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Catalytic Performance of Metal Oxide Modified SiMCM-41 Catalysts in Diphenyl Carbonate Synthesis[1]

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Abstract—Decomposition of CCl_4 into diphenyl carbonate (DPC) was examined over metal oxides modified SiMCM-41. ZnO/SiMCM-41 and Fe_2O_3/SiMCM-41 showed high activity in DPC synthesis. Although many other metal oxides, such as La_2O_3, CuO, Al_2O_3 and alkali or alkaline earth oxide, were success in destruction of CCl_4, they displayed nearly no activity on DPC synthesis. ZnO/SiMCM-41 and Fe_2O_3/SiMCM-41 were characterized by X-ray diffraction (XRD), UV-Raman, ^{29}Si MAS NMR and N_2 adsorption-desorption isotherms, and results showed that ferric and zinc oxide were supported onto SiMCM-41. The well ZnO dispersion in SiMCM-41 channels and the weak electrostatic interaction between chlorine anion and Zn^{2+} play an important role for the high activity of ZnO/SiMCM-41 in decomposition of CCl_4 into DPC.

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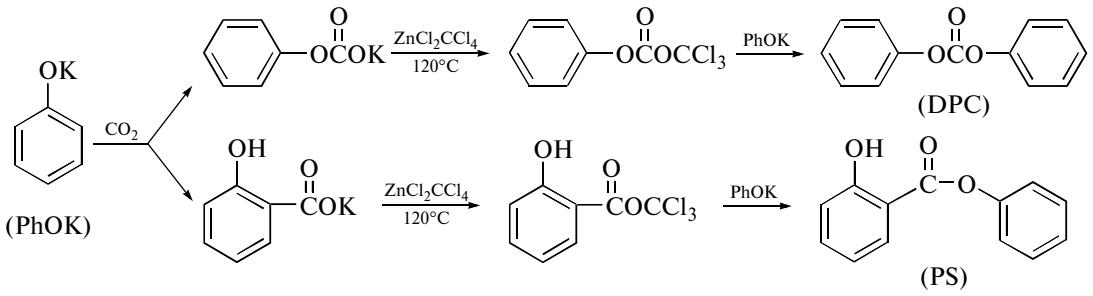
Diphenyl carbonate (DPC) is a key raw material for producing aromatic polycarbonates, and it is mainly synthesized by using severely toxic phosgene as a raw material [1], the oxidative carbonylation of phenol [2] and transesterification [3–5]. Recently, the studies on the chemical degradation of CCl_4 by phenoxide over $ZnCl_2$ were carried out, and it was found that the major DPC and minor phenyl salicylate (PS) were synthesized [6]. In this process $PhOCOO^-$ was produced from the reaction of CO_2 with phenoxide [7], and $CCl_3^{\delta+}$ could be formed from CCl_4 decomposition over Lewis acid [8, 9]. Therefore trichloromethyl phenyl carbonate was formed from CO_2 and phenoxide in CCl_4 over $ZnCl_2$, and DPC can be obtained through transesterification of trichloromethyl phenyl carbonate with phenoxide (Scheme 1) [10]. The phosgene produces from Cl_3COK in situ during the reaction and reacts with phenoxide to produce another molecular DPC [7].



Scheme 1. The synthesis of DPC from CO_2 and phenoxide in CCl_4 over $ZnCl_2$.

Although $ZnCl_2$/SiMCM-41 and $FeCl_3$/SiMCM-41 displayed high activity in decomposing CCl_4 into DPC, the main reasons for Zn^{2+} showing higher activity than Fe^{3+} in dispose of CCl_4 into DPC was still not be figured out. Herein, the decomposition of CCl_4 into DPC over metal oxide modified MCM-41 catalysts was carried out, and results showed the well ZnO dispersion in MCM-41 play an important role in decomposition of CCl_4 into DPC. The electrostatic interaction between chlorine anion and Zn^{2+} appeared to be

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Table 1. The activity of different catalysts with metal oxide loaded on SiMCM-41

