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OXIDATIVE CARBONYLATION OF PHENOL TO DIPHENYL CARBONATE BY Pd/MFe₂O₄ MAGNETIC CATALYST

Article Highlights

- MFe₂O₄ spinel ferrites were prepared by the sol-gel process as the catalysts supporter
- Pd/MnFe₂O₄ showed higher catalytic activity than other Pd/MFe₂O₄ catalysts
- The oxygen deficiency and ion transference influences the catalytic activity
- The Pd/MnFe₂O₄ catalyst showed well superparamagnetic behavior with high saturation magnetization
- The Pd/MnFe₂O₄ catalyst may be applied to the magnetically stabilized bed reactor

Abstract

In order to screen one suitable catalyst for magnetically stabilized fluidized bed (MSFB) reactor in the process of oxidative carbonylation of phenol to diphenyl carbonate (DPC), Pd/MFe₂O₄ catalysts were chosen, then prepared and characterized by XRD, H₂-TPR, XPS and vibrating sample magnetometer (VSM). Compared to the other metal ion doped spinel ferrite catalysts, the catalytic activity of Pd/MnFe₂O₄ was much higher, which the single pass yield of DPC reached 33.12% with selectivity above 99%, and turnover frequency (TOF) reached 70.56 molDPC·(molPd·h)⁻¹. The result showed that the formation of the ferrite oxygen-deficient and ion transference in the ferrites was in favor of the catalytic activity. When the support MnFe₂O₄ was calcinated at 500 °C, the saturation magnetization of the obtained catalyst Pd/MnFe₂O₄ came up to 43.1 A·m²·kg⁻¹. With good magnetic property and brilliant catalytic activity the catalyst Pd/MnFe₂O₄ may suite for industrial experiments in MSFB reactor in future.

Keywords: magnetic catalyst; oxidative carbonylation; diphenyl carbonate; spinel ferrite.

Diphenyl carbonate, as an important green chemical intermediate, is commonly used to synthesize polyaryl carbonate, mono-isocyanate and hydroxybenzoic acid polyester, especially in producing high quality polycarbonates (PC) from bisphenol A by the melt transesterification method [1-3]. There are several methods to synthesize DPC: the phosgene method, transesterification method, oxidative carbonylation method, the direct synthesis method uses carbon dioxide as the raw material, and the alcoholysis method, which uses urea as the raw material [4]. However, in the current search for environmentally benign and sustainable processes, oxidative car-

bonylation method is a promising alternative in industrial application that avoids the use of phosgene in the one-step synthesis of diphenyl carbonate (DPC). Since oxygen is used as final oxidant, the only waste product is H₂O.

Compared to homogeneous catalysts, the advantage of easy separation for solid catalysts is very attractive. Thus, improving catalysis activity and decreasing the intraparticle diffusion resistance is essential for heterogeneous catalysts to substitute homogeneous catalysts in DPC synthesis. Generally, the industrialized reactors were continuous equipments in order to get high efficiency. However, the reaction device for synthesizing DPC by the oxidative carbonylation method was only limited in stirred tank reactor and the continuous industrialized device has not yet been reported. Eishin [5] gave their reactor sketch based on palladium loaded composite solid support catalyst. Our group pioneer professor Wu [6] has rep-

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orted the heterogeneous oxidative carbonylation synthesis of DPC in fixed bed as an engineering basic research, but the yield of DPC was low. Considering the intraparticle diffusion resistance, the MSFB reactor which can strengthen mass-transfer and reduce the inhibitory effect of diffusion resistance on the yield was considered. The MSFB reactor has been used in catalytic hydrogenation [7], dust removal, dry coal separation, and biochemical separation. MSFB has emerged as the major reactor in the caprolactam hydrorefining process in China. Five industrial units of 200–400 kt/a production capacity have been built since 2003 [8]. The system of synthesis DPC by the oxidative carbonylation method was very similar to the process of caprolactam hydrorefining, which uses the amorphous Ni catalyst, because both of them were G-L-S three-phase reacting system and the reaction condition were at high temperature and pressure. Our team has explored the use of the MSFB reactor to synthesize DPC by the oxidative carbonylation method.

