

## Alkylation of naphthalene with *t*-butanol: use of carbon dioxide as solvent

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### Abstract

Organic solvent free alkylation of naphthalene and *t*-butyl alcohol (TBA) over rare earth exchanged Y zeolite (REY) has been carried out in the presence of carbon dioxide at different process conditions (temperature between 418 and 458 K, pressure between 6 and 92 bar, TBA/naphthalene mole ratios of 1:4, and different periods of time (1.5–9 h)). The results suggest that fluid carbon dioxide can replace organic solvents as a medium for butylation of naphthalene over REY without loss of its shape selective characteristics. © 2002 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

2,6-Naphthalenedicarboxylic acid (NDCA) is a valuable monomer used in the synthesis of novel polyester resins. NDCA is made by the oxidation of 2,6-dimethylnaphthalene, which is prepared by dialkylation of naphthalene with methanol. When naphthalene is alkylated, say methylated, two monomethyl naphthalenes and 10 dimethyl naphthalenes are produced in equilibrium amounts. Though the monomethyl naphthalenes can be separated by fractionation, the separation of the closely boiling dimethyl isomers is a difficult task. This has resulted in the development of expensive strategies for their separation [1,2].

If alkylation is carried out using shape selective zeolites, it is possible to produce the desired 2,6-isomer ( $\beta,\beta'$ -isomer) in larger amounts as it is

smaller in size than the other isomers. However, in the case of dimethyl naphthalenes size differences among the isomers are not large enough for discrimination inside the zeolite pores and shape selective dimethylation is difficult. On the other hand, 2,6-di-*t*-butyl naphthalene can be selectively prepared using shape selective zeolites due to the larger size differences between different butyl naphthalenes. Large pore zeolites are reported to exhibit high activity for alkylation of naphthalene in liquid phase conditions [3]. Liquid phase *t*-butylation of naphthalene in cyclohexane has been reported over a number of zeolites viz., HY, H $\beta$ , HM, SAPO-5, HZSM-5, MCM-41 [3–6] and clays [7]. Among the zeolites, HY and H $\beta$  are reported to exhibit high activity and high  $\beta$ - and  $\beta,\beta'$ -selectivities under mild conditions [3,4]. Most of the liquid phase studies have used an organic solvent such as cyclohexane as the reaction medium.

Organic solvent free alkylation is attractive, as it reduces the load on down stream separation. Isopropylation of naphthalene over zeolites in supercritical

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carbon dioxide medium is reported to reduce catalyst deactivation [8]. We have studied the isopropylation of naphthalene over different zeolites under nitrogen pressure and reported that H-beta and rare earth exchanged Y zeolite (REY) are more active than HM and HY [9]. In this paper, we present our studies on the *t*-butylation of naphthalene over REY in fluid carbon dioxide. The performance of the catalyst in different environments is also compared.

## 2. Experimental

REY was prepared from commercial Na-Y (zeolyst) by ammonium and RE exchanges. Ammonium exchange was done by stirring the Na-Y powder with a 2 M solution (10 ml/g zeolite) of  $\text{NH}_4\text{NO}_3$  for 4 h at 353 K. The mixture was cooled, the supernatant liquid was decanted and the procedure repeated twice. After the third exchange, the  $\text{NH}_4$ -zeolite was washed well with deionized water and dried at 383 K. The RE exchange procedure was similar, but a 5% solution of  $\text{RECl}_3$  (didymium chloride, supplied by Indian Rare Earths, Cochin, India; composition: Ce <2%, Nd ~35%, La/Y ~45%, Pr ~10%, other lanthanides rest; pH of solution was adjusted to ~5.2) was used and two exchanges were carried out on  $\text{NH}_4$ -Y. The sample was finally dried (383 K, 6 h) and calcined at 723 K for 4 h (heating rate = 1.5 K/min). The  $\text{RE}_2\text{O}_3$  content of the sample was 15% on dry basis. Surface area (BET) measured by  $\text{N}_2$  adsorption was  $720 \text{ m}^2/\text{g}$ . XRD patterns of the calcined sample revealed the structural integrity of the zeolite. The REY was blended and extruded with alumina (30%) and calcined at 773 K (6 h). The extrudates were sized to 1 mm length and activated at 723 K for 4 h in air before use. Naphthalene (99%) and *t*-butyl alcohol (TBA, >99%) were procured from s.d. fine chemicals, India. TBA was further purified by distillation and dried over 4A molecular sieves before use.

