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Zn-promoted synthesis of diphenyl carbonate via transesterification over Ti–Zn double oxide catalyst

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Abstract An environmentally friendly heterogeneous catalyst, Ti–Zn double oxide, was prepared using a sol–gel method and firstly used for the synthesis of diphenyl carbonate (DPC) via the transesterification of phenol and dimethyl carbonate. The catalyst exhibited excellent catalytic activity. Moreover, the effects of Ti to Zn molar ratio, calcination temperature and catalyst amount on the catalytic performances of Ti–Zn double oxide have been investigated. The characterization results of XRD, TGA–DSC, ICP-AES and NH_3-TPD showed that amorphous TiO_2 was the active sites, and amorphous ZnO was the promoter. Also the amount of Zn remarkably affected the acid amounts of the catalysts, and the calcination temperature not only influenced the acid amount, but also affected the acid strength. Besides, the weak surface acid sites were responsible for the synthesis of MPC and DPC, whereas the strong acid sites favored the formation of a by-product, anisole. The phenol conversion and the transesterification selectivity reached 41.2 and 98.2% over 0.3 g 5TiZn-250 for 8 h, respectively. Furthermore, the prepared catalyst could be reused for three runs without drastic decrease in activity. The slight decreased activity was attributed to the phase change of Ti–Zn double oxide and the leaching of Ti.

Keywords Ti–Zn double oxide · Transesterification · Diphenyl carbonate · Dimethyl carbonate

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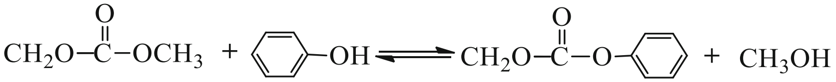
Introduction

Diphenyl carbonate (DPC) is extensively used to produce various organic compounds and polymer materials, particularly as an important intermediate for the synthesis of polycarbonate in non-phosgene processes [1–3]. The processes developed for the synthesis of DPC with different carbonyl sources involve phosgenation, oxidative carbonylation of phenol, esterification of CO_2 with phenol, phenolysis of urea, and transesterification of carbonates with phenol [4]. The phosgenation technique has the disadvantages of using corrosive and severely toxic phosgene as a raw material and the formation of corrosive hydrogen chloride as a by-product. Though the oxidative carbonylation of phenol is considered to be a prospective process for synthesis of DPC, the employment of a noble catalyst and the low yield of DPC limit its industrialization [5]. Similarly, DPC produced via direct reaction of phenol with urea or CO_2 also suffer low yield [6]. Besides, the subsequent decarbonylation of transesterification of dimethyl oxalate (DMO) and phenol to DPC hampers its application [7]. In this context, the transesterification of dimethyl carbonate (DMC) and phenol is thought to be the most suitable method for commercial production of DPC with no hazard to the environment. Generally, this route involves the transesterification of DMC and phenol to methyl phenyl carbonate (MPC; Eq. 1) followed by the further transesterification (Eq. 2) and/or a disproportionation step to DPC (Eq. 3) [8]. Moreover, side reactions also may occur in this process (Eq. 4) [9].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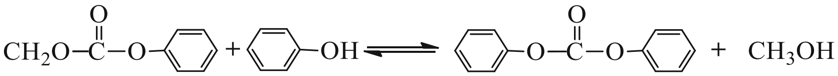
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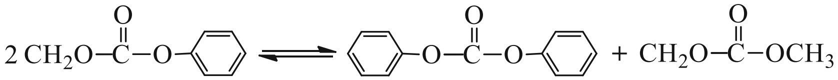
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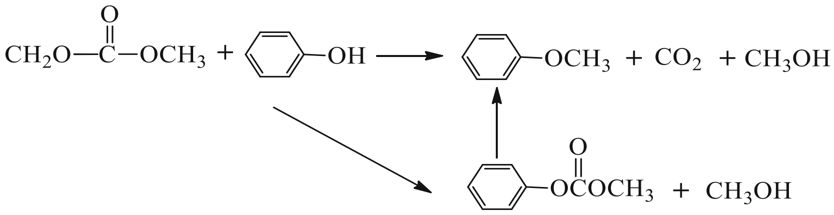
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The transesterification reaction of DMC and phenol is thermodynamically unfavorable, and the low yield and selectivity to DPC were obtained even at elevated temperatures [10]. Therefore, an effective catalyst is highly desirable for this process. The liquid-phase transesterification of DMC and phenol was usually catalyzed by homogeneous catalysts such as conventional Lewis acids, organo-titanium, and organotin compounds [11–13]. Because of the separation problems between homogeneous catalysts and DPC as well as the recovery of catalysts, more attention has been paid to heterogeneous catalysts like MoO_3/SiO_2, TiO_2/SiO_2, Ti-HMS, TiO_2/CNT, PbO/MgO, Pb–Zn composite oxide, 12-molybdophosphoric acid supported on titania (HPMo/TiO_2) and so on [14–23]. Although these catalysts had good performances in the transesterification, their stability for this process was not very satisfactory. Moreover, some catalysts containing heavy metals, supported organotin, etc., are harmful to the environment. Therefore, the development of active solid catalysts with high catalytic activity, desirable stability and nontoxicity is necessary. In transesterification, TiO_2 as catalysts have been widely studied in various fields with advantages of ease of synthesis, low cost, innocuity and environmental friendliness [24, 25]. As the activity of pure TiO_2, especially after heat treatment at high temperature, is low, some methods have been developed to improve the catalytic activity of TiO_2 including dispersion of TiO_2 on supports, complex of TiO_2 with other oxides, etc. Furthermore, it was reported that amorphous ZnO played a role as the promoter in the DPC synthesis via transesterification over lead and zinc double oxide catalyst [26]. Besides, TiO_2 shows strong interaction with transition metal oxides, which probable makes Ti–Zn double oxide stable [27]. In addition, square-shaped Zn/Ti oxides were also reported to be an excellent catalyst for the transesterification of dibutyl carbonate with phenol to synthesize DPC [28]. These facts give some credence to Ti–Zn double oxide catalyst providing preferable performance in the transesterification reaction.

