Catalysis Letters Vol. 108, Nos. 1–2, April 2006 (© 2006)
DOI: 10.1007/s10562-006-0032-z

The di-*t*-butylation of *p*-cresol with *t*-butanol in supercritical CO_2 over tungstophosphoric acid supported on ordered mesoporous silica

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Received 23 October 2005; accepted 24 January 2006

Tungstophosphoric acid (HPW) supported on MCM-41 was an excellent catalyst for the *t*-butylation of *p*-cresol to 2,6-di-*t*-butyl-4-methylphenol (2,6-DTBPC) in supercritical CO_2; however, zeolites, H-Y and H-Beta, only gave 2-*t*-butyl-4-methylphenol (2-TBPC) because of their limitation in pore size. The yield of 2,6-DTBPC was maximized at 110 °C, and further increase in temperature rather decreased the yield. The yield of 2,6-DTBPC was maximized at 10–11 MPa CO_2 pressure, and further increase of the pressure decreased in the conversion of phenol and the yield of 2,4-DTBC. The thermogravimetric analysis of used catalysts showed that the coke-formation was minimized in supercritical CO_2 compared to the other reaction media such as in liquid phase and in N_2 atmosphere.

KEY WORDS: *t*-butylation; tungstophosphoric acid; MCM-41; supercritical CO_2; *p*-cresol; 2,6-di-*t*-butyl-4-methylphenol.

1. Introduction

Increasing efforts for green chemical technologies are being made to develop chemical processes with minimized ecological impact, leading, for example, to reduce the waste or to avoid the use of hazardous or toxic organic chemicals [1]. One of important aspects in this area is a quest for the replacement of organic solvents by alternating reaction media. One such a medium, which provides the advantages of solvent for easy separation from the reaction medium and of eco-friendly nature, is supercritical CO_2 [2–5]. The supercritical CO_2 has been successfully used as solvents for acid catalyzed reactions, the oxidation, hydroformylation, and polymerization.

Friedel–Crafts alkylation is one of the industrially important reactions, which has very high commercial significance [6]. Alkylation of *p*-cresol with *t*-butanol produces industrially important organic intermediates, such as 2-*t*-butyl-4-methylphenol (2-TBPC) and 2,6-di-*t*-butyl-4-methylphenol (2,6-DTBPC), which are widely used in antioxidants and polymerization inhibitors and in the manufacture of phenol resins [7]. Recently, many workers have been attention to the liquid phase or vapor phase *t*-butylation of phenols over solid acid catalysts, such as zeolites [9–11], clays [12], metal oxides [13], and mesoporous materials [14–20] including their modified catalysts; however, there have been a few to succeed in the di-*t*-butylation of phenols. We have considered one of the reasons is the deactivation of acidic sites by coke formation.

Tungstophosphoric acid (HPW) modified mesoporous zirconia and cobalt aluminophosphate (CoAPO-5) were used for catalysts in the synthesis of *t*-butyl cresols in liquid or vapor phase [13, 14]. However, they mainly discussed on the selective synthesis of mono butyl cresols. In the present paper, we mainly focus on the use of HPW supported on MCM-41 for the synthesis of 2,6-DTPC in the *t*-butylation of *p*-cresol under supercritical CO_2 to minimize the use of organic solvents for environment conscious chemical processes (Scheme 1).

2. Experimental

2.1. Catalysts and reagents

The heteropolyacids: tungstophosphoric acid ($H_3PW_{12}O_{40}{\cdot}xH_2O$; HPW) and tungstosilicic acid ($H_4SiW_{12}O_{40}{\cdot}xH_2O$; HSiW) and zeolites: HY (Tosoh Corporation, Japan, $SiO_2/Al_2O_3 = 5.2$), dealuminated HY (Zeolyst CV, $SiO_2/Al_2O_3 = 12$, 30, 60, and 80) and H-Beta (Zeolyst CV, $SiO_2/Al_2O_3 = 25$) were obtained commercially, and used without any further treatment. Mesoporous MCM-41 was synthesized in our laboratory by standard literature method [21]. HPW and HSiW supported on MCM-41 were prepared by a procedure reported in our previous papers [22, 23]. The zeolites were modified to their protic form by calcination at 500 °C in a furnace. HPW supported on MCM-41 were prepared by impregnation method from the solutions of ethanol. *p*-Cresol and *t*-butanol were obtained commercially and used as received without further purifications.

