

Effect of solvent, catalyst type and catalyst activation on the microwave transformation of 2-*tert*-butylphenol

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Abstract

Transformation of 2-*tert*-butylphenol (2TBP) in heterogeneous solid–liquid catalytic systems has been investigated. To reach the desired temperature, reaction mixtures were heated up by conventional (CH) and microwaves (MW) methods. Solid catalysts of different acidity (zeolite HZSM5 and Mordenite, Montmorillonite KSF and K10, neutral, weakly acid and acidic alumina, Bentonite), polar and non-polar solvents, as well as the activation of the catalyst and the modality of introducing the microwave energy into the reaction mixture have been studied. Results were discussed in terms of reaction pathway, selectivity and reaction rate indicating superheating effect of catalyst. The observed unusual dilution effect resulting surprisingly in higher reaction rate was explained by a catalytic mechanism. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Microwaves; *tert*-Butylphenols; Catalyst activation; Solvent effect; Active sites

1. Introduction

Acceleration of chemical reactions by microwave dielectric heating has been widely exploited in the last years. Microwave processing is becoming an increasingly important accessory in chemical synthesis [1]. Remarkable reduction in reaction time, improved isolated yields of products and sometimes effects on chemo-, regio- and stereoselectivity have been achieved in organic synthesis [1,2]. Differences in reaction pathways and reaction products due to the microwave processing have been observed. So far, it is generally accepted that the microwave effect can

consist at least of rapid and uniform heating, inverse temperature profiles, and selective heating, all of these phenomena leading to reduced processing times and temperatures. However, the mechanism responsible for these effects is not yet well understood. Thus, the question of whether there is a non-thermal effect or whether the measured temperature does represent the true reaction temperature due to the presence of temperature gradients remains to be answered.

The simplest method for carrying out microwave-assisted synthetic reactions involves irradiation of reactants only (*solvent-free*), in an open vessel made of glass, Teflon or ceramic. The process is very limited due to the reduced number of suitable high boiling organic compounds. Two *solvent-free* techniques have been developed in the last years [3–5]: *dry media* using a solid mineral support and *solid–liquid phase transfer catalysis*.

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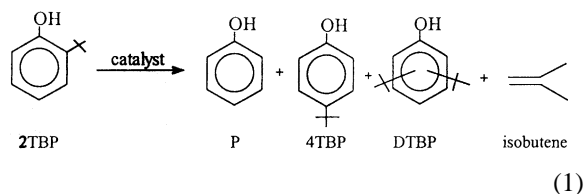
The aim of this paper was the investigation of 2-*tert*-butylphenol (2TBP) transformation in the presence of non-polar and polar solvents, the effect of different types of catalysts on the reaction pathway, as well as the method of activation of the catalyst and of introducing the microwave energy into the reaction medium.

2. Experimental

The equipment and experimental conditions for both microwave (MW) and conventional (CH) heating systems were described in detail in previous papers [6–8]. MW experiments at room temperature have been carried out by intensive cooling using a “dry ice” medium to keep the temperature $22 \pm 2^\circ\text{C}$. For the activation of KSF catalyst under microwave heating, the temperature profile was followed using a Nortech ceramic-coated optic fiber. Structure of DTBP was attributed to 2,4-di-*tert*-butylphenol (2,4DTBP) according to identical analytical data (NMR) with authentic sample.

3. Results and discussion

In continuation of our studies on the transformation of *tert*-butylphenols [6] it was found that depending on the experimental conditions, the catalytic transformation of 2TBP provides phenol (P), the isomeric 4-*tert*-butylphenols (4TBP), (2,4DTBP) and isobutene, in accordance with the following equation:



We also found [6] that the transformation of 2TBP includes isomerization, transalkylation and dealkylation reactions; their proportions being dependent on the catalyst type, reaction conditions and method of heating (CH or MW). The experiment also demonstrated that the isomerization reaction occurred via transalkylation and not by a 1,2-shift mechanism during an intramolecular rearrangement [6].

