Montmorillonite as a versatile solid acid catalyst for *tert*.-butylation of resorcinol

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Abstract

The liquid phase alkylation of resorcinol with *tert*.-butyl alcohol was carried out over HZSM-5, HY, HM, MCM-41, alumina, montmorillonite-K10 and modified montmorillonite-K10 (mont.-K10). The major products of this reaction on these catalysts were 4-*tert*.-butyl resorcinol and 4,6-di-*tert*.-butyl resorcinol. Unmodified montmorillonite-K10 shows a very low conversion compared to modified montmorillonite. The conversion in terms of catalytic activity increases in the order modified mont.-K10 ≫ HZSM-5 > HY > HM > MCM-41 > Al_2O_3 > mont.-K10. The activity and selectivity differences between the catalysts are explained based on their physical properties and acidity differences. The study brings out the significantly high butylation activity of modified montmorillonite-K10 compared to zeolite and oxide catalysts. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Butylation of dihydroxybenzenes is an industrially important reaction as the products of this reaction, butylhydroxybenzenes are useful materials in the synthesis of antioxidants, polymer stabilizers and in the treatment of mitochondrial respiration ailments. Most of the information in connection with the alkylation of dihydroxybenzenes using mineral acids are available in the form of patent literature [1]. This reaction is a Friedel-Crafts class of catalysis and generally carried out using sulfuric acid, phosphoric acid, and aqueous citric acid as catalysts [2,3]. Alkylation of aromatic compounds on modified clays have been described [5–8]. We have been using several solid acid materials, such as alumina, vanadia, zeolites, hy-

drotalcite and clays as catalysts for the alkylation of aniline and phenol [9–18]. The economics associated in the separation process and the present day's stringent environmental concerns on the disposal of spent homogeneous catalysts make it difficult to proceed with them any more. Because of the importance of the reaction and due to lack of enough available information in the open literature, we have taken the study of alkylation of dihydroxybenzenes with *tert*.-butanol, in particular resorcinol. The study assumes importance, especially in the content of enviro-catalysis as we are interested in using solid acids, which are environmentally benign in place of the conventional and hazardous mineral acid catalyst. So far there is no report available to our knowledge on the use of solid acid catalysts for the *tert*.-butylation of resorcinol. In the present study, we report, for the first time, our observation on the versatile catalytic behavior of modified montmorillonite-K10 (mont.-K10) clay for

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Table 1
Physical properties of the solid acid catalysts

Catalyst	Description	Pore-size (Å)	SiO_2/Al_2O_3	Surface area ($m^2\,g^{-1}$)
Mont.-K10	Fluka	–	–	275
Al_2O_3	Harshaw	0.6	–	190
MCM-41	Lab preparation		–	980
HM	CBV 20 A	7	20	540
HY	CBV 400	7.5	5.2	640
HZSM-5	CBV 3020	5.6	30	400

this reaction in comparison with zeolites, oxides and sulfuric acid.

2. Experimental

Experiments were carried out over HZSM-5, HY, HM, MCM-41, mont.-K10, modified mont.-K10, Al_2O_3 and H_2SO_4 catalysts. Al_2O_3, zeolites and mont.-K10 are of commercial origin. MCM-41 was prepared according to the literature procedure [4], and was crystalline as verified by XRD. The material was calcined in air at 773 K for 12 h to remove the template and surfactant. Mont.-K10 (Fluka) was modified by refluxing with 30% sulfuric acid for 60 min and filtered. The solid material was washed with distilled water until the filtrate became pH = 7. All the materials were characterized by XRD, FTIR and acidity measurements involving stepwise temperature programmed desorption of ammonia on a Micromeritics Pulse Chemisorb 2700 by bracketing the temperature of desorption. The details of acidity measurements are already described in our earlier paper [10]. Surface area, SiO_2/Al_2O_3 ratio and pore-size description details on the catalysts are given in Table 1.

