Zeolitic behaviour of paratoluenesulfonic acid-modified clay in Friedel-Crafts synthesis of raspberry ketone

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ABSTRACT: During solventless alkylation of phenol with 4-hydroxy-2-butanone under microwave irradiation, paratoluenesulfonic acid (pTSA)-modified montmorillonite clays gave, regioselectively, 4-(4′-hydroxyphenyl)-2-butanone (raspberry ketone). The duration for this reaction under microwave irradiation is much shorter than that of the conventional method. A comparative study of the alkylation reaction over a montmorillonite clay sample treated with 0.5 M-pTSA (0.5 M-pTSA clay) with that of Al-exchanged montmorillonite (Al^{3+}-Mont) and beta-zeolite (HB) was carried out. The results show that the reaction time to reach equilibrium and the product distribution pattern for the reaction over 0.5 M-pTSA clay were similar to those values for the HB. Micropores formed on the clay surface during the pTSA treatment were found to enhance the rate of formation of C-alkylation. Micropores appear to enable better access to the active sites during the course of reaction.

KEYWORDS: Friedel-Crafts alkylation, raspberry ketone, zeolitic behaviour, paratoluenesulfonic acid, micropores.

Raspberry ketone [4-(4′-hydroxyphenyl)-2-butanone] is the principal flavour and odour source in raspberries (Arctander, 1969). In addition to its application in flavour and fragrance (Smith, 1996), raspberry ketone is used in the food and cosmetics industries, otherwise known as the 'cosmaceutical industry', *e.g.* because to its ability to burn subcutaneous fat, raspberry ketone is used in dietary supplements promoting weight loss and in skin-lightening cosmetics (Ikemoto *et al*., 1998; Fukuda *et al*., 1998; Hikima *et al*., 2000; Kosjek *et al*., 2003). Industrially, raspberry ketone is prepared by using an homogeneous catalyst such as H_2SO_4, H_3PO_4, aqueous HCl (A. G. Badische Anilin-und Soda-Fabrik, 1973), or cation-exchange resin Dowex-50W (Kokai Tokkyo Koho, 1980) by the alkylation of phenol with either 4-hydroxy-2-butanone (γ-KB) or methyl vinyl ketone (MVK).

Friedel-Crafts alkylation is among the few reactions where alkyl substituents are introduced into the aromatic ring (Degnan *et al*., 2001; Venuto *et al*., 1966; Namuangruk *et al*., 2004). The alkylation can be carried out by heterogeneous as well as homogeneous acidic catalysts (Sartori & Maggi, 2009; Poh *et al*., 2006; Thomas & Thomas, 1997). Homogeneous acid catalysts are highly corrosive and generate environmentally hazardous by-products, whereas heterogeneous acidic catalysts such as clays and zeolites are eco-friendly with tunable acidity (Nagendrappa, 2011; Choudhary & Misra, 2011). Alkylation of phenol with 4-hydroxy-2-butanone (γ-KB) or methyl vinyl ketone (MVK) has been carried out in the of presence of cation-exchanged montmorillonite (M^{n+}-Mont) (Tateiwa *et al*., 1994a,b), with HCl-modified montmorillonite (Dutta & Pathak, 2011) and modified beta zeolite (Cheralathan *et al*., 2003). Raspberry ketone has also been prepared using the catalyst Amberlyst-15 (Bunce & Reeves, 1989). These syntheses were carried out under liquid-phase conditions for a duration of 48 h to give, regioselectively, 4-(4′-hydroxyphenyl)-2-butanone (para product).

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Conventionally, acid activation of clays is achieved by heating them with mineral acids for several hours, whereas under microwave heating activation is achieved within 10 min. The acid activation of montmorillonite is generally by means of treatment with mineral acids which are highly corrosive and might result in uncontrolled structural damage to the mineral (Korichi *et al.*, 2009). Activation with organic acids, however, *e.g.* moderately strong pTSA, results in the controlled dealumination of clays (Ramesh *et al.*, 2012) and zeolites (Chandrashekar *et al.*, 2011). Ramesh *et al.* (2012) studied the microwave de-alumination of montmorillonite using various concentrations of pTSA solutions and noted the formation of micropores in the octahedral sheets as a result of dealumination during the pTSA treatment. This resulted in changes in characteristics such as specific surface area, pore volume and acidity. The catalytic activity of the clays treated was studied using esterification as a model reaction. Increases in acidity and pore volume were found to influence the catalytic activity. Venkatesha *et al.* (2015) investigated the role of micropores generated in the pTSA-treated clays in the Fries rearrangement. The accessibility to the acid sites through the micropores was found to enhance the ester-to-ketone transformation.

