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The *t*-Butylation of Phenol in Supercritical Carbon Dioxide over H–Y Zeolite. Remarkable Enhancement of Catalytic Performance for the Formation of 2,4-Di-*t*-butylphenol

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Remarkable enhancement of the formation of 2,4-di-*t*-butylphenol was observed in the *t*-butylation of phenol over H–Y zeolite under supercritical CO_2 medium. Supercritical CO_2 renders active sites free for the catalysis by fast removal of coke-precursors.

Environmental concerns arising from the use of conventional organic solvents and subsequent generation of hazardous waste generated a considerable interest in developing benign chemical processes that either significantly suppresses the pollution at the source or eliminate them completely.[1]

One of the areas which promises to have significant potential for green chemical processes is supercritical fluid as reaction medium.[2–7] Supercritical CO_2 possesses intermediate properties of liquid and vapor. Supercritical solvent is an appropriate medium for dissolving the high molecular weight aromatics which causes the deactivation of the catalyst during the reaction. Recently, several researchers have successfully employed the supercritical CO_2 for the synthesis of organic compounds.[8–11]

Several industrially important compounds are produced based on the Friedel–Crafts reaction. For example, 2,4-di-*t*-butylphenol (2,4-DTBP) by the alkylation of phenol with *t*-butanol is an important intermediate for anti-oxidant, speciality chemicals, and polymers. Normally, Lewis or Brønsted acids are used as versatile catalysts for this reaction; however, they generate hazardous side products which cause environmental problems. Hence, solid acids, such as zeolites, montmorillonite, and supported heteropolyacids on mesoporous materials were applied for this reaction.[12–15] However, all these solid acids were suffered from considerable deactivation during the reaction. Moreover, *o*- and *p*-*t*-butylphenols (*o*- and *p*-TBP) was principal products and the yield for 2,4-DTBP is low in the case of modified mesoporous materials and zeolites such as Beta and SAPO-5. For example, Anand et al. found that H–Y zeolite is an appropriate candidate for the selective synthesis of 2,4-DTBP by the *t*-butylation of phenol in vapor phase, and obtained the maximum yield for 2,4-DTBP (38.1%).[7]

The advantages of supercritical fluids and H–Y zeolite prompted us to carry out the *t*-butylation of phenol in supercritical CO_2 to increase the yield for 2,4-DTBP. In the present paper, we describe merits of supercritical CO_2 medium for the selective formation of 2,4-DTBP in the *t*-butylation of phenol over H–Y zeolites.

The typical reaction procedure is as follows: the substrates (phenol(1 g)/*t*-butanol(1.57 g) = 1/2 mol/mol), H–Y zeolite (Tosoh Corporation, Japan, HSZ-320-HOA, SiO_2/Al_2O_3 = 5.2, 100 mg), and dry ice were loaded into an autoclave (100 mL). The amount of CO_2 necessary for the reaction conditions were calculated from the empty volume of the reactor. 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). Thermogravimetric analysis was carried on a Shimadzu TG-DTG-50 analyzer with temperature-programmed rate of 10 °C/min in an air stream.

Table 1. The *t*-butylation of phenol over acid catalysts in supercritical CO_2[a]

Catalyst[b]	Conv. /%	Yield/%			
		o-TBP	*p*-TBP	2,4-DTBP	Others
H–Y(5.2)	100	21.5	13.5	65.0	—
HPW/MCM-41[c]	99.0	18.2	20.5	58.5	1.8[d]
[Al]-MCM-41(30)	41.0	19.1	21.9	0	—
H-Beta(25)	72.1	17.2	52.3	2.6	—
H–Y(5.2)[e]	59.1	22.1	31.2	5.8	—
H–Y(5.2)[f]	68.0	21.8	11.1	35.1	—

[a] Reaction conditions: Catalyst: 100 mg; temperature: 130 °C; phenol/*t*-butanol: 1/2 mol/mol; CO pressure: 10 MPa; time: 6 h. [b] Values in parentheses are SiO_2/Al_2O_3 ratio. [c] 30 wt % Tungstophosphoric acid on MCM-41. [d] 2,6-Di-*t*-butylphenol (2,6-DTBP). [e] In hexane under autogeneous pressure. [f] Under 10 MPa of N_2.

Table 1 shows the effects of type of catalysts and reaction media for the *t*-butylation of phenol. H–Y gave 2,4-DTPB in high yield with the formation of *o*- and *p*-TBP. Tungstophosphoric acid supported on MCM-41 (HPW (30%)/MCM-41) also gave high yield of 2,4-DTBP although a small amount (≈2%) of 2,6-DTBP was accompanied; however, [Al]-MCM-41(30) had no activity for the di-*t*-butylation in supercritical CO_2, which indicates that the acid strength of the catalyst may also be playing an important role for this reaction. H-Beta zeolite gave principally TBP isomers: this is due to the pore size restriction of structure of Beta zeolite. The reaction in liquid phase using hexane solvent mainly yielded TBP isomers. However, the *t*-butylation under N_2 (10 MPa) gave about 32–35% yield of 2,4-DTBP.