The experiments were carried out in batch mode in a  $650 \text{ cm}^3$  stainless steel Parr autoclave. The catalyst (2 g) enclosed in a stainless steel wire mesh was attached to the stirrer blades to ensure good contact with the reacting fluids. After loading the reactor with naphthalene and TBA, it was filled with  $\text{CO}_2$  to the required pressure. After the reaction, the reactor and its contents were cooled and the product mixture was

dissolved in diethyl ether. Generally, mass balances of >95% with respect to naphthalene and alkyl naphthalenes were obtained. The products were analyzed by GC (Perkin-Elmer Auto System XL; column: Ultra 2 (cross-linked 5% PHME siloxane), film thickness:  $0.52 \mu\text{m}$ , length: 25 m, i.d.: 0.32 mm) with FID detector.

## 3. Results and discussion

The *t*-butylation of naphthalene was carried out in the presence of carbon dioxide at different process conditions (temperature between 418 and 458 K, pressure between 6 and 92 bar, TBA/naphthalene mole ratios of 1:4, and different periods of time (1.5–9 h)). The influence of reaction time on naphthalene conversion and distribution of monoalkylated (MTBN) and dialkylated naphthalenes (DTBN) in the product are given in Fig. 1. Naphthalene conversion increases from 28 to 62%, on increasing the reaction time from 1.5 to 9 h. As expected, MTBN content in the product decreases while the DTBN increases with time. The ratio of the mono- to dialkyl naphthalenes (MTBN/DTBN) decreases over the period. The

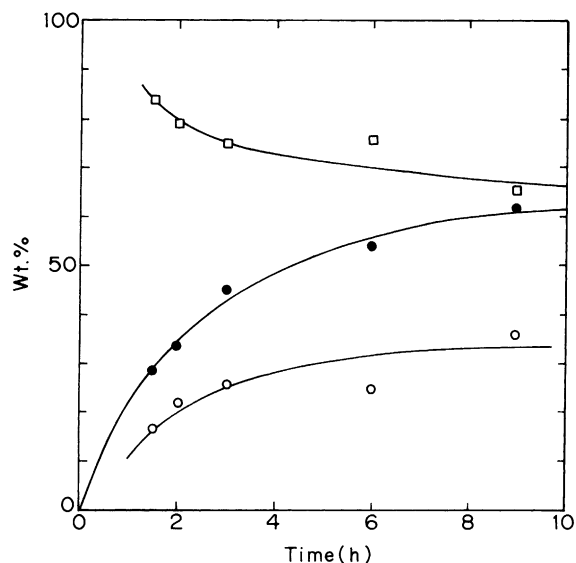


Fig. 1. Influence of reaction time on conversion of naphthalene and product distribution (temperature: 433 K, pressure: 91.8 bar, TBA/naphthalene: 2 mol, catalyst: 2 g): (●) conversion; (□) MTBN; (○) DTBN.

decrease is sharp during the initial period indicating quick consumption of MTBN and the corresponding formation of DTBN. As the DTBN concentration builds up, the yield of the dialkylated product increases at a slower rate due to increase of the reverse (dealkylation) reaction. Under the reaction conditions, equilibrium values of naphthalene conversion to *t*-butyl naphthalene calculated from thermodynamic data [10] are much larger than the observed conversions (>95%). The non-attainment of equilibrium in these experiments is probably due to poisoning and deactivation of catalyst by byproduct water and coke.