In order to make a good magnetic response to the applied magnetic field in MSFB, the catalyst loaded in MSFB should have a good magnetic property besides excellent catalytic activity. Spinel ferrite is a composite oxide mainly based on Fe, which has a crystal structure similar to spinel, $MgAl_2O_4$. Such compounds have a stable crystal structure, good magnetic property and efficient catalytic performance. When metal ions with different radii and charges were doped into the lattice system, the distribution of the original cations in the crystal lattice would change significantly, then the redox capacity and magnetic properties of the material were largely affected [9]. To the best knowledge of investigators, no systematic study of using ferrites as oxidation carbonylation catalyst supporters reported. Therefore, in the present work, using Pd/MFe_2O_4 magnetic catalyst to synthesis of DPC by oxidative carbonylation method from phenol has been carried out.

EXPERIMENTAL

Preparation of catalyst

Spinel ferrites MFe_2O_4 ($M = Co, Ni, Cu, Zn$ or Mn) supporters were prepared by the sol-gel method. Stoichiometric amount of $M(NO_3)_x \cdot nH_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ powers were homogeneously mixed with suitable amount of deionized water. The citric acid as the complexing agent was then added to the metal nitrate solution in a mole ratio (total metal ion: citric acid) of 1:1. The resulting solution was evaporated to dryness, and then the precursors were

decomposed at 200 °C until a dry gel was formed. The residual precursor was calcined in air at 500 °C for 2 h to obtain the spinel-type ferrites.

Then the catalysts were prepared by the precipitation method. Typically, 0.042 g $PdCl_2$ was dissolved in 50.0 ml aqueous solution and the pH value was adjusted to 1.0 by addition of hydrochloric acid. 5.0 g spinel ferrite supporter was dipped into the $PdCl_2$ solution in order to have a palladium mass loading of 0.5%. After stirring for 30 min, the solution was adjusted to get a pH value equal to 10.0 by addition of 0.5 mol/L sodium hydroxide solution slowly, then stirred for 30 min. The solid was separated by filtration, dried at 80 °C overnight and calcined in the resistance furnace at 300 °C for 3 h, producing Pd/MFe_2O_4 the powdery catalysts.

Characterization of catalyst

The phase identification and crystalline structure analysis were determined by X-ray diffraction (XRD) on a PANalytical X'Pert Pro X-ray diffractometer with high-intensity $CuK\alpha$ radiation ($\lambda = 0.154056$ nm). Temperature-programmed reduction (TPR) experiments were performed in a quartz reactor using a thermal conductivity detector (TCD) as detector on Micromeritics AutoChem2920 instrument. In each analysis, 50 mg samples were pretreated with helium gas by increasing the temperature from ambient temperature up to 800 °C at $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Then 10% H_2/Ar mixture at $45\text{ ml}\cdot\text{min}^{-1}$ was used and the temperature was increased at $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from ambient temperature to 900 °C. 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 $Mg\text{ K}\alpha$ X-ray radiation (1253.6 eV, 150 W). The binding energies (BEs) were calibrated using the $C1s$ peak at 284.6 eV. The magnetic properties of the samples were measured at room temperature using a HH-10 vibration sample magnetometer (VSM) manufactured by Nanjing University, China.

Activity evaluation of catalyst

DPC synthesis by oxidative carbonylation of phenol was carried out in a 250 ml stainless steel autoclave equipped with a mechanical stirrer, which was pre-filled with 50 ml dichloromethane, 1.0 g catalyst (Pd in the catalyst = 0.046 mmol), 80 mmol phenol, 3.0 mmol $(C_4H_9)_4NBr$ (tetrabutylammonium bromide, TBAB), 4 mmol hydroquinone, and 2.00 g of 4A molecular sieve used as drying agent. Then oxygen and carbon monoxide were introduced into the autoclave to the reaction pressure (5 Mpa) with the oxygen content was about 5.0%. The reaction was car-

ried out for 4 h at 100 °C at a stirring speed of 750 rpm. At the end of the reaction the autoclave was cooled to room temperature and weighed. The reaction products were identified and quantified by gas chromatography with a flame ionization detector (FID) detector (GC4000A of EAST&WEST Analytical Instruments, China).

