tert-Butylation of phenol catalysed by metal exchanged iron pillared montmorillonites

Manju Kurian, S. Sugunan *

Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, Kerala 682 022, India

Abstract

tert-Butyl phenols present an industrially important class of compounds and are prepared by the reaction between phenol and *t*-butyl alcohol over cation exchange resins. This homogeneous mechanism involves tedious work up and separation techniques. Several alternatives like zeolites and molecular sieves have been tried. The present work discusses the use of transition metal exchanged pillared montmorillonites as novel catalysts for the vapor phase *tert*-butylation of phenol. The catalytic activities of the systems depend on the amount of acid sites on the catalyst surface and the disubstituted product selectivities depend on the amount of strong acid sites.
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1. Introduction

Alkylation of hydroxy aromatic derivatives to prepare alkyl substituted phenols is an important area of fine chemical synthesis. *tert*-Butylation of phenol is a key reaction in this category as the reaction products, *tert*-butyl phenols (TBP) find a wide variety of applications in industry [1,2]. Numerous studies have been reported on the *t*-butylation of phenol using several acid catalysts like H_2SO_4, H_3PO_4 and cation exchange resins [3]. However, the homogeneous catalysts have difficulties like hazardous nature of catalysts and tedious working conditions. On the other hand, cation exchange resins cannot be used at higher temperatures. Pillared clays present a novel class of microporous materials that can be prepared easily. These materials result from a two step modification of swelling clay minerals; insertion of polyoxocations into the interlamellar space and stabilisation of the polymeric species by subsequent thermal treatment [4]. These materials have

increased surface area, porosity and intrinsic acidity suggesting potential catalytic applications [5].

2. Experimental

The pillared clay was synthesised by partial hydrolysis method. The pillaring species prepared by the hydrolysis of 0.1 M $Fe(NO_3)_3$ with 0.3 M Na_2CO_3 solution was treated with clay suspension at 80°C (OH/metal ratio, 2 and metal/clay ratio, 20 mmol/g clay). For iron–aluminium mixed pillaring, equimolar ratios of $Fe(NO_3)_3$ and $Al(NO_3)_3$ were taken. The pillared clay after repeated washings with distilled water was filtered and dried in air oven at 110 °C overnight, followed by calcination for 6 h at 450 °C in muffle furnace. Exchange with transition metals was done using 0.1 M aqueous solutions of the corresponding metal nitrate. The exchanged clay after repeated washings was filtered and dried in air oven at 110 °C overnight and calcined for 5 h at 500 °C. The prepared systems are notated as X/Fe PM or X/FeAl PM where X is V, Mn, Co, Ni, Cu and Zn.

Simultaneous determination of surface area and pore volume of the samples was done on a Micromeritics

* Corresponding author. Fax: +91 484 2577595.
  E-mail address: ssg@cusat.ac.in (S. Sugunan).

Gemini 2360 analyser. Temperature programmed desorption of ammonia was done using a conventional flow type apparatus. The samples were flushed with nitrogen for half an hour and ammonia was adsorbed on the sample by purging it with ammonia at room temperature. After 20 min, physisorbed ammonia was desorbed and the temperature increased at a rate of 5 °C/min. *tert*-Butylation of phenol was done in the vapor phase in a down flow apparatus. In a typical experiment, the reactor was charged with the activated catalyst (kept in the muffle furnace at 500 °C for 2 h) sandwiched between silica beads. The products of the reaction were collected downstream from the reactor at specified intervals and analysed by Chemito GC 8610 equipped with FID and TCD. The percentage conversion (wt %) is the total percentage of phenol transformed into products. The selectivity to a product is the amount of that product divided by total amount of products, expressed in percentage.