2.2. *t-Butylation of* p*-cresol*

In a typical reaction, *p*-cresol (9.24 mmol); *t*-butanol, (36.9 mmol) were placed with dried catalyst (100 mg) in

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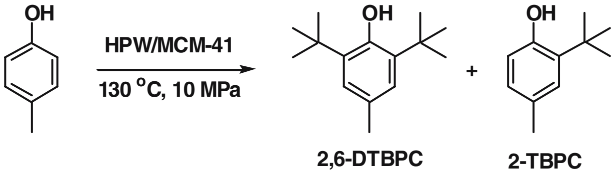

Scheme 1.

a 100 mL SUS-316 autoclave, and dry ice was loaded into the reactor. The amount of CO_2 necessary for the reaction conditions were calculated from the empty volume of the reactor [23]. The reactor was heated to a required reaction temperature and then, the reaction was started with agitation. The reactor was quenched with cold water after the completion of the reaction, and CO_2 was slowly released. The contents of the reactor were washed with acetone, and the products were analyzed by gas chromatography (GC-14A, Shimadzu Corporation) using an Ultra-1 column (15 m×0.3 mm, Agilent Technologies), and also compared with authentic samples.

2.3. Recycling of the catalyst

After finishing the reaction, the catalyst was filtered, and washed well with acetone. The catalyst was subjected to new reactions after drying at 100 °C overnight.

2.4. Characterization

Thermogravimetric analysis of used catalysts for the reaction was carried on a Shimadzu TG-DTG-50 analyzer with a temperature programmed rate of 10 °C/min in an air flow. The XRD patterns were determined by powder X-ray diffraction (XRD-6000, Shimadzu Corporation) with Cu Kα radiation ($\lambda = 0.15418$ nm). Nitrogen adsorption–desorption isotherms were measured at 77 K on a Belsorp 28SA apparatus (Bel Japan).

3. Results and discussion

Typical results of the *t*-butylation of *p*-cresol over H-Y zeolites with various SiO_2/Al_2O_3 ratios at 110 °C under 10 MPa of CO_2 pressure are summarized in Table 1. H-Y zeolites with low SiO_2/Al_2O_3 ratios gave high conversion of *p*-cresol: 2-*t*-butyl-4-methylphenol (2-TBPC) was predominantly formed, and 2,6-di-*t*-butyl-4-methylphenol (2,6-DTBPC) was in small amounts. The formation of 2,6-DTPC may be restricted by the limitation of H-Y zeolite, and occur only on its external acidic sites. The conversion of *p*-cresol decreased with the increase in SiO_2/Al_2O_3 ratio from 5.2 to 80 although 2-TBPC was obtained selectively: the catalytic activity was related to the numbers of acid sites. The catalytic activity for H-Beta zeolite was lower than that of H-Y zeolite. The alkylation is mainly acid catalyzed mechanism and requires stronger acidity. On the other hand, the conversion of *p*-cresol over H-Beta(25) zeolite was lower than that of H-Y zeolite with the similar level of SiO_2/Al_2O_3 ratio although 2-TBPC was principally obtained. These results suggest that the catalytic activity is related to the structure of zeolites, and that strong acid sites are essential for high catalytic activity because H-Beta has weaker acidity than H-Y zeolite with the similar level of SiO_2/Al_2O_3 ratio.

