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Para-selective *tert*-butylation of phenol over nano sulfated titania catalysts prepared via sol–gel route

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Titania, sulfated titania and a series of iron loaded sulfated titania catalyst with different iron loadings (3–9%) are prepared by sol–gel method and characterized by XRD, BET surface area and pore volume measurements, EDX, TG-DTG, FT-IR and TPD of ammonia. Alkylation of phenol with *tert*-butanol in the vapour phase over the prepared systems has been studied at 1 atm and 160–220 °C. The interesting aspect of this reaction is the high selectivity of alkylation at the para position. Lower flow rate and higher reactant molar ratios enhances the phenol conversion and selectivity to 2,4-di-*tert*-butylphenol while higher flow rate and lower molar ratios are helpful in producing 4-*tert*-butylphenol.

KEY WORDS: sol–gel titania; sulfated titania; *tert*-butylation of phenol; 4-*tert*-butyl phenol

1. Introduction

Short chain alkyl phenols are important intermediates for the productions of resins, antioxidants, drugs, dyes, polymer additives, agrochemicals and antiseptic substances [1]. The direct alkylation of phenol with short-chain alcohols and olefins is widely used for the preparation of these intermediates. The catalytic reaction of phenol with *tert*-butyl isobutene as well as with methyl-*tert*-butyl ether has important application, because C-alkylation products such as 4-*tert*-butylphenol (4-TBP), 2-*tert*-butylphenol (2-TBP) and 2,4-di-*tert*-butylphenol (2,4-DTBP) have great commercial significance. Some commonly used catalysts for alkylation of phenol are H_2SO_4, BF_3, aluminum phenoxide, etc., [2] alkylation of phenol using solid acid catalysts may be a very promising way for the synthesis considering the increasing demand for eco-friendly routes in the industry. It is reported that the molecular sieve based catalysts like SAPO-11 [3], zeolite [4], AlMCM-41 [5] and FeMCM-41 [6] were proved to be potential catalysts for the butylation of phenol among the various solid catalysts. However, the reaction or tertiary butylation of phenol gives numerous products depending on the nature of the catalyst as well as on the reaction temperature. Generally, in the alkylation of aromatics using catalytic activity was controlled by acidity and selectivity was controlled by pore structure and acid strength of zeolites [7–11]. Sakthivel *et al.* had reported the vapour phase tertiary butylation of phenol over sulfated zirconia catalyst with a high selectivity to *para* isomer [12]. There are only a few reports on the butylation of phenol and that too mostly in patient literature [13–16]. To our knowledge, no report is available in literature on the tertiary butylation of phenol over sulfated titania catalysts.

Titania, classified as a solid acidic oxide in both the anatase crystallographic forms, has long been known to possess catalytic activity, although anatase was found to be more active than rutile [17]. The use of sulfated metal oxide is of increasing interest because of the enhanced chemical properties imparted by the presence of sulfate groups [18,19]. The synthesis of metallic oxides by the sol–gel process is presently a widely accepted method for the preparation of such materials. The advantage of sol–gel process in general are high purity, homogeneity and low temperature. For a lower temperature process, there is a reduced loss of volatile components and thus the process is more environmental friendly. The chemical and catalytic properties of titania can be modified by the incorporation of metallic ions. In this study we report the preparation of the catalysts by sol–gel route and their physico-chemical characterization. The relationship between conversion/selectivity and the acidic nature of the catalyst for *tert*-butylation of phenol with *tert*-butyl alcohol (TBA) is explained. The important variables affecting the conversion and selectivity of the reaction such as reaction temperature, flow rate, molar ratio of phenol to TBA and time on stream is also discussed.