Catalyst	Selectivity, mol. %			Yield, mol. %
	DPC	PS	Others	
Fe_2O_3/SiMCM-41	67.2	16.8	16.0	12.1
NiO/SiMCM-41	33.2	31.5	35.3	1.1
ZnO/SiMCM-41	75.4	10.7	13.9	21.5
RZnO/SiMCM-41	73.2	11.8	15.0	19.7
RFe_2O_3/SiMCM-41	66.5	14.7	18.8	10.4
CdO/SiMCM-41	32.7	25.5	41.8	0.6
La_2O_3/SiMCM-41	22.9	29.4	47.7	0.3
Al_2O_3/SiMCM-41	30.9	28.5	40.7	0.5
CuO/SiMCM-41	10.4	14.6	75.0	0.8
Y_2O_3/SiMCM-41	31.7	26.5	41.8	0.5
RhO_2/SiMCM-41	25.6	28.4	46.0	0.4
MgO/SiMCM-41	40.8	59.2	–	0.6
MnO/SiMCM-41	22.9	51.4	25.7	0.9
Cr_2O_3/SiMCM-41	30.2	27.4	42.4	0.7

The loading of metal oxide on the support is 4 mmol/g. Reaction condition: phenol 30 mmol, K_2CO_3 15 mmol, catalyst 1.0 g, CCl_4 40 ml, $P_{CO_2} = 1.0$ MPa, 120°C, 6 h.

significantly weak which made chlorine anion much easier to divorce from zinc cation to make activity sites recycle.

EXPERIMENTAL

Pure silica MCM-41 was prepared according to the documented procedure in [10]. Metal oxides were loaded on supports by the wet impregnation of corresponding metal nitrate. After solvent was removed by evaporation at 80°C for 8 h, the catalysts were calcined at 550°C for 3 h. RZnO/SiMCM-41 and RFe_2O_3/SiMCM-41 are the secondly used catalyst and they are activated at 550°C for 3 h.

N_2 adsorption-desorption isotherms of the mesoporous and microporous samples were measured at 77 K on Micromeritics Tristar 3000 sorptometer and ASAP2000 (Micromeritics Instrument Co. USA), respectively. Prior to the measurement, all samples were outgassed at 200°C and 10^{-6} Torr over night. The surface areas of the mesoporous samples were calculated using the multiple-point Brunauer–Emmett–Teller (BET) method, and the pore size distribution curves of samples were calculated from the adsorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) method. The pore size distributions of microporous samples were determined from the adsorption branch of the isotherms employing the regularization method according to density functional theory (DFT) method. ^{29}SiMAS NMR spectra were recorded at 79.5 MHz using Varian Infinity Plus spectrometer. UV-Raman spectra were measured on a homemade V-Raman spectrometer [11, 12]. The 244 nm line from a Coherent Innova 300 Fred was used as the excitation source. The power of the UV laser lines was less than 2.0 mW. The spectral resolution was estimated to be 4.0 cm^{-1}. XRD patterns characterization of the catalyst samples were measured on a Bruker AXS (Germany) using CuK_α radiation. The date were recorded from 1° to 10° and from 10° to 70° (2θ). The Zn content in fresh ZnO/SiMCM-41 and refreshed RZnO/SiMCM-41 was measured on ICP (TJA Corporation, Astomscan 16).

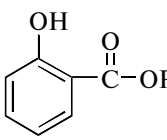
The structure of products was confirmed by GC-MS method (HP5972, capillary column: 30 m SE-30, 0.25 mm inner diameter, and 0.25 μm film thickness). Quantitative analysis was carried on a gas chromatograph (Agilent 6890N GC with a FID detector, HP-5/DB-5 capillary column) with cetane as interior standard.

A definite quantity of catalyst and reactants were firstly placed in an autoclave of 250 ml volume, the autoclave was then sealed and flushed with CO_2 to remove any air in it. After that, CO_2 was pressurized in the autoclave to given pressure and the autoclave was heated to given reaction temperature. After reactions lasted for certain duration, the autoclave was cooled down to room temperature. The contents were discharged to separate the catalyst by simple filtration.

RESULTS AND DISCUSSION

DPC is the main product of the CCl_4 transformation, and the main by-product is PS. The more precise stoichiometry of the DPC and PS synthesis was listed as the following equations:

$$4PhOH + 2K_2CO_3 + CCl_4 = 2(PhO)_2CO + 4KCl + 2H_2O + CO_2, \quad \text{(I)}$$

$$4PhOH + 2K_2CO_3 + CCl_4 = \text{  } + (PhO)_2CO + 4KCl + 2H_2O + CO_2. \quad \text{(II)}$$

Some data on the selectivity of DPC formation from CCl_4 in reaction are presented in Table 1.