In previous paper, we described the selective formation of 2,4-di-*t*-butylphenol (2,4-DTBP) in the *t*-butylation of phenol with *t*-butanol over H-Y zeolites [23]. These results from phenol correspond to the results for *p*-cresol: 2,6-di-*t*-butylation of phenol and *p*-cresol should not be allowed in the pores of H-Y zeolites.

Heteropolyacids (HPA), such as HPW and HSiW, supported on ordered mesoporous silica MCM-41 posses highly dispersed acidity with minimum pore size, and their steric restriction to access bulky molecules may be looser than those of zeolites [24, 25]. These HPA supported on ordered mesoporous silica were used successfully for the solid acid catalysts in various organic reactions [26]. The characterization of some of HPA catalysts supported on MCM-41 was described in our previous paper [22].

Typical results of *t*-butylation of *p*-cresol over HPW(30)/MCM-41[1] at 110 °C under 10 MPa of CO_2 pressure are also shown in Table 1. The yield of 2,6-DTBPC was dramatically enhanced compared to the H-Y zeolite. The increase in the yield may be due to the larger pore size availability for the diffusion of reactants and formation of products. The another reason is due to lower deactivation caused in supercritical CO_2 compared to conventional organic solvents [3]. The yield of 2,6-DTBPC (53%) observed for HPW(30)/MCM-41 was the highest yield ever observed in literature: the maximum yield of DTBC was 20% in the vapor phase reaction [14]. The *t*-butylation of *p*-cresol over relatively weaker HSiW(30)/MCM-41 resulted in lower 2,6-DTBPC yield (21.2%). [Al]-MCM-41 (SiO_2/Al_2O_3 ratio = 30) had also only low activity. These low activities are due to weaker acidities of HSiW and [Al]-MCM-41 compared to zeolites and HPA supported on MCM-41. MCM-41 had no activity for the *t*-butylation of *p*-cresol. These results suggest that MCM-41 works as

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[1] The value in parentheses shows the weight percent of HPA on MCM-41.

Table 1
The *t*-butylation of *p*-cresol over H-Y and HPA/MCM-41 catalysts[a]

Catalyst	Conversion /%	Yield /% 2,6-DTBPC	2-TBPC
H-Y(5.2)[b)]	99	3.4	96
H-Y(12)[b]	97	3.0	94
H-Y(30)[b]	98	3.7	95
H-Y(40)[b]	98	3.0	94
H-Y(60)[b]	97	3.1	92
H-Y(80)[b]	71	0.4	69
H-Beta(25)[b]	56	1.0	53
HPW(30)/MCM-41	99	53	46
HSiW(30)/MCM-41	98	24	71
MCM-41	1.0	–	1.0
[Al]-MCM-41(30)[b]	47	4.0	41
HPW(30)/MCM-41[c]	85	6.7	78
HPW(30)/MCM-41[d]	93	24	69

[a] Reaction conditions: catalyst, 100 mg; substrtate: *p*-cresol, 1.0 g (9.24 mmol) and *t*-butanol, 2.7 g (36.9 mmol); temperature, 110 °C; period, 5 h; CO_2 pressure, 10 MPa.

[b] The value in parentheses shows the SiO_2/Al_2O_3 ratio of zeolite and mesoporous silica.

[c] Hexane (15 mL) was used as solvent. Reaction conditions were the same except CO_2 pressure.

[d] The reaction was carried out under N_2 pressure. Reaction conditions were the same except CO_2 pressure.

the support for highly dispersed HPW, and provides the reaction circumstances for the formation of bulky 2,6-DTBPC by the cooperation of strong acid. The hydrophobic character of MCM-41 also enhances the diffusion of water from acidic sites.