RESULTS AND DISCUSSION

Catalytic performance analysis of spinel ferrites doped with different metal ions

XRD and H_2 -TPR characterization

Figure 1a shows the XRD patterns of spinel ferrites MFe_2O_4 . Compared with the standard JCPDS card, all the diffraction peaks of the samples were consistent with the standard diffraction peaks (2θ 30.2, 35.4, 43.1, 53.5, 56.9 and 62.5°) besides a few impurity peaks. Thus, we can conclude that the obtained samples were spinel ferrites with high-purity crystalline phase when prepared under current experimental condition.

Since the oxidation cycle regeneration efficiency of the active Pd source is the key factor in the catalytic reaction, the oxides supporters must be activated in a reducing atmosphere. In order to study this activation process, the reducibility of MFe_2O_4 systems was examined by temperature-programmed reduction and the reduction profiles are displayed in Figure 1b.

Figure 1b shows that the initial reduction peak temperature of $CuFe_2O_4$ was the lowest. Generally, it was believed that the first peak attributed to the Cu^{2+} reduction under hydrogen led to copper metal and resulted in the lowest temperature peak around 220 °C [10]. TPR curves of other MFe_2O_4 were similar and characterized by the presence of three peaks. The first peak, which was attributed to the reduction of

MFe_2O_4 to the formation of deficient ferrite [11,12] $MFe_2O_{4-\delta}$ ($\delta > 0$), was located around 300 to 500 °C. As Mn, Ni, Co and Zn are doped into the sample separately, the initial reduction peak temperature of the corresponding spinel ferrite increased in turn. The second peak was relatively near the first one, which was attributed to the reduction of MO-FeO solid solution. The third peak was relatively broad and very intense. Its position was around 600 °C and the intensity was not affected by the M chemical element species because it is attributed to the reduction of FeO to α -Fe. The comparison of the curves of all MFe_2O_4 samples indicated that copper and manganese were reduced easily at an intermediate temperature between those of CuO and Mn_2O_3 reductions. This phenomenon was in agreement with the work of Reddy [13] who studied the $CuFe_2O_4$ and $MnFe_2O_4$ spinel ferrite. It should be noted that, in all cases, the reduction temperature of $MnFe_2O_4$ was lower than other chemical element (Zn, Ni, Co) species spinel ferrite in this study. The lower the initial reduction peak temperature was, the easier the sample would change into oxygen deficient ferrite $MFe_2O_{4-\delta}$ [14]. Thereby, the doping of metal ions played a significant role in the oxygen deficiency property of corresponding ferrite. As the metal ions of Cu, Mn, Ni, Co and Zn were doped in separately, the difficulty was that the corresponding ferrite MFe_2O_4 came into oxygen deficient ferrite $MFe_2O_{4-\delta}$ grew in turn. The fact that the reduction was easier in the MFe_2O_4 supporter combinations demonstrated that there was an increase of the catalyst network oxygen mobility and improvement of the catalytic activity.

XPS characterization

XPS spectra showed further information on the structure of different irons doped Pd/ MFe_2O_4 catalysts. Figure 2a showed that no change in binding