2. Experimental

2.1. Synthesis of iron loaded sulfated titania catalyst

The nanocrystalline titania catalysts (T) reported in this study have been prepared by sol–gel method using titanium isopropoxide (Aldrich 98%). When 25 mL

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Ti $(OC_3H_7)_4$ was hydrolyzed in 300 mL water containing 2.5 mL nitric acid, precipitation occurred immediately. Precipitates were stirred continuously at room temperature to form a highly dispersed sol. To this calculated amount of iron nitrate solution is added to obtain iron loaded samples. After keeping the sol for aging it was concentrated and dried at 60 °C. Sulfation was done using 0.5 M sulfuric acid solution (2 mL g^{-1} of the hydroxide). The metal loading was varied from 3 to 9% as indicated by the number in the sample notation. The samples, after overnight drying at 110 °C, were calcined for 5 h at 500 °C.

2.2. *Catalyst characterization*

X-ray powder diffraction patterns have been recorded on a Rigaku D-max C X-ray diffractometer using Ni filtered Cu Kα radiation source (λ = 1.5406 Å). Micromeritics Gemini-2360 surface area analyzer was used to determine the BET surface area pore volume under liquid N_2 temperature using N_2 gas as the adsorbent. Thermal analysis between room temperature and 800 °C were carried out in N_2 atmosphere with a ramp of 20 °C min^{-1} using a TGAQ V2.34 thermal analyzer (TA instruments make). FT-IR spectra were recorded on a Magna 550 Nicolet instrument in the range of 4000–400 cm^{-1} phase. Quantitative elemental analysis of the samples was done by EDX measurements using EDX-JEM-35 instrument (JEOL Co. link system AN-1000 Si–Li detector). The total acidity of the samples were determined by temperature programmed desorption of ammonia (NH_3-TPD). Ammonia desorbed between 100 and 200 °C corresponds to weak acidity, those between 200 and 400 °C to medium strength, and above 400 °C is associate to strong acidity.

2.3. *Catalytic reactions*

The catalytic reactions were carried out at atmospheric pressure in a tabular, down flow reactor using 0.5 g of the catalyst by changing the reagent feed ratio, the temperature and flow rate. The catalyst was activated at 500 °C for 2 h prior to catalytic runs. The feed mixture was injected from the top using a syringe pump. The products were collected with a condenser and the liquid products were analyzed by Gas Chromatography (Chemito GC 1000) using a BP1 capillary column (12 m × 0.32 mm) with FID detector.

3. Results and discussion

3.1. *Catalyst characterization*

Figure 1 shows the powder X-ray diffraction patterns of the prepared systems. The diffractograms show the anatase and rutile phase in the pure TiO_2. But all other samples shows only the anatase phase of titania. The average crystallite size was determined using Scherrer equation [20]. It has been reported that the degree of crystallization of the sulfated oxides is much lower than that of the oxides without sulfate treatment [21,22]. The low peak intensity in the iron-incorporated sample reveals the lowering of crystallinity after iron incorporation. Sulfation retards the transformation from anatase TiO_2 crystallites sulfate surface species inhibit TiO_2 crystalline sintering leading to lower crystallite than in pure TiO_2. Pure titania shows only low surface area (table 1), while on sulfation and iron loading the surface area increases up to 138 m^2 g^{-1}. Sulfated oxides are reported to exhibit higher surface area than the pure oxide. As the amount of iron in the sample increase the surface area also increases.

The EDX analysis of the samples gives the percentage of iron and the sulfate content in the sample (table 1). Surface acidic properties of the catalysts were determined by NH_3 TPD. Sulfate modification had increased the acidity (table 2). The amount of weak medium and strong acid sites were differentiated by this method. The iron loaded samples were found to have a higher acidity as compared to the simple sulfated sample. This increase may be partially attributed to the higher sulfate content of the iron loaded samples. The structural changes accompanied by incorporation of iron moieties may be contributing to the acidity enhancement. Total acidity increases up to 6% and then suddenly drops at 9% loadings.