Therefore, in the present work, Ti–Zn double oxide, a green solid, was prepared via a sol–gel process, and first used to catalyze the transesterification of DMC and phenol. Ti–Zn double oxide catalyst revealed superior catalytic activity compared with other heterogeneous catalysts reported. The influences of molar ratio of Ti to Zn, calcination temperature and catalyst amount on catalytic behavior were also investigated.

Experimental

Catalyst preparation

Ti–Zn double oxide catalyst was prepared by a sol–gel method. An appropriate amount of zinc acetate was added to a mixed solution of ethanol (200 mL) with acetic acid (48 mL) containing 6.80 g tetra-*n*-butyl titanate [$Ti(OBu)_4$] with stirring at 80 °C for 1 h, and then the pH of the solution was adjusted to the range between 5.6 and 6 using a mixture of 2-aminoethanol and H_2O (volume ratio of 1:1), followed by evaporation of solvent at 120 °C until dry and being calcined in a muffle furnace at the desired temperature for 4 h. The prepared catalysts are denoted as *x*TiZn-*T*, in which *x* is the molar ratio of Ti to Zn, and T is the calcination temperature. TiO_2 and ZnO, as the controls, were also synthesized via the same procedure.

Characterization

Powder X-ray diffraction (XRD) was performed on a Philip X'Pert PRO MPD diffractometer using a radiation source of Cu Kα ($\lambda = 1.54056$ Å) at 45 kV and 40 mA. The samples were scanned in the 2θ ranges from 5° to 80° with a step time count of 1 s and step size of 0.02°.

The surface acid properties of the catalysts were studied via temperature programmed desorption (TPD) of NH_3 and conducted on a TPD flow system equipped with a TCD detector. Generally, the catalyst was pretreated at 250 °C for 1 h under N_2 (20 mL min^{-1}) and then cooled to 40 °C at which NH_3 was adsorbed for 2 h and sample was flushed with N_2 for 2 h to remove any physically adsorbed NH_3 followed by heating of the sample to 600 °C at 10 °C min^{-1} to desorb NH_3.

TGA–DSC experiments were carried out in a TGA/DSC 2 LF/1100/155 apparatus. About 15 mg of sample was placed in an alumina crucible. Heating was started at 15 °C min^{-1} from room temperature to 900 °C with 50 mL min^{-1} air.

The element contents were determined using an inductively coupled plasma-atomic emission spectrometry (ICP-AES) method on an IRIS 1000 instrument (Thermo Electron, USA).