Table 1

Dependence of activity of catalyst on the method of activation^a

Activity test	Initial reaction rate ($r^0 \times 10^3 \text{ s}^{-1}$)			
	A ^b	B ^c	C ^d	D ^e
CH	0.115	0.490	1.782	0.820
MW continuous	0.406	1.620	2.526	1.769
MW pulsed ^f	0.214	1.256	2.530	1.353

^a Reaction conditions: 2TBP/KSF/hexane = 20 ml/4 g/40 ml; reflux temperature, 76°C ; reaction time, 30 min; $P_{\text{MW}} = 200 \text{ W}$.

^b KSF inactivated (water content = 6.2%).

^c KSF activated for 2 h in electric oven at $120\text{--}140^\circ\text{C}$ (water content = 1.3%).

^d KSF activated for 2 h in electric oven at $320\text{--}340^\circ\text{C}$ (water content = 0.0%).

^e KSF activated for 3×10 min in domestic microwave oven (water content = 1.9%).

^f 5 s pulses in 20 s intervals.

3.1. Activation of the catalyst

Taking KSF as the representative type of acidic catalyst, experiments to investigate the influence of the activation method (A–D) on its activity were performed. The activation of the catalyst was done by heating up the catalyst in an electric oven—catalysts B and C—and in domestic microwave oven (Whirlpool)—catalyst D. Catalyst A corresponds to non-activated one.

Results are discussed using the initial reaction rate (r^0) and compared to the results obtained by using the inactivated commercial catalyst—catalyst A. The obtained data are summarized in Table 1 and Figs. 1–4.

It is evident that water content plays a very important role in catalytic activity of KSF catalyst. There were no main differences when water was removed by CH or MW heating, either continuous or pulsed system. However, microwaves required about four times shorter period of activation compared to conventional electric activation method. In all cases higher activity of the catalyst was reached when experiments were performed under MW conditions. This effect is probably caused by supplementary activation of catalyst by microwaves during the reaction (see Section 3.3.1) as indicated by induction period, Fig. 1.

3.2. Selectivity and activity of the catalyst

In order to investigate an optimal condition of activation, the activity and selectivity of eight catalysts on

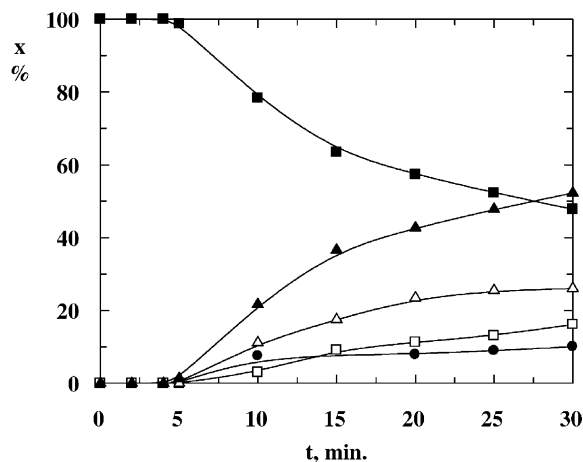


Fig. 1. MW transformation of 2TBP (2TBP, ■) at 200 W (continuous power); KSF inactivated (A); water content, 6.2%. (▲) Total conversion; (●) phenol; (□) 4TBP; (△) 2,4DTBP.

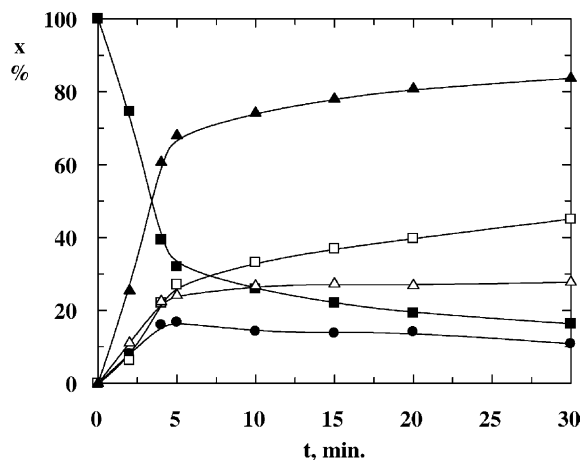


Fig. 3. MW transformation of 2TBP (2TBP, ■) at 200 W (continuous power); KSF activated for 2 h at 320–340 °C in electric oven (C); water content, 0% (loss 6.2%). (▲) Total conversion; (●) phenol; (□) 4TBP; (△) 2,4DTBP.