In comparison with pure titania the FT-IR spectrum of sulfated samples (figure 2) exhibit a broad peak with shoulders at around 1200 cm^{-1}. The peaks at 1029, 1076 and 1222 cm^{-1} are typical of the S = O mode of vibration of a chelating bidentate sulfate ion coordinated to a metal cation [23]. When SO_4^{2-} is bound to the titania surface, the symmetry can be lowered to either C_{3v} or C_{2v}. The bands obtained in the 1200–1100 cm^{-1} typical of sulfato complexes in a bidentate configuration with C_{2v} symmetry [24]. Thus the IR spectral bands of

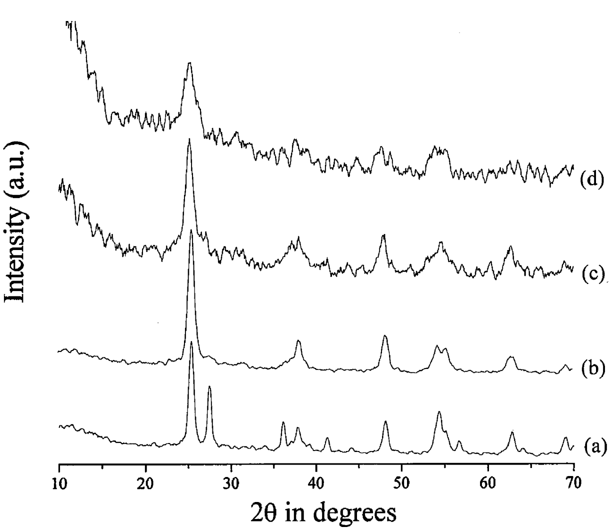

Figure 1. XRD profiles of (a) T (b) ST (c) STFe3 (d) STFe9.

Table 1
Surface parameters of the prepared systems

System	Crystallite size (nm)	Elemental composition from EDX (%)			Pore diameter (nm)	BET surface area (m^2 g^{-1})	Pore volume (cc g^{-1})
		TiO_2	SO_4	Metal			
T	12.71	100	–	–	102.8	35	0.09
ST	9.62	95.34	4.66	–	92.3	91	0.21
STFe3	10.40	89.44	7.83	2.98	65.4	104	0.17
STFe6	–	86.32	7.92	5.76	53.1	128	0.17
STFe9	135.6	82.92	10.21	6.81	49.3	138	0.17

Table 2
Acidity obtained from ammonia-TPD

System	Ammonia desorbed (mmol g^{-1})			
	Weak 100–200 °C	Medium 200–400 °C	Strong 400–600 °C	Total 100–600 °C
T	0.31	0.20	0.01	0.52
ST	0.50	0.32	0.09	0.91
STFe3	0.48	0.32	0.15	0.95
STFe6	0.44	0.53	0.30	1.27
STFe9	0.36	0.34	0.03	0.73

the samples closely agree to the bidentate sulfate complex structure having bands around 1119 and 1129 cm^{-1}. Thermal analysis of the samples showed an initial weight loss in the range of 90–150 °C and this could be attributed to the removal of surface adsorbed water. The weight loss in the temperature range of 250–300 °C is due to the transformation of amorphous titania to crystalline anatase phase. The weight loss in the temperature range 650–750 °C, is due to the decomposition of the sulfate species and evolution of oxides of sulfur. The iron promoted samples exhibited a higher thermal stability. The commencement of decomposition in these cases occured only above 700 °C. Thus, it can be inferred that, besides delaying the crystallisation process, the addition of iron also serves to stabilise the surface sulfate species.

3.2. *Catalytic reaction: tert-butylation of phenol*

In our study the major products obtained are 2-TBP, 4-TBP and 2,4-DTBP. 2-TBP easily isomerises to 4-TBP where as the reverse reaction is not significant. There is no formation of 3-TBP, which may be formed in the presence of Brönsted acid sites. In the case of our samples the Brönsted sites are weaker, and hence no 3-TBP formation is expected. Trace amount of *tert*-butyl phenyl ether (TBPE) was detected.