Reaction procedure

The transesterification of DMC with phenol was conducted in a 100-mL three-necked round-bottom flask, equipped with a magnetic stirring bar, nitrogen inlet, dropping funnel and fractionating column connected to a liquid dividing head under refluxing condition at atmosphere pressure. Typically, under nitrogen atmosphere, phenol and the desired catalyst were charged into the flask. When the mixture was heated to 175 °C, DMC was added dropwise under continuous stirring, and the reaction temperature was kept at 150–180 °C under a refluxing condition. During the reaction procedure, a distillate composed of DMC and methanol was slowly collected in a receiver flask to break the reaction equilibrium limitation to promote the reaction towards the formation of MPC and DPC. Upon completion of the reaction, the mixture was cooled to room temperature and the catalyst was separated by centrifugation, then washed with DMC and dried at 200 °C. Qualitative and quantitative analysis of the reaction products and the distillates were carried out on a HP-6890/5973 system and a gas chromatograph (Agilent Technologies 7820A) equipped with a DB-35 capillary column (30 m × 320 μm × 0.25 μm) and a flame ionization detector (FID). The conversion of phenol and the selectivity of MPC and DPC were calculated by GC results using a correction factor normalization method.

Results and discussion

Characterization

XRD patterns of the 5TiZn-*T* with varied calcination temperature were shown in Fig. 1. Below 300 °C, there was no peak in the XRD of catalysts, indicating that the Ti specie and Zn specie may exist in a microcrystalline structure or amorphous state. The characteristic peaks of anatase were observed in 5TiZn-400 and 5TiZn-500, and became sharper with calcination temperature increasing due to the improved crystallinity of TiO_2 and the particle growth. It can be deduced that increasing calcination temperature improves the crystallinity of TiO_2. In addition, the characteristic peaks of ZnO existed after reuse of 5TiZn-250 for three times. The results suggested that the additive Zn didn't change the phase of TiO_2 and was highly dispersed in the catalysts.

Figure 2 represented the NH_3-TPD characterization of TiO_2-250 and *x*TiZn-*T*. The peaks in the high and low temperature regions can be assigned to desorption of NH_3 from the strong and weak acid sites, respectively. Generally, the peaks in the high temperature ($T > 400$ °C) regions are ascribed to the desorption of NH_3 from strong acid sites, while the peaks in the low temperature ($T < 400$ °C) regions are attributed to the desorption of NH_3 from weak acid sites [29]. As shown in Fig. 2, the peaks appeared both in the low and high temperature region, confirming that there existed simultaneously weak and strong acid sites on the surface of *x*TiZn-*T*. It can also be observed clearly that the amount of weak acid sites decreased significantly with the calcination temperature of 5TiZn-*T* increasing or after reuse for three times, or with the decreased Ti content. The decreased amount of weak acid sites with the increased calcination temperature of 5TiZn-*T* might be ascribed

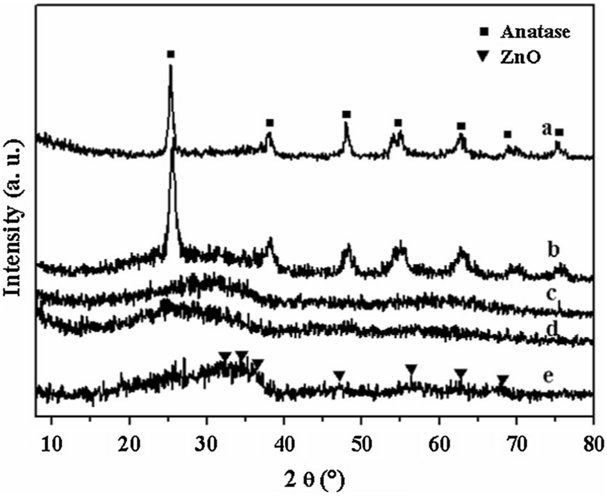

Fig. 1 XRD patterns of (*a*) 5TiZn-500; (*b*) 5TiZn-400; (*c*) 5TiZn-300; (*d*) 5TiZn-250; (*e*) 5TiZn-250 reused