3. Results and discussion

3.1. Physicochemical characterisation

A thorough characterisation of the physicochemical properties of the prepared systems has been reported elsewhere [6]. The surface areas and pore volumes of iron pillared systems are given in Table 1. As a result of pillaring, surface areas and pore volumes increase drastically. Transition metal exchange decreases the surface area and pore volume slightly. The metal exchange was done to improve the surface acidity of the acidic pillared clay systems. Results of ammonia TPD suggest that in all the prepared systems, weak and medium acid sites overshadow the strong sites (Table 1). V, Mn, Ni and Cu exchange on iron oxide pillared montmorillonite increases the amount of total acid

sites, particularly the strong sites. In the mixed pillared series also, the parent pillared system desorbs considerable amount of ammonia in the weak and medium regions and nominal acidity in strong acid region. Transition metal exchange increases the acidity in all regions, especially acidity in strong acid region. V/FeAl PM and Co/FeAl PM exhibit maximum acidity in the series owing to increased concentration of weak acid sites. But, Ni/FeAl PM displays exceptionally high acidity in strong acid region. Room temperature exchange with transition metals result in the incorporation of about 1–3% of the metal (Table 1).

3.2. tert-Butylation of phenol

We attempted to determine how the pillared clays as well as their transition metal exchanged analogues catalysed *tert*-butylation of phenol. A detailed investigation of the dependence of conversion % and product selectivity on the amount and availability of surface acid sites also is included. Table 2 depicts the activity and selectivity pattern exhibited by Fe PM, FeAl PM and their transition metal exchanged analogues. Fe PM proves to be efficient catalyst for *tert*-butylation of phenol with a monoalkylated product selectivity of 96.4%. Incorporation of transition metal decreases the activity for all iron pillared systems except Ni/Fe PM. The increase in the amount of the total phenol converted for the nickel exchanged catalyst can be credited to the higher concentration of the disubstituted product. The selectivity for monoalkylated product does deteriorate much from Fe PM for other catalysts in the series. In the mixed pillared series, FeAl PM exhibits phenol conversion of 32.3% with high selectivity towards di substituted product. All systems in the series are efficient catalysts towards *t*-butylation of phenol. Higher concentrations of 2,4-di TBP is obtained in all cases. The high activity of the pillared

Table 1
Physicochemical properties of catalyst systems in the *tert*-butylation of phenol

Catalyst	BET surface area (m² g⁻¹)[a]	Pore vol[ab] (cm³ g⁻¹)	W[cd]	M[d]	S[d]	Cumulative (mmol g⁻¹)	TM %[ae]
V/Fe PM	161	0.1991	0.722	0.159	0.088	1.068	2.33
Mn/Fe PM	194	0.2086	0.715	0.311	0.182	1.208	1.19
Co/Fe PM	178	0.1957	0.420	0.191	0.057	0.688	1.97
Ni/Fe PM	164	0.1920	0.997	0.350	0.258	1.505	1.93
Cu/Fe PM	171	0.1992	0.696	0.287	0.153	1.136	1.21
Zn/Fe PM	147	0.1857	0.592	0.112	0.080	0.784	2.26
Fe PM	194	0.2157	0.48	0.354	0.084	0.918	–
V/FeAl PM	158	0.1753	0.844	0.382	0.202	1.428	1.99
Mn/FeAl PM	156	0.1703	0.637	0.246	0.191	1.074	2.51
Co/FeAl PM	164	0.1871	1.401	0.440	0.147	1.988	1.26
Ni/FeAl PM	142	0.1673	0.524	0.224	0.299	1.047	1.3
Cu/FeAl PM	144	0.1658	0.413	0.159	0.050	0.627	1.8
Zn/FeAl PM	147	0.1635	0.449	0.163	0.112	0.724	3.18
FeAl PM	170	0.1894	0.473	0.161	0.048	0.682	–

[a] Error limit is ±5%.
[b] Total pore volume measured at 0.9976 P/P_0.
[c] Ammonia desorbed in the temperature 373–473 might contain very small amount of physisorbed ammonia too.
[d] W, M, and S stand for weak (373–473 K), medium (474–673 K), and strong (674–873 K) acidic sites.
[e] Percentage of the exchanged transition metal as obtained by EDX analysis.