3.2.1. *Effect of phenol to TBA molar ratio*

In order to understand the optimum feed mix ratio, a series of experiments were performed at 180 °C with various molar ratios of phenol to TBA over STFe6. The formation of 2-TBP, 4-TBP and 2,4-DTBP is observed at different reactant ratios. In table 3 we find that at lower reactant ratios, the production of 4-TBP is dominant and at higher ratios selectivity of 2,4-DTBP is enhanced. Phenol conversion increases on increasing TBA concentration in the feed. Higher concentration of TBA in the feed helps in promoting the cause of alkylation, provided the alkylating agent is not consumed in non-selective parallel reactions. The *p*/*o* ratio is decreasing as the amount of TBA in the feed increases. Higher concentration of TBA on the catalyst at higher reactant ratios, result in preferential phenol alkylation to form 2,4-DTBP. An optimum feed mixture of phenol to TBA in 1:2 molar ratio is chosen for further investigations, as the selectivity for 4-TBP was maximum phenol conversion.

3.2.2. *Effect of temperature*

The reaction temperature had a profound influence on the catalytic activity as well as the product selectivity. The reaction is carried out at various reaction temperature in the range of 160–220 °C. The general trend for the alkylation reaction is that the conversion usually increases with increase in temperature and reaches a steady state at high temperature. From table 4 it is, clear that the selectivity to 4-TBP was enhanced, while that of 2-TBP and 2,4-DTBP decreased with increase in reaction temperature. There is a clear cut relation between the concentration of 2-TBP and 2,4-DTBP in the products as the latter falls along with 2-TBP. It is reported in the literature [23] that the formation of 2,4-DTBP takes place in a consecutive step by alkylation of mono alkylated product and it was also observed that when a mixture of 4-TBP and 2-TBP are reacted, the latter preferably reacts to form 2,4-DTBP. Our results also demonstrate a similar trend as the fall in 2-TBP also led to fall in 2,4-DTBP selectivity. At higher reaction temperatures the formation of undesired products are enhanced and they consumes reactants (TBA) without producing the desired products, which may lead to lower phenol conversion and 2,4-DTBP selectivity. The conversion of phenol increases up to 200 °C, and after that it decreases. Considering the phenol conversion and product distribution, the proper reaction temperature chosen is 200 °C.