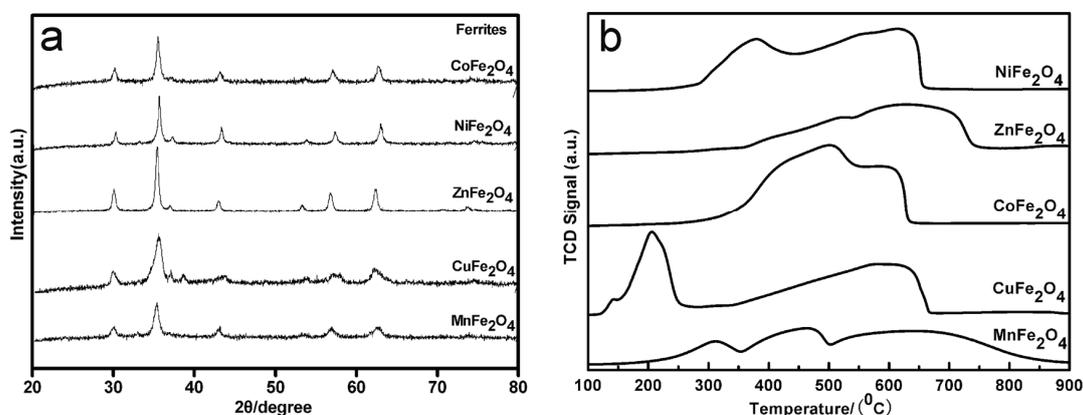


Figure 1. X-ray diffraction (XRD) patterns (a) and H_2 -TPR profiles (b) of the different iron doped ferrites (MFe_2O_4 , $M = Ni, Zn, Co, Cu$ or Mn).

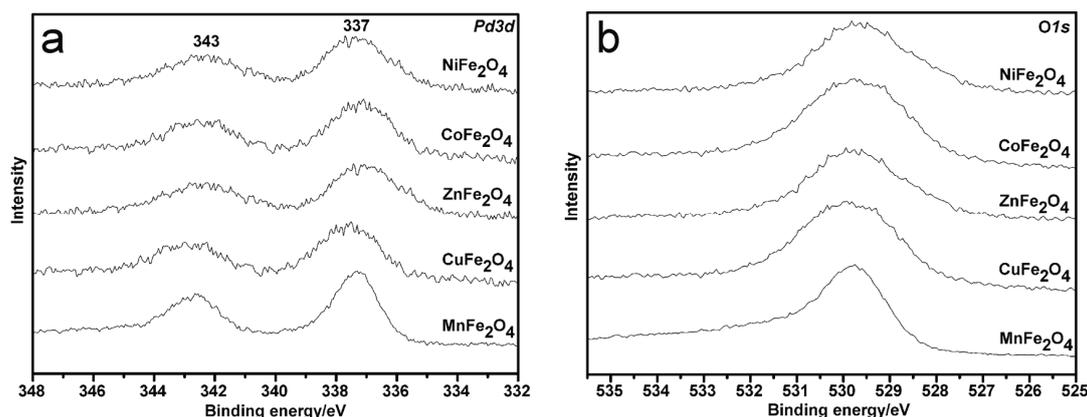


Figure 2. XPS Spectra of Pd3d (a) and O1s (b) for different iron doped ferrites catalysts (Pd/MFe₂O₄, M = Ni, Zn, Co, Cu or Mn).

energy of Pd species. The Pd 3d binding energies at 337.0 and 343.0 eV (which correspond to the Pd²⁺) were almost the same in every loaded spinel ferrite samples.

The corresponding spectra of oxygen species were presented in Figure 2b. From the figure we can see two photoemission peaks which correspond to two distinct oxygen species presented in all the samples. The line with low binding energy (about 529.5 eV) was attributed to the crystal lattice oxygen (O²⁻), and the high binding energy (about 531.3 eV) was attributed to strongly adsorbed molecular oxygen (O₂) [15]. With the Mn doped spinel ferrite catalyst, the lattice oxygen content decreased relatively and crystal defect greatly increased. Due to the defects of the lattice oxygen, large amounts of oxygen vacan-

cies were produced and the adsorption of oxygen increased in the crystal phase. The reducibility of the MFe₂O₄ supporters was closely related to the reactive oxygen species on its surfaces. Therefore, the MnFe₂O₄ spinel ferrite supporter might possess well low-temperature oxidation performance than the other metal ion doped spinel ferrite supporters, which was in accordance with the results of H₂-TPR. The content of Pd²⁺ and the proportion of different oxygen species derived from fitted O 1s spectrum are displayed in Table 1.