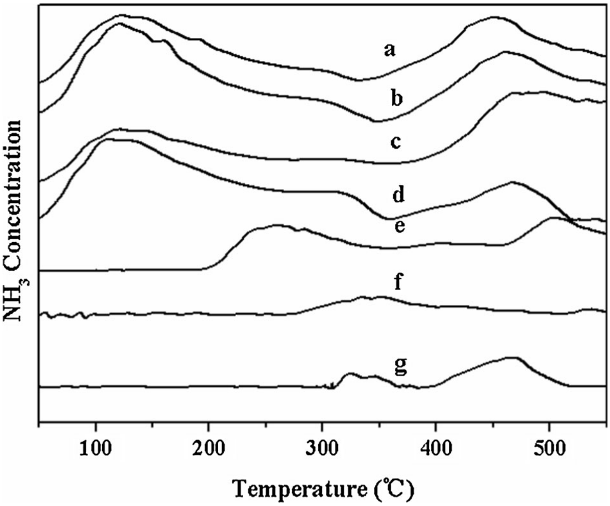

Fig. 2 The NH_3-TPD profiles of (*a*) 1TiZn-250, (*b*) 2TiZn-250, (*c*) 5TiZn-250 used, (*d*) 5TiZn-250, (*e*) 5TiZn-300, (*f*) 5TiZn-400 and (*g*) 5TiZn-500

to the decreased surface area of catalyst, the decreased amount of Ti–OH and the phase transformation from the amorphous phase to the anatase, which was demonstrated using the TGA/DSC curves of the 5TiZn-120 (Fig. 3). When catalyst was calcined at low temperature, with the calcination temperature increasing, the amount of Ti–OH decreased which led to the decreased amount of acidic sites. In addition, the peaks at high temperature for the catalysts calcined at low temperature (below 300 °C) might partly be due to the decomposition of acetate and the relative amount of strong acid sites to weak acid sites in a catalyst becoming stronger evidently with the increase of calcination temperature from 400 to 500 °C. Furthermore, in comparison with the 5TiZn-250, the peaks at low temperatures shifted toward higher temperatures with increased calcination temperature, illustrating that the strength of weak acid of 5TiZn-*T* became stronger with increasing calcination temperature. Nevertheless, the addition of Zn to TiO_2 didn't change the strength of acid sites of the *x*TiZn-250. The NH_3-TPD results indicated that the incorporation of the Zn component into Ti affected the number of acidic sites, especially the amount of weak acid sites. Also, the calcination temperature influenced the strength and the amount of acid sites.

Figure 3 showed the TGA/DSC curves of the 5TiZn-120. The TGA curve could be divided into two main weight-loss stages. The first weight loss below 250 °C could be attributed to the evaporation of solvents, such as water and alcohol, and organic acid such as acetic acid, corresponding to an endothermic peak at 120–200 °C. The second step that occurred in the temperature range of 250–500 °C resulted from the dehydroxylation of Ti–OH into TiO_2 and the decomposition of $Zn(OAc)_2$ to ZnO as corroborated by a endothermic peak at 250–350 °C and the combustion of the organic residues and the phase transformation revealed by the XRD patterns corresponding to a sharp exothermic peak at 350–500 °C [30, 31].

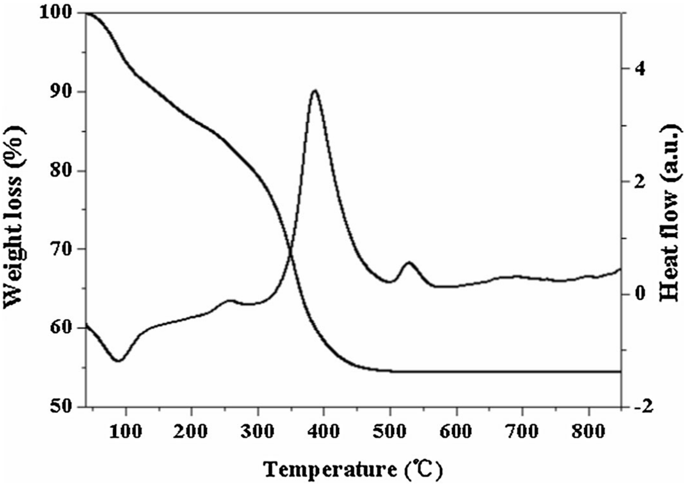

Fig. 3 TGA/DSC analysis of the 5TiZn-120

Catalytic activity

Effect of molar ratio of Ti to Zn

Table 1 showed the results of catalytic activities of *x*TiZn-250. It was notable that the phenol conversions increased steadily with increasing the molar ratio of Ti to Zn up to 3:1, followed by slowly decreasing at higher Ti content. However, the selectivity for MPC and DPC monotonously increased with the increase of Ti content. 36.4% of phenol conversion and 99.2% of selectivity for MPC and DPC over 5TiZn-250 were obtained, respectively. In the case of the absence of any catalysts, no yield of DPC was gained and only a trace amount of phenol was converted, suggesting that the transesterification was difficult to incur without catalyst.