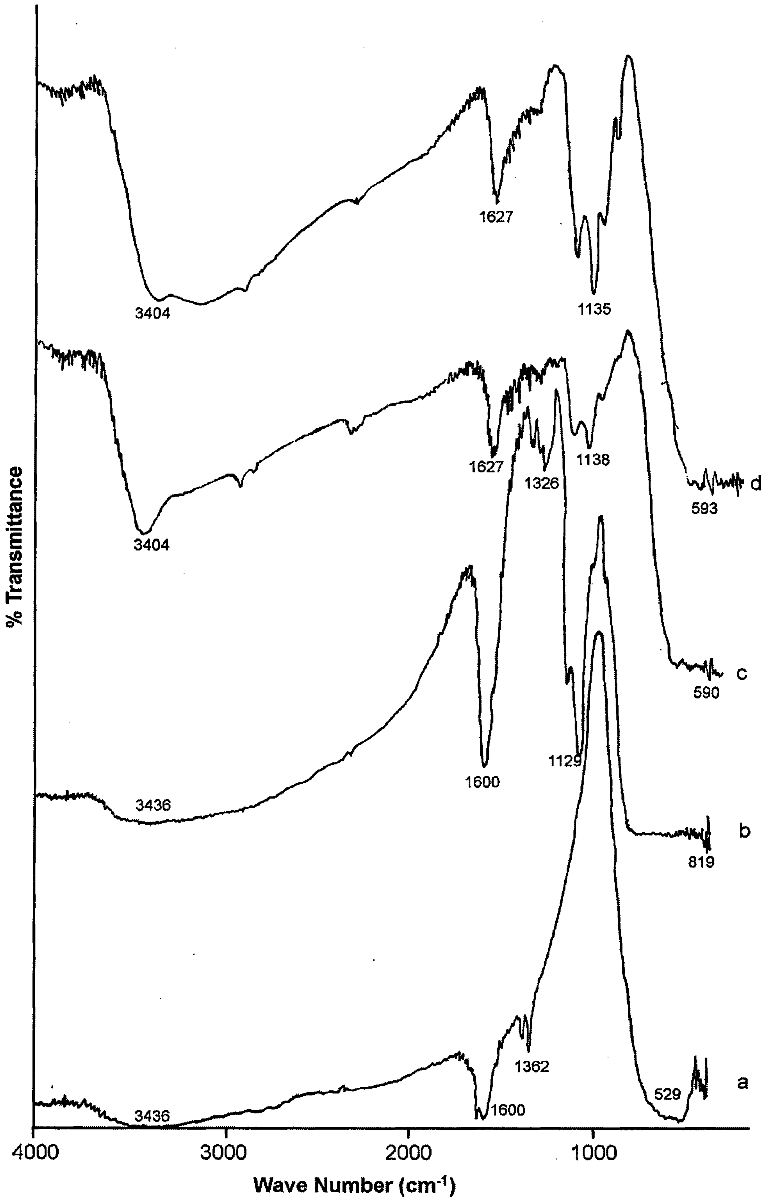

Figure 2. FT-IR spectra of (a) T (b) ST (c) STFe3 (d) STFe9.

3.2.3. *Effect of flow rate*

The contact time between the catalyst and the reactants greatly influence the reaction rate. Very low contact time (high flow rate) may woke poor reaction on account of the fast that little time is available for the adsorption of the reactants on the catalyst surface. At

Table 3
Effect of molar ratio on the conversion and product selectivity in *tert*-butylation of phenol

Phenol/TBA	Conversion of Phenol (wt%)	Product Selectivity (%)			p/o
		2-TBP	4-TBP	2,4-DTBP	ratio
1	21.02	18.49	70.48	5.93	3.81
1/2	29.25	21.93	68.75	7.47	3.13
1/4	31.04	23.51	66.22	9.49	2.82
1/6	35.60	26.15	58.53	14.24	2.24

Amount of catalyst: 0.5 g STFe6, Flow rate:4 mL h^{-1}, temperature: 180 °C, TOS: 2 h.

Table 4
Effect of temperature on the conversion and product selectivity in *tert*-butylation of phenol

Temperature (°C)	Conversion of Phenol (wt%)	Product Selectivity (%)			p/o
		2-TBP	4-TBP	2,4-DTBP	Ratio
160	29.05	23.04	65.43	7.58	2.84
180	29.25	21.93	68.75	7.47	3.13
200	32.20	20.91	70.48	7.25	3.37
220	25.30	20.05	73.42	5.34	3.66

Amount of catalyst: 0.5 g STFe6, Flow rate: 4 mL h^{-1}, TOS: 2 h, Phenol/TBA:

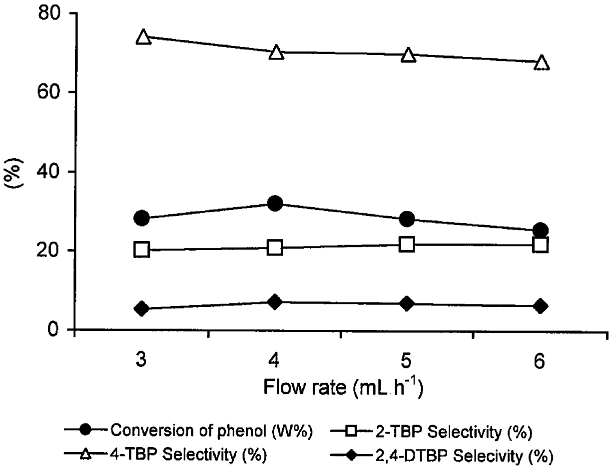

Figure 3. Effect of flow rate on the conversion and product selectivitity in the *tert*-butylation of phenol.

the same time, very high contact time (low flow rate) mostly results in undesired side reactions. Thus each reaction requires and optimum contact time with which maximum conversion and desired product yield is achieved. The reaction is carried out at various flow rates at a reaction temperature of 200 °C and with phenol to TBA molar ratio of 1:2 and is given in figure 3. As expected phenol conversion decreases with increasing flow rate, due to the shorter contact time at higher flow rate. The 2,4-DTBP selectivity is low for higher contact times whereas it improves and remains almost steady at lower contact times.