Table 2
Activity of the prepared systems for *tert*-butylation of phenol

Catalyst	Conversion %[a]	Selectivity (%)[a]	
		p-TBP[b]	2,4-di TBP[c]
V/Fe PM	32.2	93.2	6.8
Mn/Fe PM	39.6	89.2	10.8
Co/Fe PM	25.2	91.7	8.3
Ni/Fe PM	58.1	78.6	21.4
Cu/Fe PM	34.2	94.9	5.1
Zn/Fe PM	46.1	94.4	5.6
Fe PM	54.0	96.4	3.6
V/FeAl PM	45.3	84.7	15.3
Mn/FeAl PM	48.5	75.6	24.4
Co/FeAl PM	48.3	91.7	8.3
Ni/FeAl PM	16.6	70.1	29.1
Cu/FeAl PM	45.6	85.6	14.4
Zn/FeAl PM	51.0	68.8	31.2
FeAl PM	32.3	71.2	28.8

Reaction conditions – phenol/*tert*-butyl alcohol – 1/3, temperature – 200 °C, WHSV –2.6 h^{-1}, TOS – 2 h.
  [a] GC error limit is ±5%.
  [b] *p-tert*-butyl phenol.
  [c] 2,4-*tert*-butyl phenol.

systems can be credited to their high surface area. The reactants have nonrestricted access to active sites resulting in better yield. The high selectivity towards dialkylated product also confirms this observation.

tert-Butylation of phenol has been reported to occur over acidic sites present in the catalyst [7,8]. Hence an attempt was made to correlate catalytic activity of the systems with the total amount of acid sites present in the prepared systems as obtained by temperature programmed desorption of ammonia. Fig. 1 unambiguously shows that the reaction occurs over acidic sites. The superior activity of Ni/Fe PM can be attributed to higher amount of acidic sites on the catalyst surface. However, no direct correlation
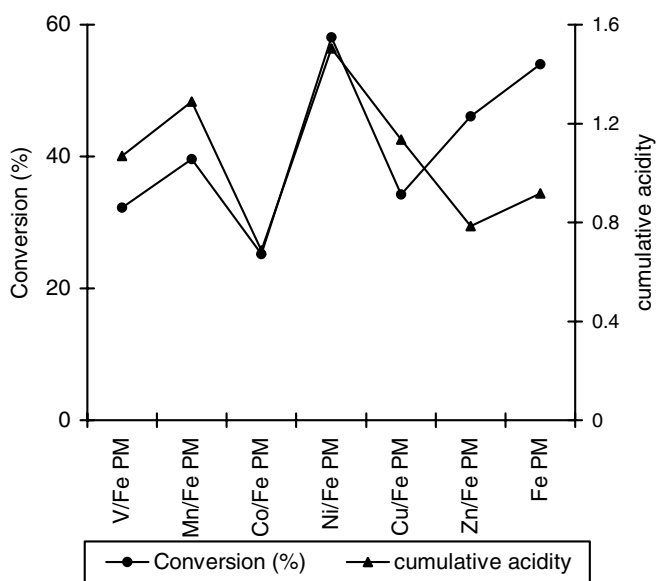
could be obtained between total acidity and conversion % in the case of mixed pillared systems.