For comparison, the transesterification over TiO_2-250 and ZnO-250 were performed and the phenol conversions and the transesterification selectivity were 15.7, 0.4% and approximatively 100, 91.4%, respectively. These results demonstrated that ZnO was the promoter, which could improve markedly the activity of the catalysts. It is well known that in this transesterification, the weak acid sites promote the synthesis of MPC and DPC, and strong acid sites are responsible for the anisole (AN) formation [32]. The decrease in phenol conversion with decreased Ti content was attributed to the decrease of weak acid sites and the decreased active sites of Ti. The decreased selectivity of MPC and DPC over catalysts with decreased Ti content was due to the decreased active sites of Ti.

Effect of calcination temperature

The effect of calcination temperature on the catalytic activity of 5TiZn-*T* was displayed in Table 2. It was observed that the conversion of phenol and the selectivity of MPC and DPC increased with the calcination temperature of 5TiZn-

Table 1 Catalytic performance of *x*TiZn-250 on the transesterification

Catalyst	Phenol conversion (%)	Yield (%)			Selectivity (%)
		MPC	DPC	AN	
None	0.86	0.86	0	0	100
TiO_2-250	15.7	10.1	5.6	0	100
10TiZn-250	35.8	19.6	16.2	0	100
5TiZn-250	36.4	20.4	15.8	0.2	99.2
4TiZn-250	38.4	20.7	17.3	0.4	98.8
3TiZn-250	41.2	20.4	17.2	3.6	91.1
2TiZn-250	33.2	18.0	9.1	6.1	81.6
1TiZn-250	24.6	7.1	9.3	8.2	66.4
ZnO-250	0.4	0.3	<0.1	<0.1	90.0

Reaction conditions: phenol 10 g, *n*(phenol) = *n*(DMC), catalyst 0.15 g, reaction time 8 h, reaction temperature 160–180 °C

Table 2 Effect of calcination temperature of 5TiZn-*T* on the transesterification

T (°C)	Phenol conversion (%)	Yield (%)			Selectivity (%)	
		MPC	DPC	AN	MPC + DPC	DPC
200	34.7	21.5	12.4	0.8	97.6	35.7
250	36.4	20.4	15.8	0.2	99.2	43.3
300	28.4	14.9	12.6	0.9	96.9	44.4
400	24.6	13.0	4.5	7.1	81.7	18.3
500	6.6	2.7	0.3	3.6	45.2	4.5

Reaction conditions: phenol 10 g, *n*(phenol) = *n*(DMC), catalyst 0.15 g, reaction time 8 h, reaction temperature 160–180 °C

T increasing from 200 to 250 °C, then decreased afterwards. The maximum phenol conversion of 36.4% and transesterification selectivity of 99.2% were obtained with 5TiZn-250, which was higher than that over other catalysts [4]. The decreased catalytic performance of 5TiZn-*T* with increasing calcination temperature was ascribed to the decreased amount of weak acid sites, which was the active site in the transesterification of phenol and DMC [28], and was also due to the formation of anatase possessing low catalytic activity [33]. The low selectivity at higher calcination temperature was attributed to the acid strength becoming stronger and the increased relative amount of strong acid sites to weak acid sites, which favor the formation of AN [28]. The results elucidated that the composition of production was closely related to the calcination temperature of 5TiZn-*T*.

Effect of catalyst amount

The effect of 5TiZn-250 amount on the transesterification was determined in Fig. 4. The phenol conversion increased significantly with the catalyst amount increasing

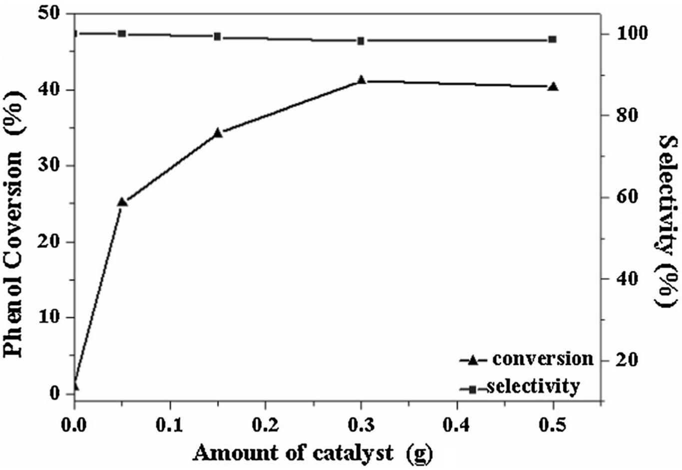

Fig. 4 Effect of catalyst amount on the catalytic performance of 5TiZn-250. Reaction conditions: phenol 10 g, n(phenol) = n(DMC), reaction time 8 h, reaction temperature 160–180 °C