2TBP transformation were tested and the results are summarized in Table 2.

The activity of the catalysts was found to decrease in the order KSF = K10 = HZSM5 = Mordenite > Bentonite > Al₂O₃ a > Al₂O₃ wa > Al₂O₃ n in relation to their acidity. The selectivity of the catalyst increased in the opposite direction, in accordance with the rule, lower activity led to higher selectivity.

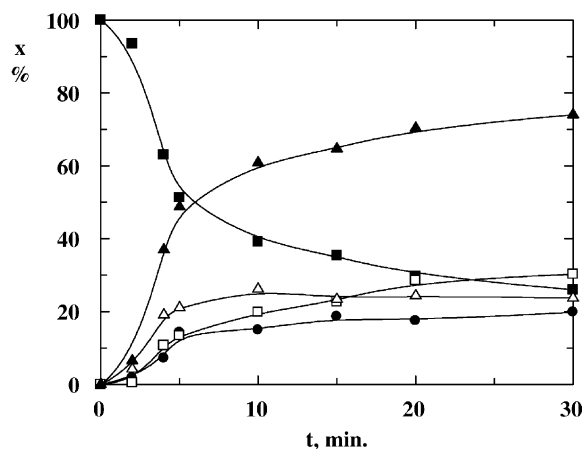


Fig. 2. MW transformation of 2TBP (2TBP, ■) at 200 W (continuous power); KSF activated for 2 h at 120–140 °C in electric oven (B); water content, 1.3%. (▲) Total conversion; (●) phenol; (□) 4TBP; (△) 2,4DTBP.

The transformation of 2TBP in the presence of strong acidic catalysts (Montmorillonites KSF and K10, zeolites HZSM5 and Mordenite) was very fast even at 105 °C. None of the low acidic or neutral catalysts reacts at temperatures below 105 °C in either MW or CH heating systems. However, a major difference in selectivity was recorded when carrying out the reaction in the presence of strong acid catalysts

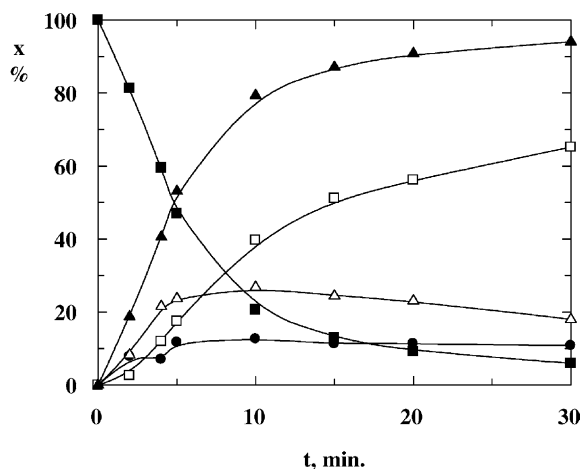


Fig. 4. MW transformation of 2TBP (2TBP, ■) at 200 W (continuous power); KSF activated for 3 × 10 min at 750 W in domestic microwave oven (D); water content, 1.9%. (▲) Total conversion; (●) phenol; (□) 4TBP; (△) 2,4DTBP.