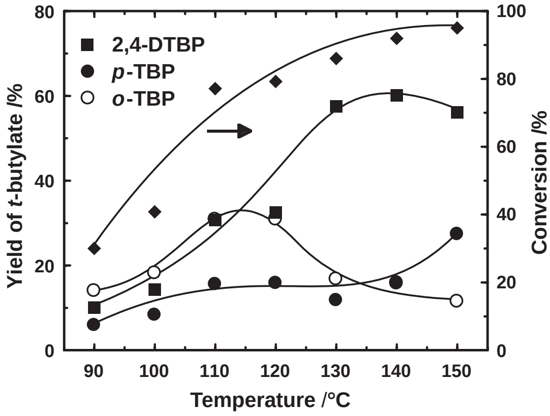

Figure 1. Effects of reaction temperature on the *t*-butylation of phenol under supercritical CO_2. Reaction conditions: phenol/*t*-butanol = 1/2 (mol/mol); catalyst, H–Y, 100 mg; CO_2 pressure: 10 MPa; time: 4 h.

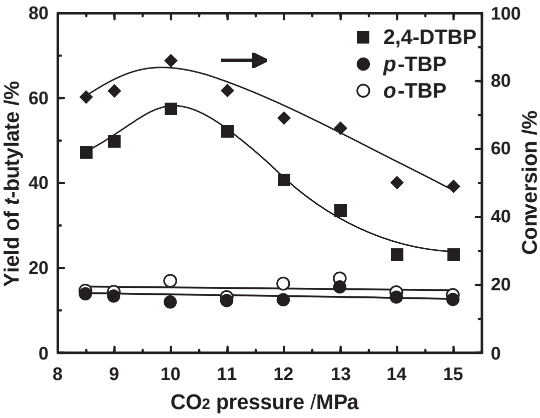

Figure 2. Effects of CO_2 pressure on the *t*-butylation of phenol under supercritical CO_2. Reaction conditions: phenol/*t*-butanol = 1/2 (mol/mol); catalyst, H–Y, 100 mg; temperature, 130 °C; time, 4 h.

The effects of reaction temperature on the *t*-butylation of phenol over H–Y are shown in Figure 1. The conversion of phenol and the yield of 2,4-DTBP increased with increasing reaction temperature, and particularly, they were enhanced at a higher temperature than 120 °C: 65% yield of 2,4-DTBP was achieved at 130 °C and CO_2 pressure at 10 MPa. The yield for 2,4-DTBP was considerably higher than *o*- and *p*-TBP isomers at all temperatures. However, liquid phase reaction in hexane or the reaction under N_2 pressure gave lower yield of 2,4-DTBP as shown in Table 1. H–Y zeolite was rapidly deactivated by heavy aromatics formed under vapor-phase reaction conditions.[7] The increase in the yield of 2,4-DTBP is mainly due to the effects of supercritical CO_2 to keep the acid sites of H–Y zeolite to be rendered free for the dialkylation because heavy aromatics should be removed by their dissolution in supercritical CO_2. The enhancement is because of the availability of the free active site during the course of the reaction in supercritical CO_2 medium. Supercritical fluids provide the advantage of the higher dissolution power and also possess intermediate properties in comparison with the reaction under liquid and vapor phase, which facilitates the better mass transfer of the reactants, and products thus maintaining the activity of the catalyst with considerably lower deactivation even at longer reaction times.

Figure 2 summarizes the effects of the CO_2 pressure on this reaction. We should notice that an increase in the reaction pressure from 8.5–10 MPa has increased the conversion of phenol by the increase in the solubility of the reactants; however, the decrease of phenol conversion occurred by further increase in the pressure (>11 MPa). CO_2 with higher density at higher operating pressures disturbs the access of the reactant to catalytic active center by its preferential interaction with the zeolite.[6] From these reasons, the yield of 2,4-DTBP increased with the CO_2 pressure; however, it decreased with the increase in the pressure although the system was under supercritical region in both cases.

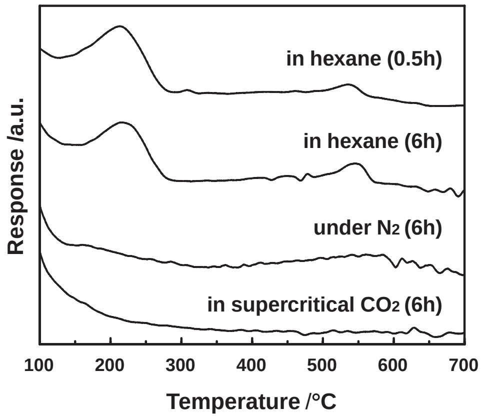

Figure 3. Thermogravimetric profiles of H–Y zeoltie used for the reaction.

Thermogravimetric profiles of H–Y zeolites used in the reaction were given in Figure 3. Almost no coke-deposition was observed for H–Y zeolites in supercritical CO_2. However, coke was found for the catalyst for liquid-phase reaction in hexane. Almost the same amount of coke was observed by the reaction for 30 min and 6 h: the deactivation in hexane occurs in short time. The coke formation was also found under N_2 atmosphere. These observations unambiguously prove the minimal deactivation in supercritical CO_2.

We have also studied the recyclability of the H–Y catalyst in supercritical CO_2, and found reasonably good activity for the catalyst even after the three reaction cycles.

From these results, we can conclude that supercritical CO_2 can remarkably enhance the formation of 2,4-DTBP in the *t*-butylation of phenol because supercritical CO_2 keeps acid site of H–Y zeolite free for the dialkylation by efficient dissolution of heavy aromatics, coke precursors. The current process is the most selective for the formation of 2,4-DTBP among the processes in the literatures. This study exemplifies that the use of supercritical CO_2 medium is a potential way for the prevention of the deactivation of the catalysis by severe coke-formation. Moreover, the proposed process is greener, and ensures the least pollution thus showing a cleaner way for further the Friedel–Crafts chemistry.

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