Previous studies of the synthesis of raspberry ketone using other catalysts have limitations with respect to longer reaction times. In the present study, the role played by micropores in pTSA-modified montmorillonite during the synthesis of raspberry ketone is reported. The reaction was conducted in solvent-free conditions under microwave irradiation to examine the effect on the reaction time in comparison with that of beta zeolite.

MATERIALS AND METHODS

The bentonite, Na^+-Mont, used here, was provided by Ashapura Chemicals, India. 4-Hydroxy-2-butanone was obtained from Sigma-Aldrich (Germany); pTSA and phenol by S.D. Fine Chemicals (India). The Na^+ form of beta zeolite with a Si:Al ratio of 30 was provided by Süd-Chemie, India Ltd. All commercially available organic and inorganic compounds were used without purification.

Preparation of the catalyst

The bentonite was modified by treatment with different concentrations of pTSA and subjected to microwave irradiation in a lab station START-S (Milestone, Italy), with built-in infrared automatic temperature control and magnetic stirrer. The bentonite was treated with 0.1 M, 0.2 M, 0.5 M and 1 M pTSA aqueous solutions as described by Ramesh *et al.* (2012) and the acid-activated clays were designated as 0.1 M-, 0.2 M-, 0.5 M- and 1 M-pTSA clay, respectively.

Al-exchanged clay (Al^{3+}-Mont) was prepared by treating the bentonite with aqueous Al chloride solution following the method described by Reddy *et al.* (2004). Beta zeolite was converted into the H-form by ion exchange with 1 M ammonium nitrate solution for 8 h with subsequent calcination at 823 K in air for 8 h and the mineral was designated as HB.

Catalyst characterization

X-ray diffraction data were recorded on a Philips X'pert PRO X-ray diffractometer with monochromatic (graphite monochromator) CuKα radiation (λ = 1.5405 Å). The BET specific surface area measurements were carried out using a QuantaChrome Nova-1000 surface analyzer at liquid nitrogen temperature. Nitrogen adsorption-desorption isotherm measurements were carried out in order to study the evolution of porosity and textural properties of the pTSA-treated and Al-exchanged clay samples. Full adsorption-desorption cycles were determined up to the saturation vapour pressure of nitrogen at 77 K. Pore-size distribution was calculated from adsorption data using the Barrett-Joyner-Halenda (BJH) method. The total acidity of the clay samples was measured by temperature programmed desorption (TPD) of ammonia studies. The Brønsted and Lewis acidity were measured by Fourier transform infrared (FTIR) spectroscopy using pyridine as the probe molecule. The FTIR spectra of the samples were recorded in the range 1400–1600 cm^{-1} using an IRAffinity-1 spectrometer (Shimadzu, Japan) with a resolution of 4 cm^{-1} with 40 scans. All clay samples were heated at 393 K for 2 h and cooled in a desiccator prior to analysis.

Catalytic test

All reactions were performed under microwave irradiation using microwave lab station START-S (Milestone, Italy) with a built-in infrared automatic temperature control and magnetic stirring, at desired temperatures ranging from 373 to 433 K. In a typical reaction, 20 mmol of phenol, 10 mmol of γ-KB and 0.5 g of the catalyst were placed in a 50 mL glass reactor along with a magnetic stirrer fitted with an air-cooled condenser. The mixture was then microwave irradiated at the reaction temperature for 60 min.
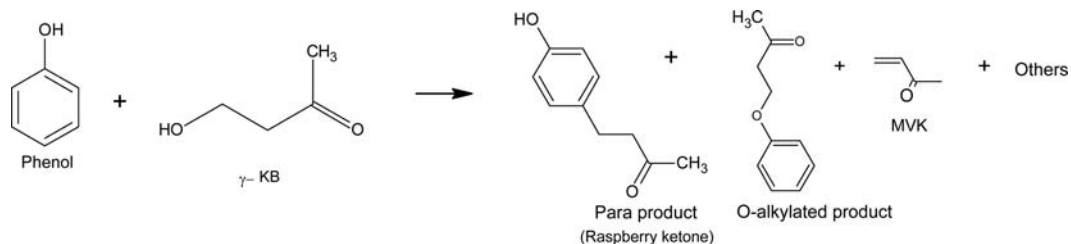
F_{IG}. 1. Alkylation of phenol with γ-KB catalysed by a pTSA-modified clay catalyst.