Selected XPS spectra of Fe 2p and Mn 2p core-level photoemission peaks for Pd/MnFe₂O₄ sample were shown in Figure 3. Very similar spectra of Fe 2p were obtained for the other samples. In Figure 3a shown that the Mn 2p_{3/2} and Mn 2p_{1/2} core-level peaks

Table 1. Pd and different oxygen species content on different catalysts

Pd 3d and oxygen species content, %	Catalyst				
	Pd/CoFe ₂ O ₄	Pd/NiFe ₂ O ₄	Pd/CuFe ₂ O ₄	Pd/ZnFe ₂ O ₄	Pd/MnFe ₂ O ₄
Pd	1.61	1.85	1.48	1.79	2.0
O ²⁻	48.64	47.48	49.66	45.21	38.32
O ₂	0.38	0.41	0.35	0.32	19.78

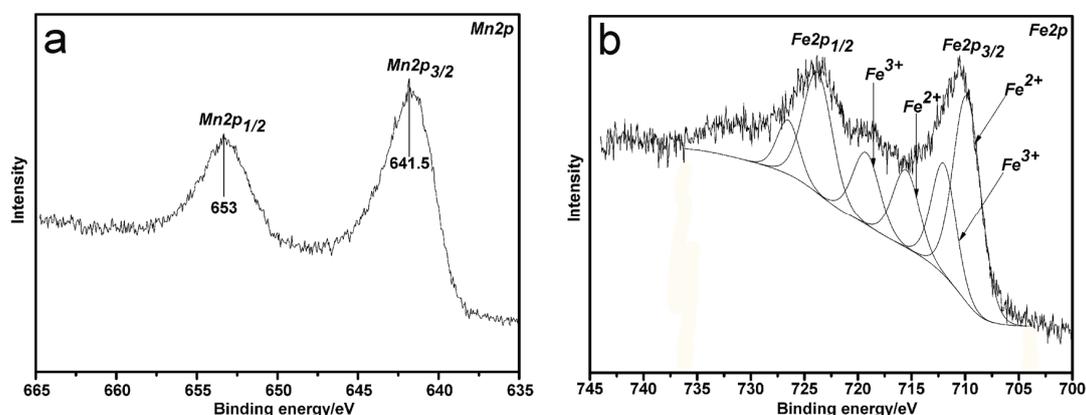


Figure 3. XPS Spectra of Mn 2p (a) and Fe 2p (b) for Mn doped ferrite catalyst (Pd/MnFe₂O₄).

were centered at 641.5 and 653.0 eV. Thus, the $Mn2p_{3/2}$ peak was observed between those of MnO (641 eV) and Mn_2O_3 (641.6 eV) and the energy separation between the $Mn2p_{3/2}$ and $Mn2p_{1/2}$ states was 11.5 eV [16]. The peak positions and the intensity ratio of $Mn2p_{3/2}$ and $Mn2p_{1/2}$ could infer that the manganese was existed as Mn^{2+} and Mn^{3+}/Mn^{4+} states in the synthesized catalysts.

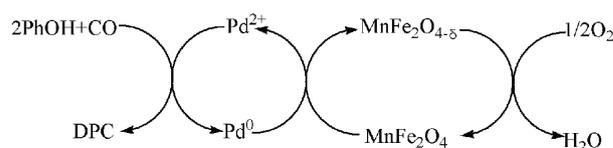
Accord to the reference [17], the $Fe^{2+}2p_{3/2}$ peak at 709.5 eV was always associated with a satellite peak at 6.0 eV above the principal peak whereas $Fe^{3+}2p_{3/2}$ peak at 711.2 eV was associated with a satellite peak at 8.0 eV. From Figure 3b for the Mn doped ferrite catalyst, the binding energy values of $Fe2p_{3/2}$ were observed at 711.2 and 709.7 eV, and distinct satellite peaks were observed at around 8.0 and 6 eV above the main peak. So it could confirmed that the presence of Fe^{3+} and Fe^{2+} state in the sample. This was in accordance with the XRD results.