Table 2
Selectivity dependence on the catalyst type^a

Catalyst	CH			MW				
	Conversion (%)	Selectivity ^b (%)			Conversion (%)	Selectivity ^b (%)		
		Phenol	4TBP	Dialkyl		Phenol	4TBP	Dialkyl
Al ₂ O ₃ n ^c	5.73	85.69	8.73	5.58	8.61	90.34	6.04	3.60
Al ₂ O ₃ wa ^c	6.98	89.54	6.73	3.87	6.84	81.43	9.36	4.97
Al ₂ O ₃ a ^c	19.25	76.42	17.14	12.57	38.17	81.34	14.46	8.17
Bentonite	62.84	38.12	35.92	25.95	74.65	40.69	41.56	17.74
K10	97.46	27.35	61.00	11.65	98.74	53.18	40.77	6.06
KSF ^c	98.32	41.28	47.12	8.26	98.89	53.70	40.00	5.27
HZSM5 ^d	97.32	25.45	68.29	6.44	97.47	32.10	63.36	4.53
Mordenite ^d	97.21	36.19	58.95	4.86	98.02	47.98	50.04	1.98

^a Reaction conditions: 2TBP/catalyst = 5 ml/1 g; reflux temperature, 190–196 °C; reaction time = 30 min; P_{MW} = 550 W; each catalyst activated ~2 h at 340 °C in electric oven.

^b Selectivity was calculated with the relation:

$$\text{selectivity} = \frac{C_P}{\sum C_P} \times 100\%$$

where C_P is the molar concentration of phenol and $\sum C_P = C_P + C_{4TBP} + C_{DTBP}$.

^c n—Neutral; wa—weakly acidic; a—acidic (5% SO₄²⁻).

^d 2TBP/catalyst = 10/1.

^e The selectivity for trialkylphenols was determined: CH = 3.34%; MW = 1.03%.

at reflux temperature (196–199 °C) under both MW and CH conditions. While under MW conditions, isobutene was vigorously evolved for all the four catalysts used, under CH conditions its evolution was either very poor or absent. These results can be explained by *superheating* of the catalyst by microwaves, when higher temperature of catalyst (or its active sites [9]) is favorable for dealkylation reactions.

3.3. Solvent and dilution effect

In order to investigate the 2TBP transformation in the presence of the acidic type catalysts in more detail, the reaction rate was lowered by the decrease of the reaction temperature, dilution with polar and non-polar solvents and the reduction of the catalyst concentration.

Commercial Montmorillonite KSF was chosen to represent acidic catalysts. The results obtained under identical CH and MW experimental conditions were compared using the initial reaction rate (r^0).

3.3.1. Solvent effect

(a) *Non-polar solvents*: Using non-polar solvents such as heptane and hexane at their reflux temperature

(105 and 75 °C), the rate enhancement factor between MW and CH experiments of the transformation reaction had the same trend as without solvent. Moreover, the rate enhancement factor was more evident at lower temperatures, see Table 3. However, the rate enhancement factor in the presence of non-polar solvents was reduced. This effect can be explained by a better elimination of temperature gradients in the presence of a solvent compared to experiment in the neat medium.

(b) *Polar solvents*: In the presence of polar solvents, represented by methanol and tetrahydrofuran, no reaction was noted either for MW or CH experiments. This effect was attributed to the stronger adsorption of these solvents compared to phenols, indicating that 2TBP does not react without adsorption. When carrying out the reaction in the absence of catalyst or in the presence of a low acidic or neutral catalyst, none or weak adsorption of 2TBP was noted and therefore no conversion was observed.

Similarly, water has been found to have a strong inhibitory effect on the reaction rate. However, an interesting effect of partial inhibition of catalyst activity by the addition of a small amount of water was observed,

Table 3

Catalytic transformation of 2TBP—initial reaction rate (r^0) dependence on the catalyst concentration and dilution by solvent at the ratio 2TBP/hexane = 1/0.5 ml and 1/0 ml^a

KSF/2TBP (g/ml)	CH			MW		
	$r_{1/0.5}^0 \times 10^{-3} \text{ s}^{-1}$	$r_{1/0}^0 \times 10^{-3} \text{ s}^{-1}$	$r_{1/0.5}^0/r_{1/0}^0$	$r_{1/0.5}^0 \times 10^{-3} \text{ s}^{-1}$	$r_{1/0}^0 \times 10^{-3} \text{ s}^{-1}$	$r_{1/0.5}^0/r_{1/0}^0$
0.0125	0.05	0.02	2.50	0.13	0.11	1.18
0.025	0.15	0.07	2.14	0.18	0.16	1.13
0.05	0.86	0.41	2.10	1.19	1.18	1.09
0.2	2.92	1.40	2.09	2.93	2.85	1.03

^a Reaction conditions: catalyst KSF; reflux temperature = 75 °C, reaction time = 30 min, $P_{\text{MW}} = 550 \text{ W}$.