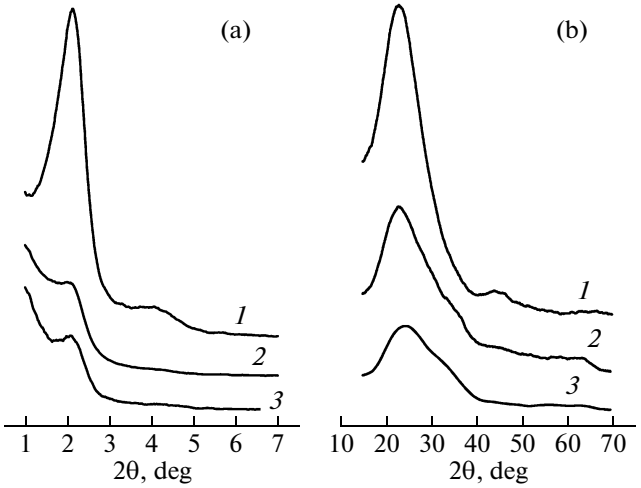


Fig. 1. Small angle XRD (a) and extensive XRD (b) spectrums of different catalysts: *1*—SiMCM-41, *2*—Fe_2O_3/SiMCM-41, *3* —ZnO/SiMCM-41.

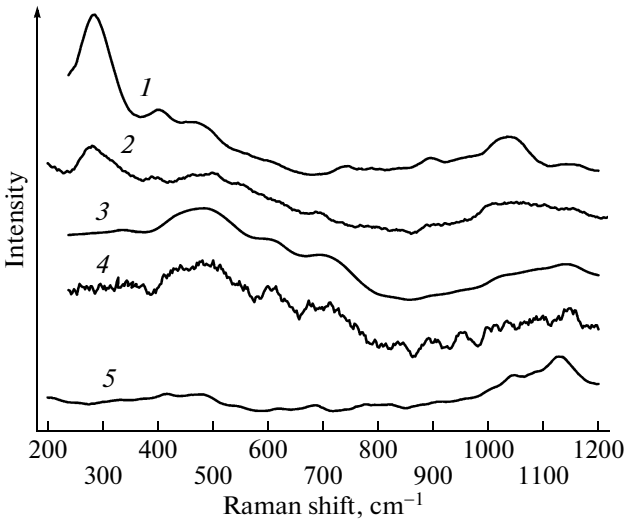


Fig. 2. UV-Raman spectra of fresh and refreshed catalysts with 4 mmol/g loading fresh ZnO/SiMCM-41 (*1*), refreshed ZnO/SiMCM-41 (*2*), fresh Fe_2O_3/SiMCM-41 (*3*), refreshed Fe_2O_3/SiMCM-41 (*4*), and SiMCM-41 (*5*).

Metal oxides, such as La_2O_3 [8, 13], CuO [14], Al_2O_3 [15] and alkali or alkaline earth oxide [16], were success in destruction of CCl_4, but they displayed nearly no activity in decomposition of CCl_4 into DPC. However, when ZnO/SiMCM-41 acted as catalyst, DPC yield amounted to 21.5%, and DPC selectivity achieved 75.4%. When reaction was carried out over Fe_2O_3/SiMCM-41, DPC yield and selectivity declined to 12.1 and 67.2%, respectively. The used ZnO/SiMCM-41 was refreshed, and it displayed high activity for DPC synthesis, which indicated ZnO/SiMCM-41 could be recycled.

Although ZnO/SiMCM-41 and Fe_2O_3/SiMCM-41 displayed high activity in decomposing CCl_4 into DPC, the main reasons for ZnO showing higher activity than Fe_2O_3 in dispose of CCl_4 into DPC was still not be figured out. Here, the XRD patterns of ZnO/SiMCM-41 and Fe_2O_3/SiMCM-41 were listed in Fig. 1. The peaks (100) intensity at 2° still existed when ZnO and Fe_2O_3 were loaded (Fig. 1a), which suggests that the mesoporous structure of SiMCM-41 existed in ZnO/SiMCM-41 and Fe_2O_3/SiMCM-41. No metal oxide crystallite diffraction peaks were detected and only one strong SiO_2 diffraction peak appeared in extensive XRD spectra of different catalysts (Fig. 1b), which indicated the metal oxides were well dispersed on SiMCM-41.