3.2.4. *Effect of time on stream*

The effect of time on stream is expected to throw light on deactivation of a particular catalyst and its influence on product selectivity. The performance of the reaction for a continuous 7 h run tests the susceptibility of deactivation of the catalyst. The products were collected and analyzed after every 1 h. Figure 4 represents the phenol conversion of representative systems towards time on stream. In the initial hours the catalyst might absorb phenol strongly and after 2 h, the catalyst activity established an equilibrium level. The conversion of phenol gradually increased with time on stream in the initial reaction period for 2 h, and then the conversion level attained a steady value for 5 h and after that it decreases slowly. This could, however be due to the formation of water molecules during the reaction, which may convert some of Lewis acid sites into Brönsted sites [23,25]. The deactivation of the catalyst increases after some time and hence there is a reduction in conversion.

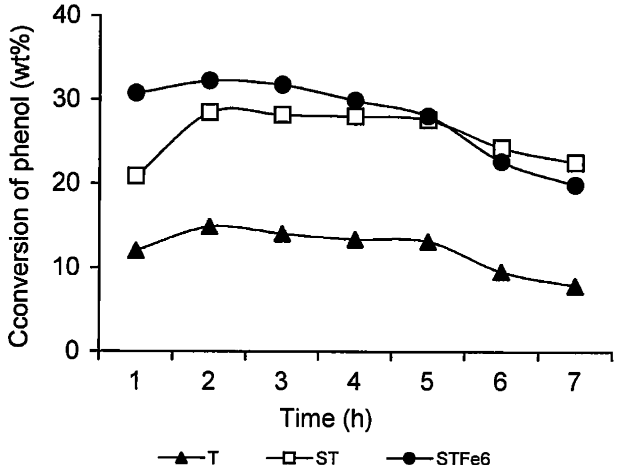

Figure 4. Effect of time on stream on the conversation in the *tert*-butylation of phenol.

3.2.5. *Effect of iron content*

An attempt to investigate the influence of the metal loading on catalytic activity is quite reasonable. As expected, variation in metal loading had a significant impact on the catalytic activity. An increase in metal content resulted in enhanced catalytic activity. As the Fe loading is increased from 0 to 6% the conversion gradually increases, thereafter the conversion declines. Incorporation of iron had increased the total acidity of the catalyst there by an increase in conversion is obtained. At high loadings of iron, the sulfate content is high (from EDX) and so polysulfate formation may occur, which may decrease the acidity of the system, and thus the conversion. The reaction did not show any conversion without catalyst. In all the cases *para* isomer is the major product. The Brönsted acid sites in sulfated titania catalysts are weaker than in H-ZSM-5 and therefore no *meta*-product is expected. Selectivity to 4-TBP and 2,4-DTBP also changes with respect to the metal loading (figure 5) present study the reaction is promoted by medium and strong acid sites. Strong acid are necessary to get higher selectivity of 2,4-DTBP while medium acid sites art helpful in enhancing the selectivity of 4-TBP. Medium acid sites may promote the isomerization or transalkylation reaction of *o*-TBP to *p*-TBP, while strong acid sites are helpful in forming 2,4-DTBP. Zhang *et al.* [26] also reported that the strong acidity is required for the formation

Table 5
Catalytic activity and product selectivities over the prepared systems

System	Conversion of Phenol (wt%)	Product Selectivity (%)			*p*/*o* ratio
		2-TBP	4-TBP	2,4-DTBP	
T	14.90	23.53	50.64	2.54	2.15
ST	28.45	19.81	65.64	5.44	3.31
STFe3	28.95	19.95	66.63	6.82	3.34
STFe6	32.20	20.91	70.48	7.25	3.37
STFe9	29.47	20.04	67.32	4.62	3.36