Product selectivity shown by an acid catalyst depends on the acid site distribution on the catalyst surface. The di substituted product has been suggested to be formed by the alkylation of monoalkylated product. Zhang et al. proposed that strong acid sites are required for the formation of 2,4-di TBP [9]. Hence selectivity of di substituted product was correlated to the amount of strong acid sites, obtained from NH$_3$-TPD measurements (Fig. 2). The figure suggests that strong acidity plays a key role in the alkylation of monobutylated product. Enhanced formation of 2,4-di TBP over Ni/Fe PM and Mn/Fe PM can be traced to higher amount of strong acid sites. Also, lower amounts of strong acid sites on the surface of Co/FeAl PM and Cu/FeAl PM explains the diminutive selectivity towards 2,4-di TBP. In clays, the strong sites are present mainly in the outer surface. Aluminium in threefold coordination, perhaps occurring at an edge, or arising from a Si–O–Al rupturing dehydroxylation of the Brönsted site, would correspond to a Lewis site. An octahedral Al^{3+}, located at a platelet edge, also function as a Lewis site after thorough dehydration [10]. Hence, the strong sites which are present mainly in the outer surface, catalyses the conversion of the produced monoalkylated products to di substituted ones.

The reaction conditions play an imperative role in deciding the catalytic activity and product distribution. Temperature plays a vital role in the *t*-butylation of phenol (Table 3). Increase in temperature increases the phenol conversion as well as monoalkylated product selectivity. Maximum conversion is shown at 200 °C. After this optimum temperature, activity decreases with no apparent deterioration in

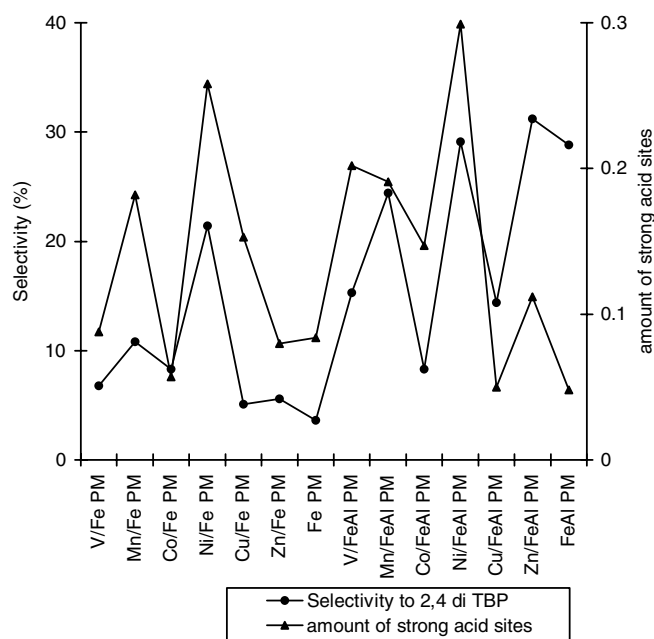Fig. 1. Correlation of conversion (%) on total acidity.

Fig. 2. Correlation of 2,4-di TBP selectivity on the amount of strong acid sites.

Table 3
Effect of reaction variables on *tert*-butylation of phenol

Reaction variable		Conversion (%)[a]	Selectivity (%)[a]	
			p-TBP[b]	2,4-di TBP[c]
Temperature (°C)	160	37.5	65.0	35.0
	180	48.2	74.3	25.7
	200	54.0	96.4	3.6
	220	31.7	95.9	4.1
	240	23.2	97.7	2.3
Phenol:TBA	2:1	30.2	98.3	1.7
	1:1	48.7	93.5	6.5
	1:2	44.0	92.9	7.1
	1:3	54.0	96.4	3.6
	1:5	41.4	86.3	13.7
WHSV (h^{-1})	1.7	44.5	88.3	11.7
	2.6	54.0	96.4	3.6
	3.5	33.8	94.1	5.9
	4.3	34.0	89.1	10.9

Reaction conditions – phenol/*tert*-butyl alcohol – 1/3, temperature – 200 °C, WHSV – 2.6 h^{-1}.
[a] GC error limit is ±5%.
[b] *p-tert*-butyl phenol.
[c] 2,4-*tert*-butyl phenol.