The physical properties of catalysts are listed in Table 2. The BET surface (*S*) of ZnO/SiMCM-41 and Fe_2O_3/SiMCM-41 was 546 and 703 m^2/g, respectively. The sequence of pore volume (v) of catalyst declined as follows: SiMCM-41 > Fe_2O_3/SiMCM-41 > ZnO/SiMCM-41. The fact that the pore diameter (*d*) of Fe_2O_3/SiMCM-41 did not decrease could suggested that most Fe_2O_3 did not fill the pore channels of SiMCM-41, but rather cover the pore mouth. The difference in pore diameter between ZnO/SiMCM-41 and Fe_2O_3/SiMCM-41 was only 0.1 nm, but this characterized results suggested that ZnO was well dispersed in the pore channel of SiMCM-41. The well ZnO dispersion over SiMCM-41 might result in ZnO/SiMCM-41 showing high activity.

Figure 2 showed UV-Raman spectra of the fresh and refreshed catalysts. In the spectrum of SiMCM-41, the bands at 490 and 613 cm^{-1} were assigned to the three and four siloane rings, and the band at 810 cm^{-1} was the symmetric stretching mode of the [SiO_4] tetrahedron [17–20], which was the unit of the MCM-41 framework. Fe_2O_3/SiMCM-41 exhibited new bands at 524, 1126, and 1152 cm^{-1}. The chemical analysis of SiMCM-41 and Fe_2O_3SiMCM-41 showed that the iron was the only difference in chemical composition of these samples, and the new bands must be attributed to the iron species [21]. A new Raman band at 283 cm^{-1} was observed in the spectrum of ZnO/SiMCM-41 which must be caused by zinc species. The bands at 283, 491, 810, and 1046 cm^{-1} still existed in refreshed ZnO/SiMCM-41, which implied that the structure of SiMCM-41 was not destroyed during reaction. However, the band at 283 cm^{-1} in refreshed ZnO/SiMCM-41 declined greatly, which

Table 2. The properties of catalysts

Catalyst	*S*, m^2/g	v, cm^3/g	*d*, nm
SiMCM-41	820	1.06	2.7
ZnO/SiMCM-41	546	0.63	2.6
Fe_2O_3/SiMCM-41	703	0.76	2.7

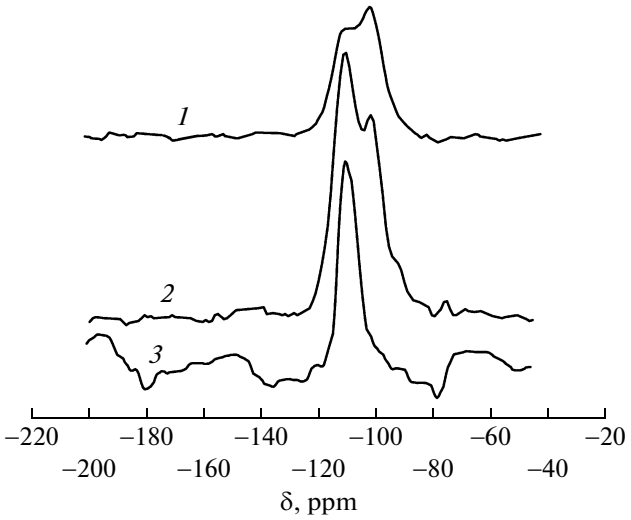
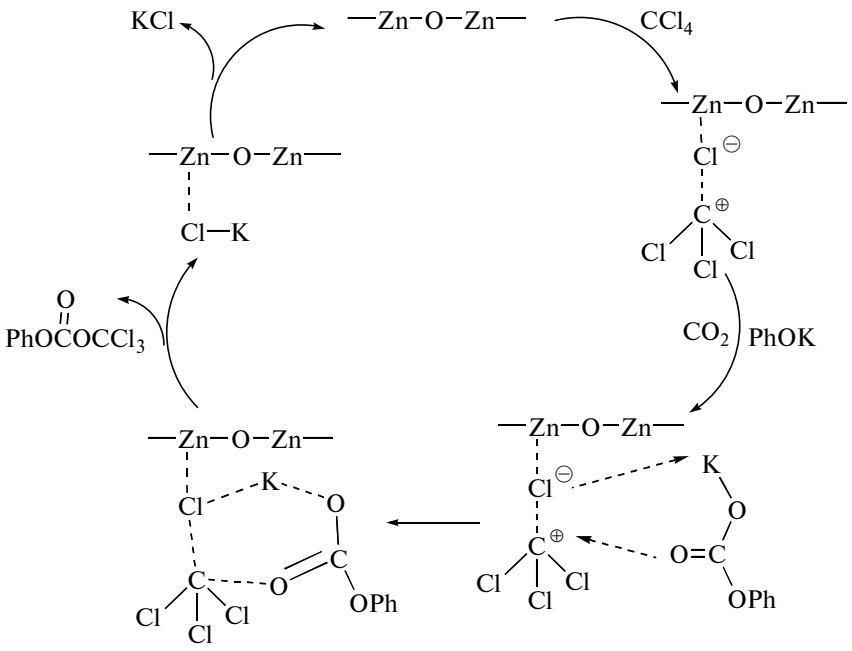