Amount of catalyst: 0.5 g, Flow rate: 4 mL h^{-1}. TOS:2 h, Phenol/TBA: 1/2, Reaction temperature: 200 °C

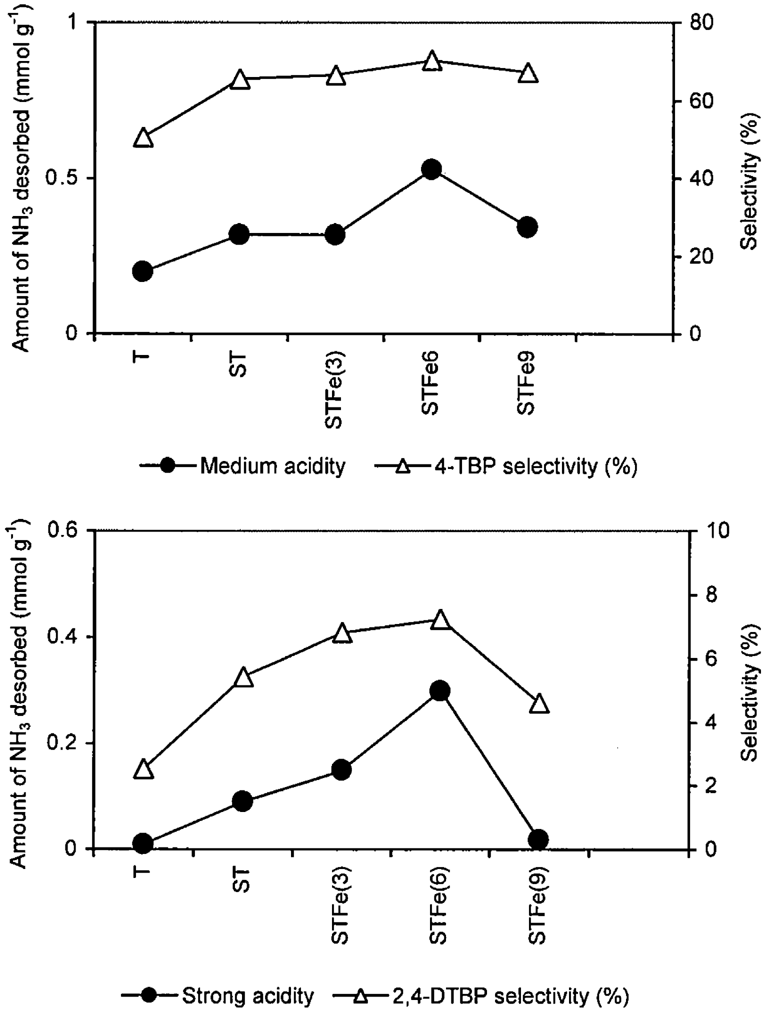

Figure 5. Correlation between product selectivity and acitidy from ammonia TPD.

2,4-DTBP and acid sites of medium strength are responsible for the formation of 4-TBP. Further, it is interesting to note that the catalytic activity remained the same even after several hours. Comparison of the present system with already reported systems for this reaction is given in table 6. Present systems show high 4-TBP selectivity within 2 h, compared with other reported systems.

4. Conclusion

The present study demonstrates sulfated titania catalyst and its modified forms are promising for the vapour phase butylation of phenol. Among the catalysts STFe6 is found to be the best catalyst for this reaction. A good substrate and excellent selectivity of the products are obtained. In order to promote the

Table 6
Comparision of phenol conversion and 4-TBP selectivity over sulfated titania with other catalysts under optimum conditions

Catalyst	Conversion of Phenol (wt%)	Product Selectivity (%)		Temp (°C)	Time (h)	Phenol: TBA
		2-TBP	4-TBP			
T [this work]	14.90	23.53	50.64	200	2	1:2
ST [this work]	28.45	19.81	65.64	200	2	1:2
STFe6 [this work]	32.20	20.91	70.48	200	2	1:2
USY10 [27]	37.70	60.70	27.30	70	3	1:0.6
Beta 15 [27]	35.0	16.90	82.50	70	3	1:0.6
AlMCM-41 [5]	35.9	8.10	83.4	175	1.5	1:2
SAPO-11 [3]	59.0	5.0	43.8	175	2	1:2
Sulfated zirconia [12]	57.8	6.8	86.5	175	4	1:2

formation of 4-TBP at higher conversions of phenol, a proper reaction temperature, lower reactant ratio and medium acidity on the sulfated titania based catalysts are recommended.