Results and discussion of activation evaluation

As shown in Table 2, the catalytic activity of catalyst Pd/MnFe₂O₄ was the highest compared with other metal ion doped spinel ferrites catalysts. As Cu, Ni, Co and Zn were doped separately, the catalytic activity of the corresponding catalysts decreased in turn. According to the mechanism of the oxidative carbonylation reaction of phenol to DPC, the oxidation cycle regeneration efficiency of the active palladium source was the key factor in the entire catalytic reaction. It is generally believed that the performance of the ferrite oxide meets the Mars-Van-Krevelen redox mechanism in the catalytic reaction. Therefore, it can be inferred that, in the procedure of the oxidation cycle regeneration of the active palladium, the lattice oxygen in the ferrite support first affected on Pd⁰, oxygenized the inactive reduced Pd⁰ into Pd²⁺ and at the same time the support was reduced to oxygen deficient ferrite MFe₂O_{4-δ}. Furthermore, the oxygen deficiency in the crystal could absorb gaseous oxygen in the gas phase and weaken the chemical bonds, which can activate the adsorbed oxygen. Thus, the oxygen deficient ferrite MFe₂O_{4-δ} would be oxygenized into ferrite MFe₂O₄ by the active adsorbed oxygen. In addition, it is believed that, due to the instability of the crystal lattice structure caused by lattice defects, oxygen deficient ferrite needs to capture O²⁻

to fill the absence of oxygen [18]. Meanwhile, the more stable the ferrite, the stronger its reduction capability. So the oxidation cycle regeneration efficiency of the active palladium source could be affected greatly by the occurrence of oxygen deficiency. Namely, the more easily the oxygen deficiency occurred, the more efficient the oxidation cycle regeneration of the active palladium source, and the higher the activation of the corresponding catalyst were. So as Cu, Ni, Co and Zn were doped separately, their yields of DPC decreased in turn, which was accordance with the order of H₂-TPR result above.

According to the redox potential theory, when the high valence ion oxidizes Pd⁰ to the active component Pd²⁺, the reduced low valence ion must be oxygenized rapidly to a high valence ion. Considering the redox potential of these samples with different ions doped in, the only one between φ_{Pd^{2+}/Pd^0} (0.99 eV) and φ_{O_2/H_2O} (1.23 eV) was MnO₂/Mn²⁺ which lying in the support of MnFe₂O₄, was exactly 1.224 eV. From the XPS results, the existence of high valence manganese was confirmed. Considering that Mn³⁺ was more easily oxidized by oxygen than Mn²⁺, the existence of high valence manganese benefited the ion transference in support and the oxidation cycle regeneration of the active palladium, which improves the catalytic efficiency of the catalyst. As a result, with the coaction of oxygen deficiency and the ion transference of the high valence manganese in the MnFe₂O₄ support, the catalyst Pd/MnFe₂O₄ had the highest catalytic activity. Accordingly, the possible reaction mechanism oxidation carbonylation of phenol to DPC over the supported catalyst Pd/MnFe₂O₄ is shown in Scheme 1.



Scheme 1. Reaction mechanism for Pd/MnFe₂O₄ catalyzed oxidative carbonylation of PhOH to DPC.

VSM Characterization

The hysteresis loops of the catalyst Pd/MnFe₂O₄ was characterized by VSM at room temperature. As shown in Figure 4, the remanent magnetization and

Table 2. Catalytic performance of the different iron doped catalysts (Pd/MFe₂O₄)

Catalytic performance	Pd/NiFe ₂ O ₄	Pd/ZnFe ₂ O ₄	Pd/CoFe ₂ O ₄	Pd/CuFe ₂ O ₄	Pd/MnFe ₂ O ₄
Yield of DPC, %	3.77	0.42	0.70	16.04	33.12
Selectivity of DPC, %	98.45	99.05	99.31	98.89	99.12
TOF, mol DPC·(mol Pd·h) ⁻¹	8.03	0.8825	1.49	34.17	70.56

coercivity of the catalyst was low, indicating that the sample was in line with the properties of the soft magnetic material. Moreover, the specific saturation magnetization of the catalyst was over $10 \text{ A}\cdot\text{m}^2\cdot\text{kg}^{-1}$ (exactly $43.1 \text{ A}\cdot\text{m}^2\cdot\text{kg}^{-1}$), which could meet the requirements of the specific saturation magnetization of the magnetic particles applied in MSFB [8].