Figure 1 shows the influences of reaction temperature on the *t*-butylation of *p*-cresol over HPW(30)/MCM-41 under 10 MPa of CO_2 pressure. The conversion of the *p*-cresol was 23% at 90 °C. However, the catalytic activity increased rapidly with increasing the reaction temperature from 100 to 140 °C. The yield of 2,6-DTBPC was enhanced with increasing of temperature and reached the maximum (53%) at 110 °C, and it decreased to some extent with further increase in the temperature. The decline in the yield of 2,6-DTBPC is ascribed to its de-alkylation at higher reaction temperatures: the formation of 2-TBPC was observed by the contact of 2,6-DTBPC with the catalyst at 140 °C in supercritical CO_2.

The influence of CO_2 pressure on the *t*-butylation of *p*-cresol is shown in figure 2. The conversion of *p*-cresol was not significantly influenced by CO_2 pressure in the range of 8–11 MPa; however, dramatically dropped down with further increase in CO_2 pressure to result in the decrease of the yield of 2,6-DTBPC. Similar phenomena were also observed in our previous work [23]. High pressure CO_2 above the optimum pressures retards the *t*-butylation of *p*-cresol. Supercritical CO_2 at high pressures is dense enough to hinder the access of reactant molecules to the catalytic centre, and decreases the conversion and the yield of 2,6-DTBPC. The influence of the weight of the catalyst on the catalysis was examined; however, any significant change was not observed in the conversion or yield of the products.

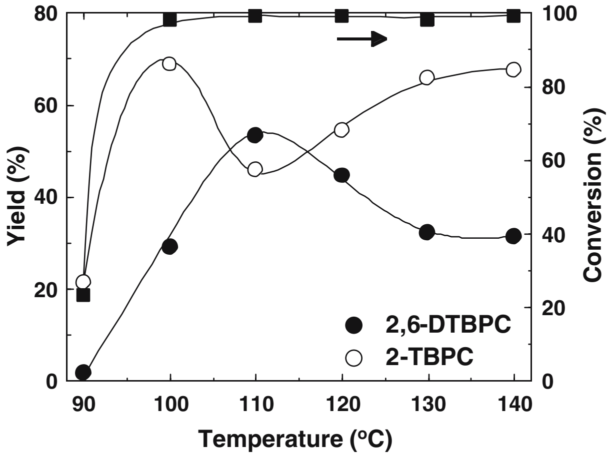

Figure 1. The influences of reaction temperature on the *t*-butylation of *p*-cresol over HPW(30)/MCM-41. Reaction conditions: catalyst: HPW(30)/MCM-41, 100 mg; *p*-cresol, 1.0 g (9.24 mmol); *t*-butanol, 2.7 g (36.9 mmol); period; 5 h; CO_2 pressure, 10 MPa.

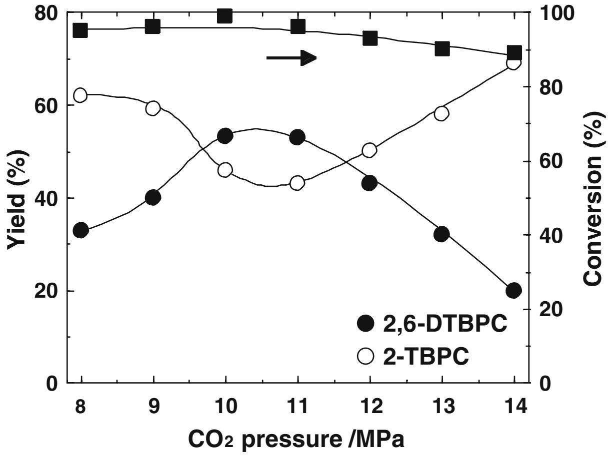

Figure 2. The influences of CO_2 pressure on the *t*-butylation of *p*-cresol over HPW(30)/MCM-41. Reaction conditions: catalyst: HPW(30)/MCM-41, 100 mg; substrate: *p*-cresol, 1.0 g (9.24 mmol) and *t*-butanol, 2.7 g (36.9 mmol); temperature, 110 °C; period: 5 h.