from 0.05 to 0.30 g, with the selectivity decreasing slightly, and remained almost constant with the further increase of catalyst amount. The conversion of phenol and the selectivity of the transesterification reached 41.2 and 98.2%, respectively, with 0.30 g of catalysts, which was significantly higher than that with V–Cu composite oxide (37.0% of phenol conversion and 96.8% of selectivity, respectively) [34]. Nevertheless, with the increase of catalyst amount, the decarboxylation of MPC to AN increased, which decreased the selectivity of the transesterification [20]. Therefore, the optimal amount of catalyst was 0.3 g.

Reusability test of catalyst

The reusability of 5TiZn-250 was investigated and the results are listed in Table 3. The used catalyst was filtered and washed with DMC, and dried at 200 °C. As shown in Table 3, the phenol conversion slowly decreased from 41.2 to 37.5%, with the transesterification selectivity slightly improving, indicating that the catalyst could be reused. XRD results suggested that the characteristic peaks of ZnO appeared in the used catalyst, implying that the structural change occurred during the reaction, which may be the reason for the decreased phenol conversion for the spent catalyst. In addition, the total acidic amount of reused catalyst reduced, leading to the catalytic activity decrease. Furthermore, the molar ratio of Ti to Zn dissolved in solution was 15:1.35 in the first run, which also caused the decreased activity of the catalyst. On the whole, 5TiZn-250 was more stabilized than other TiO_2 -based catalysts and other metal-based catalysts [14, 26]. The excellent stability of 5TiZn-250 maybe a result from the strong interaction between TiO_2 and ZnO [27].

Table 3 The reusability of 5TiZn-250

Run time	Phenol conversion (%)	Yield (%)		Selectivity (%)	
		MPC	DPC	MPC + DPC	DPC
1	41.2	22.9	17.6	98.2	42.7
2	38.7	21.5	17.1	99.7	44.2
3	37.5	21.0	16.5	>99.9	44.0

Reaction conditions: phenol 10 g, *n*(phenol) = *n*(DMC), catalyst 0.15 g, reaction time 8 h, reaction temperature 160–180 °C

Conclusions

A green and economic catalyst of Ti–Zn double oxide was prepared employing a sol–gel method and firstly used as a heterogeneous catalyst for the transesterification of DMC and phenol with excellent catalytic activity and high stability. The molar ratio of Ti to Zn and calcination temperature significantly affected the catalytic performance of the catalysts. 41.2% of phenol conversion and 98.2% of selectivity were achieved over 0.3 g of 5TiZn-250. Moreover, the 5TiZn-250 catalysts could be used for three times with the phenol conversion slowly decreasing from 41.2 to 37.5%, the stabilization of which was ascribed to the strong interaction of TiO_2 with ZnO. The decreased catalytic activity was caused by the phase change and the leaching of Ti.