### 3.1. Effect of temperature

The effect of temperature on naphthalene conversion, concentrations of mono- and dialkylates and the ratio of MTBN isomers are presented in Fig. 2. Conversion increases from nearly 15% at 418 K to 75% at 448 K. Beyond 448 K, the increase in conversion is not as rapid. There is a steady decrease in the quantity of MTBN in the product accompanied by an increase in DTBN with increase in temperature. These results indicate that secondary reactions take place more

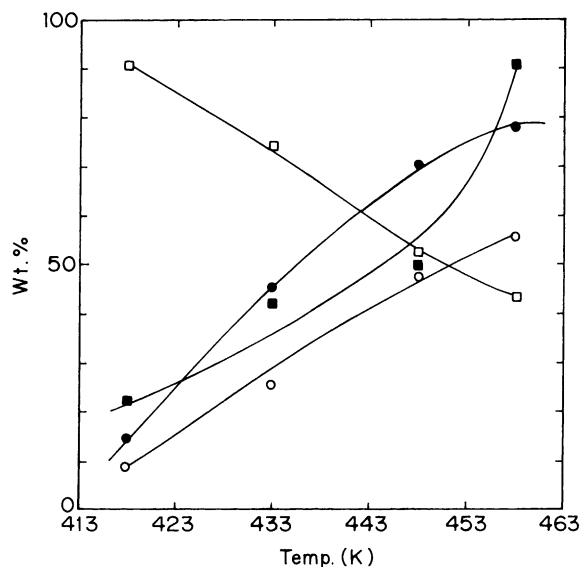


Fig. 2. Influence of temperature on the conversion of naphthalene and product distribution (initial  $\text{CO}_2$  pressure: 61.2 bar, TBA/naphthalene: 2 mol, catalyst: 2 g): (●) conversion; (□) MTBN; (○) DTBN; (■)  $\beta/\alpha$  (MTBN) ratio.

readily at higher temperatures. It may be noted that the reaction time for the temperature studies was 3 h. From Fig. 1, it is observed that the reactions do not equilibrate within this period and the overall reaction is under kinetic control.

The apparent activation energy was calculated from the naphthalene conversion–temperature data in the temperature range 418–448 K and found to be 22 kcal/mol. Though the 12 membered channels of REY are easily accessible to the reactants naphthalene and TBA, the transport of the products MTBN and DTBN through its channels could be restricted due to their bulkiness. The reasonably large activation energy obtained by us suggests that the reaction, under our experimental conditions, is not mass transfer controlled. It has been suggested that the use of supercritical fluids as reaction medium can eliminate transport limitations as the transport properties of reactants and products are altered by supercritical media [11]. To what extent these arguments are applicable in our case is not clear as supercritical behavior of  $\text{CO}_2$  is not expected inside small zeolite pores. At the conditions of the above experiments,  $\text{CO}_2$  ( $P_c = 72.9$  bar,  $T_c = 31^\circ\text{C}$ ) is expected to be in the supercritical state.

### 3.2. Effect of pressure

Reaction pressure was increased (70–92 bar) by increasing the amount of  $\text{CO}_2$  charged into the reactor. Influence of pressure on reaction behavior and a comparison with the results when the reaction is carried out under self-generated pressure (in the absence of  $\text{CO}_2$ ,  $\text{N}_2$  or any organic solvent) are presented in Table 1. There is an increase in naphthalene conversion and the amount of DTBN in the product on use of carbon dioxide as the reaction medium (reaction pressure: 69.7 bar). This is accompanied by a decrease in the (2,6- + 2,7-DTBN) selectivity and increase in the (2,6-/2,7-) selectivity ratio. The observed changes with  $\text{CO}_2$  as the medium may be due to more uniform distribution of the reactants in the  $\text{CO}_2$  phase.

Although  $\text{CO}_2$  is not expected to react, the relative sorption/concentration of the reactants at the catalyst surface may decrease due to sorption of  $\text{CO}_2$  on REY. However, the absence of a decrease in conversion suggests that  $\text{CO}_2$  behaves as a neutral diluent and its adsorption on the acidic sites surface is very weak.