Figure 3 shows the influences of reaction period on the *t*-butylation of *p*-cresol over HPW(30)/MCM-41 at 110 °C under 10 MPa of CO_2 pressure. The formation of 2-TBPC was predominant at the early stages; however, the yield of 2,6-DTBPC was increased with the increase in reaction period. The reaction is completed after 6 h, and no further change in the yields of the products was observed with longer reaction periods. These results show that the di-*t*-butylation occurs *via* a consecutive introduction of *t*-butyl groups in *p*-cresol.

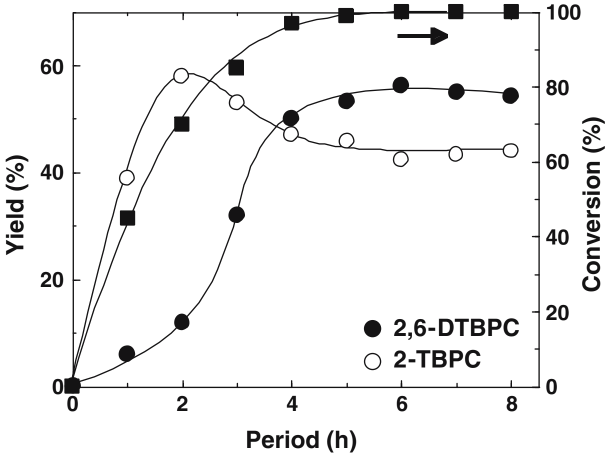

Figure 3. The influences of reaction period on the *t*-butylation of *p*-cresol over HPW(30)/MCM-41. Reaction conditions: catalyst: HPW(30)/MCM-41, 100 mg; substrate: *p*-cresol, 1.0 g (9.24 mmol) and *t*-butanol, 2.7 g (36.9 mmol); temperature, 110 °C; CO_2 pressure, 10 MPa.

Only small change of the XRD patterns was observed on of the catalyst before and after using the *t*-butylation of *p*-cresol in supercritical CO_2 (Figure not shown). These results mean that the mesoporous structure of HPW(30)/MCM-41 was not destroyed significantly by the water formed by the dehydration of water from *t*-butanol. Mesoporous structure of MCM-41 is sometimes destroyed by water; however, the stability of mesoporous structure in this study should be due to the rapid diffusion of water from *t*-butanol. Surface area of HPW(30)/MCM-41 was decreased from 645 m^2/g for fresh catalyst to 625 m^2/g for recovered catalysts: this change of surface area during the catalysis suggests almost no decline of the catalyst structure because the encapsulated products reduce the surface area.

It is very important to know the coke-formation during the catalysis. Figure 4 shows thermogravimetric profiles from 250 to 800 °C of the HPW(30)/MCM-41 used for the catalysis under different reaction media. The coke-formation occurred in almost all reaction environments in the range of 400–700 °C, however, the amounts of the coke were depended on the reaction media. The catalysts used in supercritical CO_2 had the slight weight loss at *ca.* 450 °C; however, this loss is much less than the catalysts used in the other reaction media. On the other hand, no significant coke formation was observed for the H-Y zeolites in supercritical CO_2. Similar results were obtained in the *t*-butylation of phenol [23]. These differences of the coke-formation between HPW(30)/MCM-41 and H-Y zeolites in the *t*-butylation of *p*-cresol are explained by the stronger acidity of the HPW/MCM-41 catalysts compared to that of H-Y zeolites. The coke-precursors, such as polynuclear aromatics from *p*-cresol and isobutene oligomers from *t*-butanol, should be difficult to be cleaned completely from on HPW(30)/MCM-41 even in supercritical CO_2 although it is the best medium for removing them. On the other hand, the severe coke formation was observed for the other reaction media. Amounts of the coke after 20 min and 6 h were in the same level for liquid phase reaction in hexane over HPW(30)/MCM-41. These results indicate that the coke-formation in liquid phase catalysis occurred particularly at initial stages. The *t*-butylation of phenol under N_2 atmosphere also accompanied the coke-formation: the amount of the coke was in the similar level of the case of liquid phase reaction. The coke-formation caused the deactivation of the catalysts, and resulted in the decrease of the yield of 2,6-DTBPC (Figure 4).