Variable power up to 1000 watts was applied by the microprocessor-controlled single magnetron system. The reaction mixture was cooled, extracted into 10 mL of toluene and the catalyst filtered off. The sample was analysed by gas chromatography (Chemito model GC 1000, FID detector, India) using methyl salicylate as internal standard in a TR-Wax capillary column (30 m × 0.32 mm). Products were further confirmed by gas-chromatography-mass spectrometry. To compare the performance of catalyst samples, alkylation reactions were also carried out under conventional heating in a stainless steel autoclave reactor heated to a desired temperature in a hot air oven.

RESULTS AND DISCUSSION

The alkylation of phenol with γ-KB catalysed by a pTSA-modified clay catalyst is illustrated graphically in Fig. 1. When the reaction was conducted under solvent-free microwave irradiation, a para product was formed along with an O-alkylated product, a methyl vinyl ketone (MVK) and other polymerized products. The conversion and selectivity of γ-KB and that of different products formed using different pTSA-modified clay samples as catalysts are listed in Table 1. The conversion of γ-KB was nearly 100% for all the modified pTSA clays. The reactions carried out at 433 K gave mainly the para product with a maximum selectivity of ~28% for 0.5 M- and 1 M-pTSA clay-catalyst samples. As the temperature increased from 353 to 403 K the selectivity of the O-alkylated product decreased from 34% to 10% and almost disappeared at 433 K. The formation of MVK and its polymers always occurred during the alkylation of ketones in the presence of solid-acid catalysts as reported in earlier studies (Tateiwa *et al.*, 1994a,b; Cheralathan *et al.*, 2003).

A comparison of the conversion under microwave heating with that of the conventional methods using 0.5 M-pTSA clay, under optimized conditions, showed

that the former method was much quicker than the latter. The reaction reached equilibrium under conventional heating over a period of 48 h while the same was achieved within 1 h using microwave heating. An increase in the formation of other products during conventional heating was also noted.

Further work was carried out with a view to understanding the formation of the para product. This necessitates the optimization of reaction conditions and relating the formation of the para product with the characteristics of the catalyst samples. Some of the characteristics of the acid-treated and Al^{3+}-Mont catalyst samples are listed in Table 2.

Increases in the pTSA concentration for treatments from 0.1 to 0.5 M, resulted in an enhancement of the specific surface area, acidity and both micro- and meso-porosities. Further increase in the pTSA concentration, beyond 0.5 M, showed negligible changes in the structural characteristics of the clay. This increase in the acidity of the clay due to pTSA treatment was due to the gradual increment in the amount of interlayer Al^{3+} ions (Venkatesha *et al.*, 2015). 0.5 M-pTSA clay possesses acidity comparable to that of the acidity of the Al^{3+}-Mont catalyst. The XRD data (Fig. 2) indicated no loss in structural integrity during the process.

Role of microporosity in the formation of para product

The role of micropores in the pTSA-modified clay in the alkylation of phenol with γ-KB was investigated by carrying out a comparative study between different pTSA-modified clay samples. The results of a set of reactions performed under optimized conditions, *i.e.* at a temperature of 373 K, at a 1 : 1 mole ratio of phenol: γ-KB, with 0.5 g of the desired catalyst, and a reaction period of 60 min, are presented in Table 3.

TABLE 1. Alkylation of phenol with γ-KB over different modified bentonite clay catalysts.

Catalyst	% conversion of γ-KB	% selectivity		
		Para	MVK	Others
Indian bentonite	32.31	–	26.66	6.45
0.1 M-pTSA clay	97.45	7.65	81.32	6.96
0.2 M-pTSA clay	99.60	12.28	69.86	17.82
0.5 M-pTSA clay	99.70	27.82	57.08	16.96
1 M-pTSA clay	99.88	26.45	49.41	14.70

Others: MVK polymers.
Reaction conditions: temperature: 433 K; molar ratio (Phenol: γ-KB): 2:1;
catalyst weight: 0.5 g; Time: 60 min.