Table 4
Effect of time on stream on activity

Time on stream (h)	Conversion (%)[a]	Selectivity (%)[a]	
		p-TBP[b]	2,4-di TBP[c]
1	52.5	97.3	2.7
2	54.0	96.4	3.6
3	53.8	94.1	5.9
4	51.2	92.1	7.9
5	50.0	91.5	8.5

Reaction conditions – phenol/*tert*-butyl alcohol – 1/3, temperature – 200 °C, WHSV – 2.6 h^{-1}.
[a] GC error limit is ±5%.
[b] *p-tert*-butyl phenol.
[c] 2,4-*tert*-butyl phenol.

TBP selectivity. The decrease in phenol conversion at higher temperatures refers to an increase in the amount of phenol in the reaction mixture, which can be attributed to the dealkylation of the alkylated products at higher temperatures [9]. Increase in *t*-butyl alcohol in the reaction mixture increases the phenol conversion as expected. The activity reduces after a phenol to tert-butyl alcohol ratio of 1:3. The selectivity to 2,4-di TBP is high at larger concentrations of *t*-butyl alcohol. Decreased conversion of phenol at phenol/*t*-butyl alcohol ratio of 2/1 can be attributed to the higher amount of phenol at this ratio. It has been demonstrated that polar molecules such as methanol and higher alcohols compete with phenol for the adsorption sites with increasing molar excess of the alkylating agent and hence phenol conversion increases [11]. Increase in 2,4-di TBP can be attributed to higher concentrations of the *t*-butyl carbenium ions in the reaction mixture, bringing about further alkylation of the produced monobutylated product. Feed rate is another important parameter that has an influence on the activity as well as selectivity pattern in gas phase reactions. Increase in space velocity increases the phenol conversion. Maximum conversion is shown at a space velocity of 2.6 h^{-1}, where after the conversion decreases. Thus, there is an optimum contact time for *t*-butylation to occur over clay catalysts. The selectivity to monoalkylated product also shows a decrease first followed by an increase. The reduction in conversion at higher space velocities can be simply due to high diffusion of the reactant molecules from the catalyst active sites. On the other hand, the low conversion at lower space velocity could be attributed to the dealkylation of butyl phenols to phenol as well as coke formation.

Another set of experiments was conducted to evaluate the stability of the systems with reaction time. The pre-pared clay catalysts show appreciable activity for the reaction even after 5 h (Table 4). The selectivity to 2,4-di TBP increases with time on stream. The slight decrease in catalytic activity with increase in time on stream can be attributed to the deactivation of the catalyst active sites. This can be due to either coke formation or poisoning of the active sites with products. However, the latter seems to be more feasible because there is an increase in the di substituted product with increase in time on stream. Generally in Friedel Crafts alkylations, further alkylation of the monoalkylated product is observed with increase in reaction time [12].

t-Butylation of phenol just like alkylation of any other aromatic compound follows the Friedel Crafts mechanism. The generally accepted mechanism for the reaction is that the carbenium ion interacts with adsorbed phenol forming the pi complex, which then rearranges to sigma complex by the electrophile attacking a ring carbon atom. The sigma complex on proton elimination gives *t*-butyl phenol. The disubstituted product is formed by further alkylation of the *t*-butyl phenols.

4. Conclusions

The various points that can be summarised from a systematic study of the catalytic activity and product selectivity towards *t*-butylation of phenol are:

- Iron pillared and mixed iron pillared systems are efficient catalysts for *t*-butylation of phenol in the gas phase.
- Catalytic activity of the systems can be correlated to the total amount of acid sites present in the catalysts.
- Di substituted product selectivity exhibit direct correlation with amount of strong acid sites.
- The reaction is highly sensitive towards reaction temperature. An optimum temperature of 200 °C was detected.
- Increase in amount of *t*-butyl alcohol increases the conversion.
- An optimum feed rate of 2.6 h^{-1} is required for maximum conversion of *t*-butyl alcohol as well as monoalkylated product selectivity.

- The prepared clay catalysts show appreciable activity even after 5 h. This can be ascribed to the stability of active sites under the reaction conditions.

Acknowledgment

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