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References

1. W.B. Kim, U.A. Joshi, J.S. Lee, Ind. Eng. Chem. Res. **43**, 1897 (2004)
2. J. Haubrock, M. Raspe, G.F. Versteeg, H.A. Kooijman, R. Taylor, J.A. Hogendoorn, Ind. Eng. Chem. Res. **47**, 9854 (2008)
3. K.M. Deshmukh, Z.S. Qureshi, K.P. Dhake, B.M. Bhanage, Catal. Commun. **12**, 207 (2010)
4. Q. Wang, C.H. Li, M. Guo, S.J. Luo, C.W. Hu, Inorg. Chem. Front. **2**, 47 (2015)
5. H.Y. Niu, J. Yao, Y. Wang, G.Y. Wang, Catal. Commun. **8**, 355 (2007)
6. W. Xue, J. Zhang, Y. Wang, X. Zhao, Q. Zhao, Catal. Commun. **6**, 431 (2005)
7. X. Ma, J. Gong, S. Wang, F. He, H. Guo, X. Yang, G. Xu, J. Mol. Catal. A Chem. **237**, 1 (2005)
8. H. Lee, S.J. Kim, B.S. Ahn, W.K. Lee, H.S. Kim, Catal. Today **87**, 139 (2003)
9. Y. Ono, Appl. Catal. A Gen. **155**, 133 (1997)
10. X. Yin, Y. Zeng, J. Yao, H. Zhang, Z.Y. Deng, G.Y. Wang, Ind. Eng. Chem. Res. **53**, 19087 (2014)
11. H.Y. Niu, J. Yao, Y. Wang, G.Y. Wang, J. Mol. Catal. A Chem. **235**, 240 (2005)
12. H.J. Lee, J.Y. Bae, O.S. Kwon, S.J. Kim, S.D. Lee, H.S. Kim, J. Organomet. Chem. **689**, 1816 (2004)
13. Z.P. Du, W.K. Kang, T. Chen, J. Yao, G.Y. Wang, J. Mol. Catal. A Chem. **246**, 200 (2006)
14. Y.T. Kim, E.D. Park, Appl. Catal. A Gen. **356**, 211 (2009)
15. U.A. Joshi, S.H. Choi, J.S. Jang, J.S. Lee, Catal. Lett. **123**, 115 (2008)
16. S.W. Luo, T. Chen, D.S. Tong, Y. Zeng, Y.C. Lei, G.Y. Wang, Chin. J. Catal. **28**, 937 (2007)
17. X. Zhou, X. Ge, R.Z. Tang, T. Chen, G.Y. Wang, Chin. J. Catal. **35**, 481 (2014)

18. M. Cao, Y.Z. Meng, Y.X. Lu, Catal. Commun. **6**, 802 (2005)
19. Z.H. Li, Y.J. Wang, X.S. Ding, X.Q. Zhao, J. Nat. Gas Chem. **18**, 104 (2009)
20. S.L. Wang, R.Z. Tang, Y.Z. Zhang, T. Chen, G.Y. Wang, Chem. Eng. Sci. **138**, 93 (2015)
21. D.S. Tong, J. Yao, Y. Wang, H.Y. Niu, G.Y. Wang, J. Mol. Catal. A Chem. **268**, 120 (2007)
22. R.Z. Tang, T. Chen, Y. Chen, Y.Z. Zhang, G.Y. Wang, Chin. J. Catal. **35**, 457 (2014)
23. Y. Zhang, S. Wang, Z. Xiao, T. Chen, G. Wang, Res. Chem. Intermed. (2016). doi:10.1007/s11164-016-2530-y
24. X. Liu, M.M. Yu, Z.Q. Zhang, X. Zhao, J. Li, Res. Chem. Intermed. **42**, 5197 (2013)
25. N. Ganji, A. Allahverdi, F. Naeimpoor, M. Mahinroosta, Res. Chem. Intermed. **42**, 5395 (2016)
26. W. Zhou, X. Zhao, Y. Wang, J. Zhang, Appl. Catal. A Gen. **260**, 19 (2004)
27. S. Wang, Y. Liu, Y. Shi, X. Ma, J. Gong, AIChE J. **54**, 741 (2008)
28. P. Wang, S. Liu, F. Zhou, B. Yang, A.S. Alshammaric, Y. Deng, RSC Adv. **5**, 84621 (2015)
29. Y. Liu, X. Ma, S. Wang, J. Gong, Appl. Catal. B Environ. **77**, 125 (2007)
30. S.F. Wang, F. Gu, M.K. Lu, C.F. Song, S.W. Liu, D. Xu, D.R. Yuan, Mater. Res. Bull. **38**, 1283 (2003)
31. Z.Q. Wang, X.G. Yang, S.Y. Liu, J. Hu, H. Zhang, G.Y. Wang, RSC Adv. **5**, 87311 (2015)
32. S. Wang, X. Ma, J. Gong, N. Gao, H. Guo, X. Yang, G. Xu, Catal. Today **93–95**, 377 (2004)
33. X. Ge, B. Li, J. Hu, T. Chen, G. Wang, X. Hu, Chem. Eng. (China) **39**, 61 (2011)
34. D. Tong, T. Chen, J. Yao, Y. Wang, G. Wang, D. Shi, Z. Li, Z. Chen, Chin. J. Catal. **28**(3), 190 (2007)