Untreated bentonite was ineffective in the alkylation reaction and showed no product formation. A maximum selectivity of ~12% for the para product was observed for the 0.5 M-pTSA clay. An increased selectivity in the O-alkylated product was observed for the 0.1 M-pTSA clay which decreased gradually from ~23 to 7% with a concomitant increase in the para product selectivity when the catalyst changed from 0.1 to 0.5 M-pTSA clay. The 1 M-pTSA clay catalyst gave similar results to those for the 0.5 M-pTSA clay. This increase in the conversion of γ-KB and in the selectivity of para product may be attributed to the increased total acidity, specific surface area and pore volume of the clay with increase in pTSA concentration.

In order to understand the individual role of acidity, specific surface area and pore volume in the conversion of the reactants and the selectivity of the para and O-alkylated products, the alkylation reaction was conducted under similar reaction conditions over Al^{3+}-Mont. The latter clay is known to possess mainly Brønsted acid sites (Reddy *et al.*, 2004, 2009; Varma, 2002). The results were compared mainly with that of 0.5 M-pTSA-modified clay as both had similar interlayer Al and acidity but with a noticeable difference in the pore volume and surface area. Al^{3+}-Mont showed 54% γ-KB conversion with a maximum selectivity of 24% for the O-alkylated product and a selectivity of only 7% for the para product over a period of 60 min.

The Al^{3+}-Mont has similar Brønsted acidity and interlayer Al content to that of 0.5 M-pTSA clay but smaller specific surface area and pore volume. The Al^{3+}-Mont with small specific surface area and porosity values is not effective at the formation of para product. The degree of conversion, shown in Table 3, for samples treated with different concentrations of pTSA, is

TABLE 2. Amount of interlayer Al, TPD ammonia, pore volumes for pTSA-clay samples and Al^{3+}-Mont catalyst.

| Catalyst	Interlayer Al (mmol/kg of clay)	TPD ammonia desorbed (μmol/ g of clay)	Micropore* volume (cm³/g)	Mesopore** volume (cm³/g)	Total pore volume (cm³/g)	Specific surface area (m²)
Indian bentonite (untreated)	–	–	0.011	0.067	0.078	29.6
0.1 M-pTSA clay	27.7	63	0.015	0.068	0.083	92.1
0.2 M-pTSA clay	43.3	152	0.019	0.074	0.093	110
0.5 M-pTSA clay	75.5	218	0.024	0.076	0.100	133
1 M-pTSA clay	77.7	218	0.026	0.094	0.12	135
Al^{3+}-Mont	68.8	220	0.011	0.067	0.078	22.8

*For pore size <20 Å.
**For pore size of 20–500 Å.
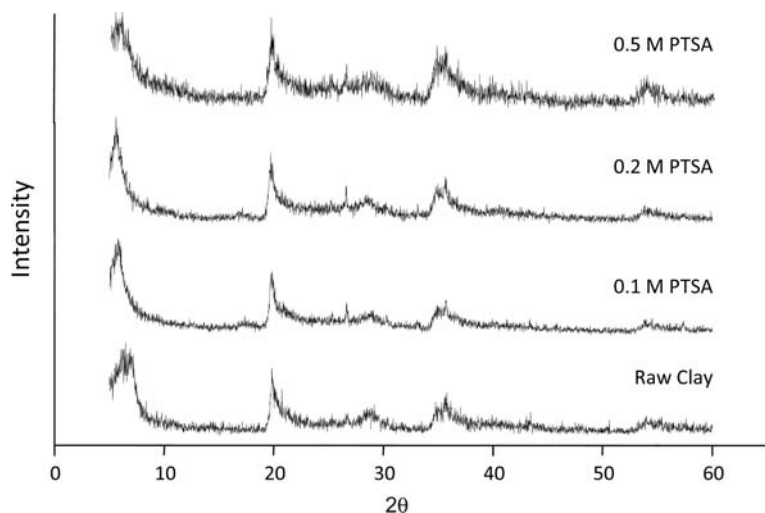
FIG. 2. XRD patterns of untreated and pTSA-treated clays.

compared with the clay properties in Table 2. From these results it becomes evident that the micropores generated due to acid treatment play a role in the formation of the para product, as shown by the increase in specific surface area and pore volume (micropore volume = 0.027 cm^3/g). To further substantiate the role of zeolitic-type pores in the para-selectivity, the reaction was conducted with zeolite HB which is known to have more micropores (micropore volume = 0.43 cm^3/g).