Table 1

Influence of pressure on the butylation of naphthalene (N) with TBA over REY (temperature: 433 K, TBA/N: 2 mol, reaction time: 3 h, catalyst: 2 g)

| P (bar)      | Conversion (%) | Product distribution (%) |      |        | (2,6- + 2,7-)<br>selectivity (%) <sup>a</sup> | Selectivity ratios                   |                               |
|--------------|----------------|--------------------------|------|--------|---|--------------------------------------|-------------------------------|
|              |                | MTBN                     | DTBN | Others |   | MTBN <sup>b</sup> ( $\beta/\alpha$ ) | DTBN (2,6-/2,7-) <sup>c</sup> |
| <sup>d</sup> | 42.0           | 67.8                     | 31.9 | 0.3    | 99.9  | 46.3                                 | 4.6                           |
| 69.7         | 46.3           | 66.2                     | 33.4 | 0.4    | 85.2  | 36.9                                 | 5.5                           |
| 91.8         | 45.0           | 74.5                     | 25.5 | –      | 94.9  | 42.2                                 | 5.5                           |

<sup>a</sup> Selectivity = (wt.% of 2,6-DTBN and 2,7-DTBN/wt.% of all the DTBN in the product)  $\times$  100.

<sup>b</sup> Ratio of 2-*t*-butyl naphthalene to 1-*t*-butyl naphthalene.

<sup>c</sup> Ratio of 2,6-DTBN to 2,7-DTBN in the product.

<sup>d</sup> No CO<sub>2</sub>; self-generated pressure.

Table 2

Influence of mole ratio on the butylation of naphthalene (N) with TBA over REY (temperature: 433 K, pressure: 91.8 bar, reaction time: 3 h, catalyst: 2 g)<sup>a</sup>

| TBA/N (mol) | Conversion (%) | Product distribution (%) |      |        | (2,6- + 2,7-)<br>selectivity (%) | Selectivity ratios      |                  |
|-------------|----------------|--------------------------|------|--------|----------------------------------|-------------------------|------------------|
|             |                | MTBN                     | DTBN | Others |                                  | MTBN ( $\beta/\alpha$ ) | DTBN (2,6-/2,7-) |
| 1           | 63.1           | 54.8                     | 43.8 | 1.3    | 91.8                             | 123                     | 3.9              |
| 2           | 45.0           | 74.5                     | 25.5 | –      | 94.9                             | 42.2                    | 5.5              |
| 4           | 2.6            | 89.3                     | 10.7 | –      | 100                              | 25.3                    | –                |

<sup>a</sup> See footnotes in Table 1.

### 3.3. Effect of mole ratio of reactants and catalyst quantity

The influence of TBA/naphthalene mole ratio and catalyst quantity on conversion and selectivity are presented in Tables 2 and 3. Naphthalene conversion decreases considerably with increase in the TBA/naphthalene ratio above 2 mol. An increase in mole ratio leads to an increase in the TBA concentration on the catalyst surface, compared to naphthalene. This may promote reactions between TBA molecules (such as dehydration, addition and cracking) more

compared to reactions between TBA and naphthalene. Separate experiments have revealed that the dehydration of TBA molecules proceeds at a faster rate compared to the alkylation reactions between naphthalene and TBA. The water formed in the reaction can act as a poison for the catalyst. A significant decrease in catalyst activity at TBA/naphthalene ratio above 2 mol has already been reported by Liu et al. [3]. A similar effect has also been reported by Song and Kirby [12] in the isopropylation of naphthalene with isopropanol on mordenite. The authors explain this effect as being due to passivation of active sites

Table 3

Influence of catalyst quantity on the butylation of naphthalene (N) with TBA over REY (temperature: 433 K, pressure: 91.8 bar, TBA/N: 2 mol, reaction time: 3 h)<sup>a</sup>

| Catalyst (g) | Conversion (%) | Product distribution (%) |      |        | (2,6- + 2,7-)<br>selectivity (%) | Selectivity ratios      |                  |
|--------------|----------------|--------------------------|------|--------|----------------------------------|-------------------------|------------------|
|              |                | MTBN                     | DTBN | Others |                                  | MTBN ( $\beta/\alpha$ ) | DTBN (2,6-/2,7-) |
| 1            | 24.0           | 82.5                     | 17.4 | 0.1    | 95.7                             | 31.8                    | 4.3              |
| 2            | 45.0           | 74.5                     | 25.5 | –      | 94.9                             | 42.2                    | 5.5              |
| 4            | 69.7           | 53.5                     | 45.6 | 0.8    | 95.1                             | 48.8                    | 5.6              |

<sup>a</sup> See footnotes in Table 1.