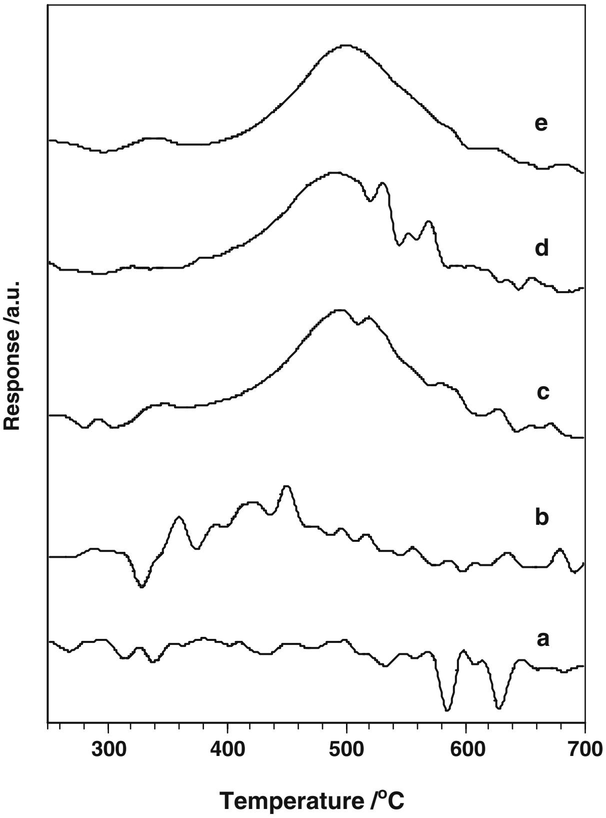

Figure 4. TG profiles of the catalysts used for the *t*-butylation of *p*-cresol. Sample: 10 mg; Programmed rate: 10 °C/min; under air stream. Reaction conditions: catalyst, HPW(30)/MCM-41, 100 mg; substrate: *p*-cresol, 1.0 g (9.24 mmol) and *t*-butanol, 2.7 g (36.9 mmol); temperature, 110 °C; period, 5 h. Samples: (a) fresh catalyst before use, (b) the catalyst used in supercritical CO_2, (c) the catalyst used under N_2 pressure, (d) the catalyst used in hexane for 20 min, (e) the catalyst used in hexane for 6 h.

From these results, we can emphasize that supercritical CO_2 is the best medium for the *t*-butylation of *p*-cresol with *t*-butanol over HPW(30)/MCM-41 although there is a limitation to dissolve coke-precursors formed during the reaction.

4. Conclusion

HPW(30)/MCM-41 and H-Y zeolites are excellent solid acid catalysts for the *t*-butylation of *p*-cresol with *t*-butanol in supercritical CO_2. The catalytic activity to yield 2,6-DTBPC over HPW(30)/MCM-41 was much higher than that over H-Y zeolites. HPW(30)/MCM-41 gave the highest yield of 2,6-DTBPC (53%) among the catalysts. These differences are ascribed to the availability of the free catalytically active centers: the pores of MCM-41 are big enough for the formation of 2,6-DTBPC, and H-Y cannot allow its accommodation. The coke formation over HPW(30)/MCM-41 and H-Y catalysts was very less in supercritical CO_2 during the catalysis. These results emphasize that supercritical CO_2 is an appropriate solvent for the synthesis of 2,6-DTBPC compared to conventional organic solvents: this is the biggest merit of supercritical CO_2 using as a medium in the acid catalysis.

Acknowledgments

A part of this work was financially supported by a Grant-in Aid for Scientific Research (B) 16310056, the Japan Society for the Promotion of Science (JSPS). G. Kamalakar is grateful to JSPS for the postdoctoral fellowship.

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