The results of a set of alkylation reactions carried out over HB from 5 to 60 min are shown graphically in Fig. 5. These reactions were carried out under optimized reaction conditions of: temperature = 373 K, a 1:1 mole ratio of phenol: γ-KB and 0.5 g of HB catalyst. The results for Al^{3+}-Mont and 0.5 M-pTSA clay samples are also presented for comparison in Figs 3 and 4. The duration and the proportion of reactants converted to reach equilibrium for HB were similar to that of 0.5 M-pTSA under similar reaction conditions. The conversion with HB catalyst reached a maximum of 96% in 60 min, with a selectivity of 10% for the para product and 7% for the O-alkylated product, which was comparable to that of the 0.5 M-pTSA clay. The similarity of results for the HB and 0.5 M-pTSA clay shows that the micropores generated on the clay sample after pTSA treatment are responsible for the para selectivity. The O-alkylated product is formed initially without para product formation (Figs 3–5), the latter increasing proportionately with the decrease in the O-alkylated product. This data trend suggests that the micropores formed facilitate the conversion of the O-alkylated product formed initially into the para product.

Para-product selectivity in the presence of mixed catalysts

A good correlation was noted between the amount of para product formed and microporosity ($r^2 = 0.99$) and total acidity ($r^2 = 0.99$). The correlation between para product formed and the mesoporosity of the catalyst samples was relatively poor ($r^2 = 0.76$). This shows the involvement of micropores which seem to facilitate access by reactants to the Brønsted and Lewis acid sites as a result of pTSA treatment.
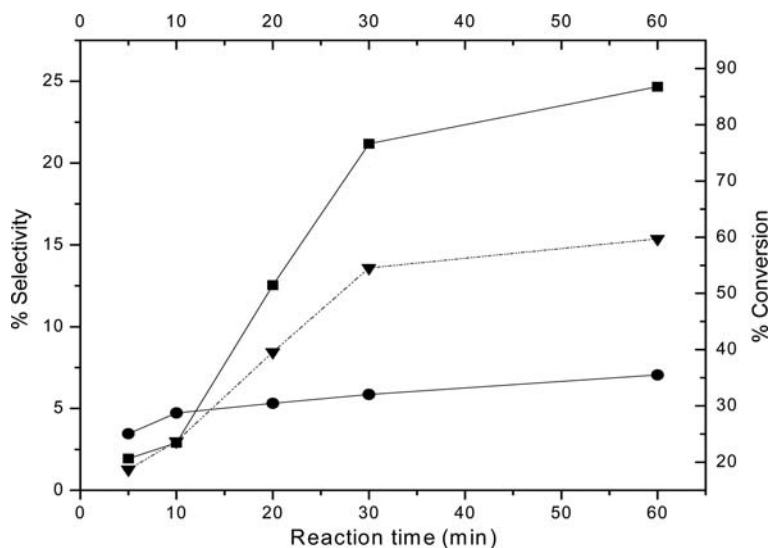
TABLE 3. Alkylation of phenol with γ-KB at 373 K with modified catalysts.

Catalyst	% Conversion of γ-KB	% Selectivity	
		O-alkylated	Para
Indian bentonite	10.23	–	–
0.1 M-pTSA clay	81.26	23.55	9.60
0.2 M-pTSA clay	99.60	9.39	10.58
0.5 M-pTSA clay	99.70	7.49	12.85
1 M-pTSA clay	99.86	7.21	12.31
Al^{3+}-Mont	59.70	24.66	7.05

Reaction conditions: temperature: 373 K; molar ratio (phenol: γ-KB): 1:1; catalyst weight: 0.5 g; time: 60 min.

FIG. 3. The effect of reaction time on the selectivity of para and O-alkylated product and conversion of γ-KB using an Al³⁺-Mont catalyst. Temperature: 373 K; molar ratio 1:1 (phenol: γ-KB); catalyst weight: 0.5 g. ● Para-; ■ % O-alkylated; ▼ γ-KB.