Fig. 3. Solid state ^{29}Si MAS NMR spectra of catalysts SiMCM-41 (*1*), ZnO/SiMCM-41 (*2*), and Fe_2O_3/SiMCM-41 (*3*).

displayed a part of Zn species might leach out of ZnO/SiMCM-41.

Figure 3 shows ^{29}Si MAS NMR spectra of SiMCM-41, ZnO/SiMCM-41, and Fe_2O_3/SiMCM-41. ^{29}Si NMR spectra could be deconvolved into three Gaussian peaks with chemical shift of −113.0(Q^4), −100.1(Q^3) and −90.31(Q^2) ppm corresponding to $Si(OSi)_4$, $Si(OSi)_3OH$, and $Si(OSi)_2-(OH)_2$, respectively [22]. These NMR peaks were used to monitor the relative concentration variety of the silicon species. After ZnO and Fe_2O_3 were loaded on the surface of SiMCM-41, the intensities of $Si(O-Si)_3OH$ and $Si(O-Si)_2(OH)_2$ signals decreased while that of Q^4 signal increased by the contribution of $Si(OSi)_4-n(OM)_n$ species (n = 0, 1, 2) [23], which suggested that a part of ferric and zinc ions were fixed onto SiMCM-41 framework by the reaction between metal ions and silanol groups [24].

The Zn^{2+} and Fe^{3+} content on the surface of fresh and refreshed catalyst were summarized in Table 3. The characterized results showed that a small amount of Zn species leached out of ZnO/SiMCM-41 during reaction. The loss of Zn species belonged to no fixed Zn species which resulted in the appearance of UV-Raman band at 283 cm^{-1}. However, nearly no Fe^{3+} species was leached out from Fe_2O_3/SiMCM-41. The refreshed ZnO/SiMCM-41 displayed high activity for DPC synthesis, which indicated the leached Zn species in solution has little effect on decomposition of CCl_4 into DPC, and supported ZnO was main activity site for DPC synthesis.



Scheme 2. Reaction mechanism for DPC synthesis over ZnO/SiMCM-41.

In order to figure out the main reasons for Zn^{2+} showing higher activity than Fe^{3+} in decomposition of CCl_4 into DPC, a possible reaction path was suggested in Scheme 2. PhOCOOK interacted with CCl_3^+ to form $PhOCOOCCl_3$ which further reacted with another PhOK to form DPC [25]. After transesterification of $PhOCOOCCl_3$ with phenoxide, the phosgene produces from Cl_3COK in situ during the reac-

Table 3. The metal content on the surface of fresh and refreshed catalyst

Catalyst	Metal content, wt %	
	fresh	used
ZnO/SiMCM-41	19.7	16.3
Fe_2O_3/SiMCM-41	27.3	26.2

tion and reacts with phenoxide to produce another molecular DPC. The electrostatic interaction between chlorine anion and Zn^{2+} appeared to be significantly weaker, which resulted in chlorine anion being easier to divorce from Zn^{2+} than from Fe^{3+}, i.e., the electrostatic interaction between chlorine anion and Zn^{2+} appeared to be significantly weak which made chlorine anion much easier to divorce from zinc cation to make activity sites recycle.

Thus, ZnO/SiMCM-41 displayed higher activity than Fe_2O_3/SiMCM-41 in DPC synthesis because chlorine anion was easier to divorce from Zn^{2+} than from Fe^{3+} to keep catalyst from deactivation. Metal ions were bound to the wall of SiMCM-41, which resulted in leaching of a small amount of metal species from catalyst during reaction. The well ZnO dispersion in SiMCM-41 pore channels also played an important role in decomposition of CCl_4 into DPC.

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