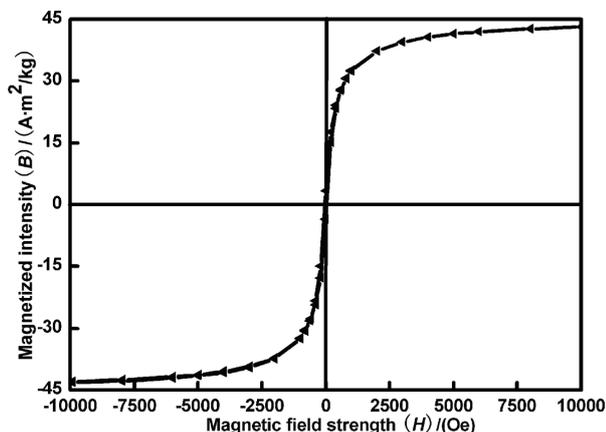


Figure 4. The hysteresis loops of Pd/MnFe₂O₄ catalyst.

CONCLUSIONS

The spinel ferrite MFe₂O₄ was successfully prepared by the sol-gel method as a catalyst supporter for oxidative carbonylation of phenol to diphenyl carbonate. Compared to the other metal ion doped spinel ferrite catalysts, the catalytic activity of Pd/MnFe₂O₄ was much higher, with the single pass yield of DPC reaching 33.12% with selectivity above 99%, and TOF reaching $70.56 \text{ mol DPC}\cdot(\text{mol Pd}\cdot\text{h})^{-1}$. The H₂-TPR characterization result showed that the formation of the ferrite oxygen-deficient in MnFe₂O₄ was much easier than other metal ion doped spinel ferrite catalysts. The XPS result showed that manganese existed in various states in the Pd/MnFe₂O₄ catalyst. The formation of the oxygen-deficient ferrite and ion transference in the Pd/MnFe₂O₄ might favorably affect the catalytic activity. When the support MnFe₂O₄ was calcinated at 500 °C, the saturation magnetization of the obtained catalyst Pd/MnFe₂O₄ was $43.1 \text{ A}\cdot\text{m}^2\cdot\text{kg}^{-1}$.

With good magnetic property and excellent catalytic activity, the catalyst Pd/MnFe₂O₄ may be well suited for industrial experiments in MSFB reactors in the future.

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OKSIDATIVNA KARBONILACIJA FENOLA DO DIFENIL KARBONATA POMOĆU Pd/MFe₂O₄ MAGNETSKOG KATALIZATORA

U cilju skrininga pogodnog katalizatora za reaktor sa magnetno stabilisanim fluidizovanim slojem (MSFB) u procesu oksidativne karbonilacije fenola do difenil-karbonata (DPC), izabrani su, pripremljeni i okarakterisani katalizatori Pd/MFe₂O₄. Njihova karakterizacija je izvršena metodama XRD, H₂-TPR, XPS i VSM. U poređenju sa drugim spinel feritnim katalizatorima, dopiranim pomoću metalnog jona, katalitička aktivnost Pd/MnFe₂O₄ je mnogo veća, usled čega je prinos DPC 33,12 %, selektivnost iznad 99%, a obrtna frekvencija 70,56 mol DPC·(mol Pd·h)⁻¹. Rezultat pokazuje da formiranje ferita sa manjkom kiseonika i transfer jona u feritu idu u prilog katalitičkoj aktivnosti. Sa kalcinacijom MnFe₂O₄ na 500 °C, zasićena magnetizacija dobijenog katalizatora Pd/MnFe₂O₄ dostiže vrednost 43,1A·m²·kg⁻¹. Uz dobre magnetne osobine i odličnu katalitičku aktivnost, katalizator Pd/MnFe₂O₄ se može upotrebiti na industrijskom nivou u MSFB reaktoru.

Ključne reči: magnetski katalizator; oksidativna karbonilacija; difenil-karbonat; spinel ferit.