The present results therefore seem to suggest that catalyst microporosity determines the alkylation of phenol by γ-KB with 0.5 M-pTSA clay. This was further investigated by performing the alkylation reaction under similar reaction conditions over a mixture of 0.5 M-pTSA clay and HB (1:1 catalyst ratio). The results were compared with different catalysts as shown in Table 4. Comparison of these results showed a similar product distribution pattern for mixed catalyst as well as for 0.5 M-pTSA clay and HB, both having micropores. The final product compositions for Al³⁺-Mont-catalysed alkylation reaction, over a period of 60 min, was different, although the total acidity of Al³⁺-Mont was comparable to that of 0.5 M-pTSA clay. This further emphasizes the influence of the micropores
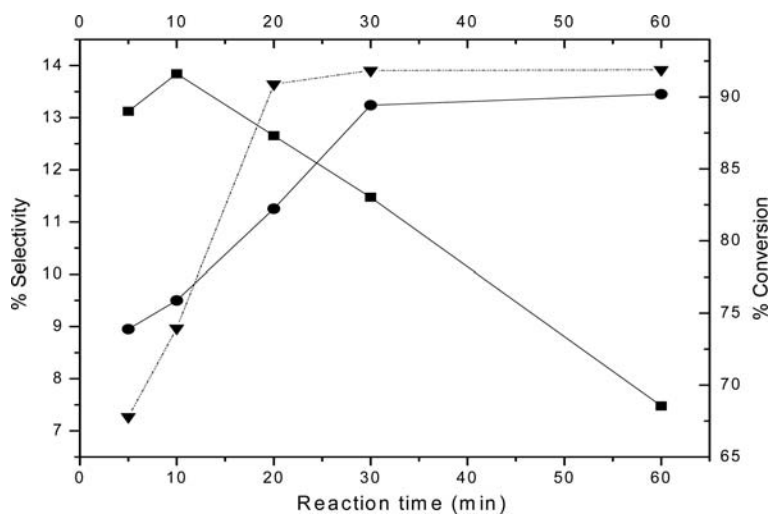

FIG. 4. The effect of reaction time on the selectivity of para and O-alkylated product and conversion of γ-KB on 0.5 M-pTSA clay. Temperature: 373 K; molar ratio 1:1 (phenol: γ-KB); catalyst weight: 0.5 g; ● Para-; ■ O-Alkylated; ▼ γ-KB.
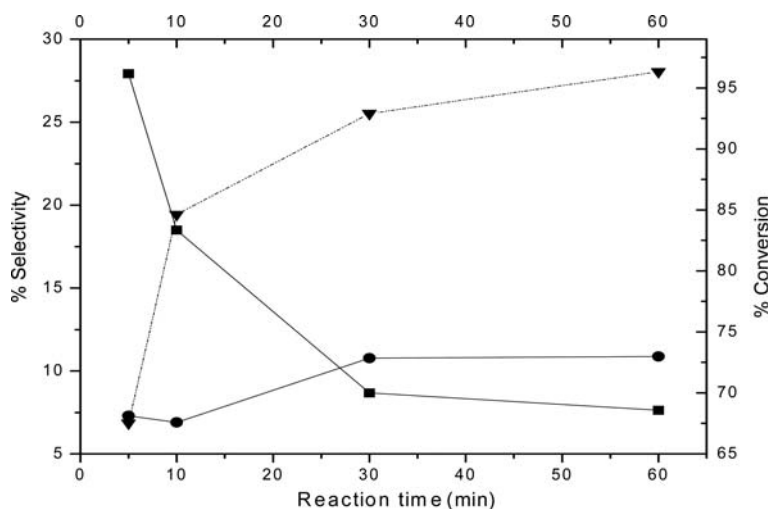
FIG. 5. The effect of reaction time on the selectivity of para and O-alkylated product and conversion of γ-KB on beta zeolite. Temperature: 373 K; molar ratio 1:1 (phenol: γ-KB); catalyst weight: 0.5 g. ● Para-; ■ O-alkylated; ▼ γ-KB.

present on the catalyst surface in the alkylation of phenol with γ-KB.

pTSA probably gains access through the hexagonal cavities of the tetrahedral sheet and forms soluble cationic complex species with Al in the octahedral sheet, thereby dislodging the Al into the interlayer in the form of a soluble Al-pTSA complex. The displacement of Al ions creates cavities of micropore dimensions through which access to the interlayer ions is facilitated (Ramesh *et al.*, 2012). The soluble Al-pTSA complex ions hydrolyse to form cationic species of hydrated Al hydroxide which remain in the interlayer as exchangeable ions and act as potential

Brønsted acid sites. Exposed broken edges in the micropore explain the origin of the Lewis acid sites. Thus pTSA treatment results in new acid sites and this explains the increase in acidity with organic-acid treatment (Table 2). Diffusion of the reactants through these micropores during alkylation of phenol with γ-KB facilitates access to the active sites.

