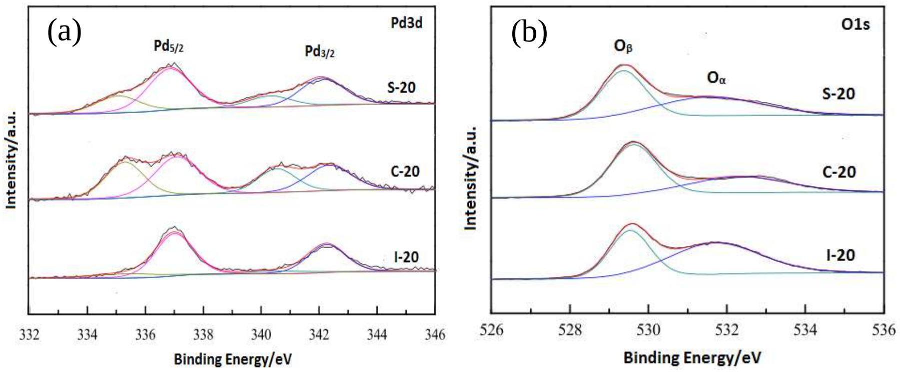

Fig. 7. XPS spectrum of a silicon-based composite aerogel supported Pd catalyst: (a) Pd3d , (b) O1s.

In order to study the loading of the active component Pd and to compare the surface structure of the catalyst, X-ray photoelectron spectroscopy was performed on the sample, and the XPS spectra of the Pd3d and O1s orbits were compared. The results are shown in Fig. 7. After peak-differenating analysis, the binding energy of $Pd3d_{3/2}$ and $Pd3d_{5/2}$ in the XPS photoelectron spectroscopy of Pd on the surface of catalyst I-20, is basically at 342.3 eV and 337.0 eV, which is basically consistent with the XPS binding energy of standard PdO [**26**], indicating that the active component supported on the surface of the catalyst is mainly in the form of Pd^{2+}, which will be very beneficial for the oxidative carbonylation of phenol to DPC. However, the Pd3d tracks of the other two catalysts S-20 and C-20, shift to a lower binding energy position significantly, corresponding to Pd^0 after peak-differenating analysis. The results show that the content of active components Pd^{2+} in these two catalysts is decreased, which is not conducive to the catalytic reaction.

Two different oxygen species, adsorbed oxygen (O_α) and the lattice oxygen (O_β) respectively correspond to two emission peaks of similar binding energy: a high binding energy (about 531.6 eV) showing strongly adsorbed oxygen (O_α), low binding energy (about 529.5 eV) representing lattice oxygen (O_β) [**27**]. Comparing the XPS spectra of O ls tracks of catalysts prepared by three methods (Fig. 7 (b)), it can be found that these surface oxygen species of three aerogel catalysts mainly exist in the form of lattice oxygen [**28**], but with different content of adsorbed oxygen species.

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Among them, the content of adsorbed oxygen species in catalyst I-20 was the highest, and the content of adsorbed oxygen species in catalyst C-20 was the lowest, which was consistent with the results of O_2-TPD. The main reason is that the average grain sizes of the material particles are different, the lattice distortions are also different, and the number of oxygen vacancies are different, ultimately leading to different numbers of adsorbed oxygen. The adsorbed oxygen species present on the surface of the catalysts can effectively promote the redox cycle of the active component Pd^{2+}. Thus in the oxidative carbonylation of phenol to DPC, catalyst I-20 has relatively high catalytic activity, so the impregnation method are more suitable to produce silicon-based composite aerogel support Pd catalysts.

4. Conclusion

A series of metal cerium manganese silicon-based composite aerogel supported Pd catalysts were prepared by the in-situ method, precipitation method and impregnation method respectively, and these catalysts were applied to the synthesis of DPC by oxidative carbonylation of phenol. The effects of different preparation methods and the content of cerium manganese oxide on the catalytic activity were investigated. The results show that the catalyst prepared by the impregnation method has relatively good catalytic activity, mainly due to: 1. the catalyst prepared by impregnation has a large specific surface area and a small particle size, contributing to the dispersion of active centers and the increase of active sites, improving the catalytic activity; 2. the catalyst prepared by the impregnation method has better low temperature oxidation performance and more surface adsorption oxygen, which will help to improve the multi-step electron transfer efficiency and promote the regeneration of the active component Pd^{2+}, thereby increasing the catalytic activity.

Conflicts of interest

There are no conflicts to declare.

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Highlights

1. Catalysts were prepared by the in-situ method, the precipitation method and the impregnation method.
2. The composite method affect the particle size and specific surface area.
3. The composite method affect the surface oxygen species.

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Declaration of Interest Statement

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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