2% (p.w.) of water added to the reaction mixture causing a drastic reduction of catalytic activity. Reaction rate under CH conditions was reduced 44 times and under MW conditions 10 times. Rate enhancement factor 6.2 can be attributed to the partial reactivation of catalyst in situ by effective removal of water by microwaves as was indicated by induction period [6].

3.3.2. Dilution effect

The dilution of the reaction mixture with a limited amount of hexane led to a surprising result. When the transformation was performed under CH conditions and the reaction mixture (2TBP + KSF) was diluted by hexane at volume ratio 2TBP/hexane = 1/0.5, the reaction rate was unexpectedly higher (about twice) for all concentrations of catalyst investigated, KSF/2TBP = 0.2–0.0125/1, Table 3. Under MW conditions, the dilution effect was not so evident because of the higher reaction rate, even without dilution.

By investigation of different degrees of dilution ratio 2TBP/hexane, it was found that this effect took place only at the ratio of 1/0.5. In every case, the reaction rate in MW experiment was higher than in CH experiment, Table 4.

For these unexpected and unique results—when a reaction rate is higher under reduced concentration of catalyst by dilution—we looked for the following possible explanations:

1. Diffusion effect,
2. Inhibition effect,
3. Mechanistic effect.

Under experimental conditions no internal or external diffusion could be possible because an efficient stirring and very fine catalyst particles (10–15 μm)

Table 4

The effect of dilution by hexane on the CH and MW transformations^a

2TBP/hexane (ml/ml)	$r_{\text{CH}}^0 \times 10^{-3} \text{ s}^{-1}$	$r_{\text{MW}}^0 \times 10^{-3} \text{ s}^{-1}$	$r_{\text{MW}}^0/r_{\text{CH}}^0$
1:0	1.40	2.85	2.04
1:0.5	2.92	2.93	1.00
1:1	0.65	2.26	3.48
1:2	0.49	1.62	3.31
1:4	0.24	0.82	3.41

^a Reaction conditions: catalyst KSF; 2TBP/KSF = 5 ml/1 g; reflux temperature = 75 °C; reaction time = 30 min; $P_{\text{MW}} = 550 \text{ W}$.

were used. Inhibition of the catalyst by products is also improbable because no deactivation of the catalyst was observed. For this reason the first two possible explanations were excluded. Thus we assume that the increase of reaction rate by dilution is caused by mechanistic reasons related to the number of active sites needed for the surface reaction of corresponding catalytic mechanisms. The results indicate that at least one free active site should be available for the surface reaction of the adsorbed reactant species on other site. In the absence of a solvent, a limited number of free sites is probably available for the surface reaction, while in high dilution the absorption of reactant competes in adsorption with the solvent. Only in a narrow range of concentration of solvent in reaction mixture the higher reaction rate can be detected, which was the case of 1/0.5 ratio of dilution.

4. Conclusions

In spite of the complexity of the studied process, it can be concluded that microwaves did have a strong

influence on the reaction rate and on the activity and selectivity of the catalyst in transformation of alkylphenols. Two new interesting results have been found:

1. A rare favorable dilution effect on reaction rate of catalytic reaction. This effect is explained in terms of mechanistic reasons, which consist of at least one free active site available for the surface reaction of adsorbed molecule of the reactant.
2. Results concerning MW effect on reaction rate and selectivity indicate possible superheating of catalyst (or its active sites). Evolution of isobutene at refluxing reaction mixture and the highest rate enhancement factor at low (room) temperature supports superheating of catalyst.

The results gained at very low temperatures (below 0) where no reaction proceeded under conventional conditions but significant reaction rate was recorded under microwave conditions will be published in a subsequent paper [9].

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