Table 4

Influence of different media on the butylation of naphthalene (N) with TBA over REY (temperature: 433 K, TBA/ N: 2 mol, reaction time: 3 h, catalyst: 2 g)<sup>a</sup>

| P (bar)           | Conversion (%) | Product distribution (%) |      |                     | (2,6- + 2,7-) selectivity (%) | Selectivity ratios      |                 |
|-------------------|----------------|--------------------------|------|---------------------|-------------------------------|-------------------------|-----------------|
|                   |                | MTBN                     | DTBN | Others <sup>b</sup> |                               | MTBN ( $\beta/\alpha$ ) | DTBN (2,6-/2,7) |
| 6.8 <sup>c</sup>  | 42.0           | 67.8                     | 31.9 | 0.3                 | 99.9                          | 46.3                    | 4.6             |
| 20.4 <sup>d</sup> | 40.6           | 61.3                     | 34.8 | 3.9                 | 100                           | –                       | 3.7             |
| 91.8 <sup>e</sup> | 45.0           | 74.5                     | 25.5 | –                   | 94.9                          | 42.2                    | 5.5             |

<sup>a</sup> See footnotes in Table 1.

<sup>b</sup> Unidentified products.

<sup>c</sup> No solvent, no N<sub>2</sub>, no CO<sub>2</sub>.

<sup>d</sup> Solvent: 100 ml cyclohexane, N<sub>2</sub>, reaction time: 2 h.

<sup>e</sup> No solvent, CO<sub>2</sub>.

by strong adsorption of excess alcohol or the water produced by the dehydration of alcohol. The other possible reasons suggested are a counter diffusion effect of alcohol and its products that may reduce the diffusion rate of naphthalene in or out of the zeolite channels and deactivation by oligomerization of excess olefin produced by dehydration. As the TBA concentration increases, the distribution of monoalkylate in the product increases, while that of dialkylate decreases due to the low overall conversion.

Naphthalene conversion increases with increase in catalyst quantity, as can be seen from Table 3. The distribution of higher alkylates in the product also increases, and that of monoalkylate decreases. There is not much change in the (2,6- + 2,7-DTBN) selectivity, but the selectivity ratio shows that 2,6-DTBN is favored at higher catalyst concentrations. At higher catalyst concentrations, the active surface available for the reactants is larger and both mono-alkylation and di-alkylation rates are larger.

### 3.4. Effect of different media

It is interesting to compare the reaction behavior in the presence of different environments. Table 4 compares the reaction behavior under different environments, i.e. neat (no solvent, no added gas), in presence of cyclohexane and nitrogen and in presence of carbon dioxide under pressure. The reaction behavior in the three environments is comparable. Byproducts are more when cyclohexane is used as solvent as can be seen from the product distribution. Conversion is slightly higher when carbon dioxide

is used. Though selectivity for 2,6- and 2,7-DTBN is less (94.9%), the selectivity for 2,6-DTBN is higher (2,6-/2,7-ratio = 5.5) when CO<sub>2</sub> is used as the medium. The results indicate that CO<sub>2</sub> under pressure may be a better medium for the *t*-butylation of naphthalene.

## 4. Conclusions

Carbon dioxide can replace organic solvents as a medium for butylation of naphthalene on REY without loss of its shape selective characteristics. The relatively high apparent activation energy in carbon dioxide suggests that the reaction is not hindered by mass transfer resistance inside the pores of the catalyst. High conversion and DTBN selectivity are obtained at a TBA/naphthalene ratio of 2 mol. At higher ratios, conversion of naphthalene decreases significantly due to side reactions and catalyst poisoning by byproduct water.

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