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References

[1] J.S. Beck and W.O. Haag, in: *Handbook of Heterogeneous Catalysis*, G. Ertl, H. Knozinger, and J. Weitkamp (eds) Vol. 5, (Wilely-VCH, Weinheim, 1997) p. 2131.

[2] J.F. Lorenc, G. Lambeth and W. Scheffer, in: *Kirk-Othmrer Encyclopedia of chemical technology 4th ed.*, M. Howe-Gmt and J.L. Kroschwitz (eds) Vol.2, (Wiley, New York, 1992) p. 113.

[3] S. Subramanian, A. Mitra, C.V.V. Satyanarayana and O.K. Chakrabarty, Appl. Catal. A 159 (1997) 229.

[4] K. Zhang, C. Huang, H. Zhang, S. Xiang, S. Liu, D. Xu and H. Li, Appl. Catal. A 166 (1988) 89.

[5] A. Sakthivel, S.K. Badamali and P. Selvam, Micropor. Mesopor. Mater. 39 (2005) 457.

[6] S.K. Badamali, A. Sakthivel and P. Selvam, Catal. Lett. 65 (2000) 153.

[7] G. Bellussi, G. pazzuconi, C. Perego, G. Girotti and G. Terzoni, J. Catal. 157 (1995) 227.

[8] S. Namba, T. Yashima, Y. Itaba and N. Hara, Stud. Surf. Sci. Catal. 5 (1980) 105.

[9] J. Cejka, N.Zilkova, B. Wiehterlova, G. Eder-Mirth and J.A. Lercher, Zeolites 17 (1996) 265.

[10] S.J. Chu and Y.W. Chen, Appl. Catal. A. Gen. 123 (1995) 51.

[11] J.L.G. Almeida, N. Dufauz, Y. B. Taarit and C. Naccache, Appl. Catal. A.Gen. 114 (1994) 141.

[12] A. Sakthivel, N. Saritha and P. Selvam, Catal. Lett. 72 (2001) 225.

[13] A. Carma, H. Garcia and J. Primo, J. Chem. Res. (1988) 40.

[14] C.D. Chang and S.D. Hellring, US Patent, 5 288 927, (1994).

[15] M. Yamamoto and A. Akyama, Japanese Patent, 6 122 639, (1994).

[16] A.U.B. Queiroz and L.T. Aikawa, French Patent, 2 694 000, (1994).

[17] H. Urabe and F. Sato, “Lewis acids in organic synthesis”, Hisashi Yamamoto 2 (1999) 653.

[18] M. Signoretto, F. Pinna and G. Strukul, Catal. Lett. 36 (1996) 129.

[19] K. Tanabe, Mater. Chem. Phys. 13 (1985) 347.

[20] M.S. Dieekmann and K.A. Gray, Water Res. 30 (1996) 1169.

[21] M.M. Dubinin, Chem. Rev. 60 (1960) 235.

[22] M.P. Rosynek and P.T. Magnuson, J. Catal. 46 (1977) 402.

[23] G.D. Yadav and J.J. Nair, Micropor. Mesopor. Mater. 33 (1999) 1.

[24] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th edition*, (Wiley, New York, 1986).

[25] E. Iglesia, S.L. Soled and G.M. Kramer, J. Catal. 144 (1993) 238.

[26] K. Zhang, H. Zhang, C. Hung, S. Xiang, S. Liu, D. Xu and H. Li, Appl. Catal. A. 166 (1) (1988) 89–95

[27] E. Dumitriu and V. Hulea, J. Catal. 218 (2003) 249.