In order to establish the role of micropores in the synthesis of para product, another set of reactions was carried out in two stages. In the first stage, alkylation of

TABLE 4. Effect of alkylation of phenol using γ-KB with mixed catalyst.

Catalyst	% Conversion of γ-KB	% Selectivity	
		O-alkylated	Para
0.5 M-pTSA clay + HB*	96.93	6.83	14.09
HB	96.31	7.63	10.21
0.5 M-pTSA clay	99.70	7.49	12.85
Al^{3+}-Mont	59.7	24.66	7.05

*Weight of HB: 0.25 g; Weight of 0.5 M-pTSA clay: 0.25 g; time: 60 min.
Reaction conditions: temperature: 373 K; Molar ratio (phenol: γ-KB): 1:1; catalyst weight: 0.5 g.

TABLE 5. Alkylation of phenol with γ-KB over different catalysts after the reaction with Al^{3+}-Mont.

Catalyst added in Stage 2	*Time (min)	% Conversion of γ-KB	% selectivity	
			O-alkylated	Para
0.5 M-pTSA clay	10	94.42	12.29	17.24
	30	96.50	4.88	29.43
HB	10	96.78	7.53	23.03
	30	97.10	3.56	29.61

Reaction conditions: (1st stage) Temperature: 373 K; Molar ratio (Phenol: γ-KB): 1:1; Catalyst: Al^{3+}-Mont; catalyst weight: 0.5 g; Time: 60 min (γ-KB conversion = 59.7%; O-alkylated product = 24.7%; para product = 7.05).
*(2nd stage) catalyst weight: 0.25 g; Temperature: 373 K.

phenol with γ-KB was conducted over Al^{3+}-Mont at 373 K for 60 min and the reaction was further continued under similar conditions after *in situ* addition of 0.5 M-pTSA-Mont or HB (second stage). The results are summarized in Table 5 for reaction times of 10 and 30 min. After the first-stage reaction with Al^{3+}-Mont, the major selectivity was for the O-alkylated product. The addition of the extra, fresh catalyst to the reaction in the second stage accelerated the rearrangement of the O-alkylated product to the para product in the case of both 0.5 M-pTSA clay and HB. These results support the zeolitic-type behaviour of the 0.5 M-pTSA clay.

Although the overall reaction mechanism is uncertain, the formation of the para product 4-(4′-hydroxyphenyl)-2-butanone is likely to occur by an intermolecular rearrangement of the O-alkylated product selectively for the para product (Tateiwa *et al.*, 1994a,b; Cheralathan *et al.*, 2003).

CONCLUSIONS

pTSA treatment of Indian bentonite clays removes structural Al from the octahedral sheet leading to an increase in acidity, surface area, pore volumes and in the formation of micropores. Micropores generated upon pTSA treatment of the bentonite sample show zeolitic micropore behavior and this is observed in the conversion of O-alkylated to C-alkylated (para) product during the microwave-irradiated, solventless synthesis of 4-(4-hydroxyphenyl)-2-butanone (raspberry ketone). The role of micropores in the selective formation of raspberry ketone (para product) was established by varying the micropore volume and the acidity by using different concentration of pTSA. Al-exchanged clay with less microporosity, showed less selectivity for the desired para product. The participation of micropores in the pTSA-treated clay is further supported by its comparable behaviour with that of HB zeolite and in the presence of mixed catalyst of HB zeolite, pTSA-treated and Al^{3+}-clays. The results demonstrate that the micropores formed in pTSA-modified clay as a result of the selective dealumination from octahedral sheets show zeolitic behaviour. These micropores induce better access to the active sites present in the catalyst thereby increasing the rate of the C-alkylation (para product).

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