The alkylation reaction was carried out by taking 1 g of resorcinol, 2.8 ml of *tert*.-butyl alcohol and 200 mg of the catalyst powder in a round bottom (RB) flask. The molar ratio of resorcinol to *tert*.-butyl alcohol was 1:3. The weight ratio of resorcinol to catalyst was 1:5. The reaction mixture was refluxed at 353 K for 8 h. The effect of reaction temperature was studied on the conversion of resorcinol and selectivity of products. In the case of sulfuric acid catalyzed reaction, the molar ratio of resorcinol:*tert*.-butyl alcohol:sulfuric acid was maintained at 1:3:0.4. Here again, 1 g of resorcinol and 2.8 ml of *tert*.-butyl alcohol were taken in a

50 ml RB flask and were refluxed with 0.22 ml of 1 M sulfuric acid at 353 K for 8 h. After completion of the reaction, 5 ml of methanol was added to make the end product mixture less viscous and easy for filtration. The product mixture was analyzed by a Chemito 8510 gas chromatography (GC) using 20% SE-30 column, coupled with FID. The products mixture was separated by silica-gel chromatography and were identified using standards. GC-MS and ^{1}H-NMR spectra of the products confirm them to be 4-*tert*.-butyl resorcinol and 4,6-di-*tert*.-butyl resorcinol. ^{1}H-NMR data for 4-*tert*.-butyl alcohol is $\delta = 1.4$, s, 9H (*tert*.-butyl), 5.75, brs, 2H (OH), 6.2, dd, 1H (Ar–H), 6.34, dd, 1H (Ar–H), 7.1, d, 1H (Ar–H). and for,4,6-di-*tert*.-butyl resorcinol is $\delta = 1.4$, s, 18H (*tert*.-butanol), 4.65, s, 2H (OH), 6.0, s, 1H (Ar–H), 7.1, s, 1H (Ar–H).

3. Results and discussion

The reaction is carried out by refluxing a mixture of *tert*.-butanol and resorcinol using zeolites and modified mont.-K10 as catalysts. The product analysis revealed that 4-*tert*.-butyl resorcinol and 4,6-di-*tert*.-butyl resorcinol were formed indicating that butylation took place selectively at 4 and 6, positions of resorcinol. The differences in the conversion of resorcinol and selective formation of 4-*tert*.-butyl and 4,6-di-*tert*.-butyl resorcinol over various solid acid catalysts along with the findings on the sulfuric acid catalyzed reaction is shown in Fig. 1. Unmodified or non-acid treated mont.-K10 clay shows a very low conversion (<5%) where as the modified or the acid treated mont.-K10 shows a very high conversion (>95%). The conversion in terms of catalytic activity increases in the order modified mont.-K10 $\gg$ HZSM-5 > HY > HM > MCM-41 > Al_2O_3 >
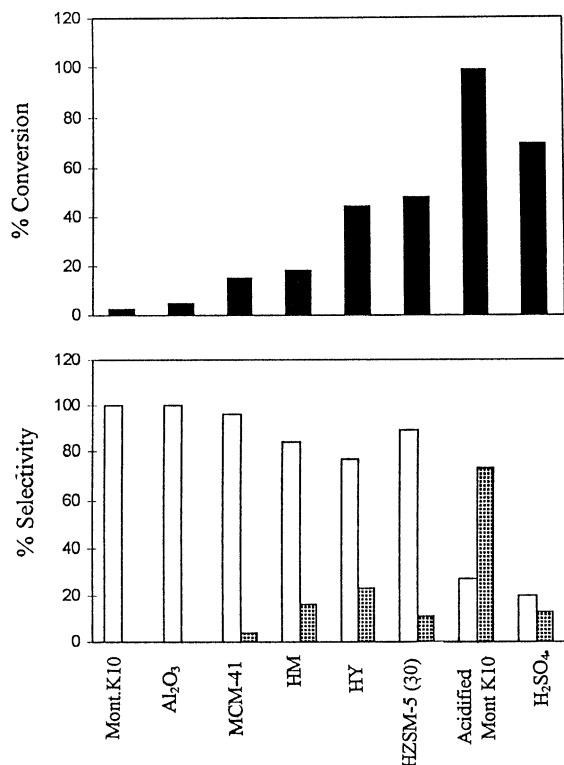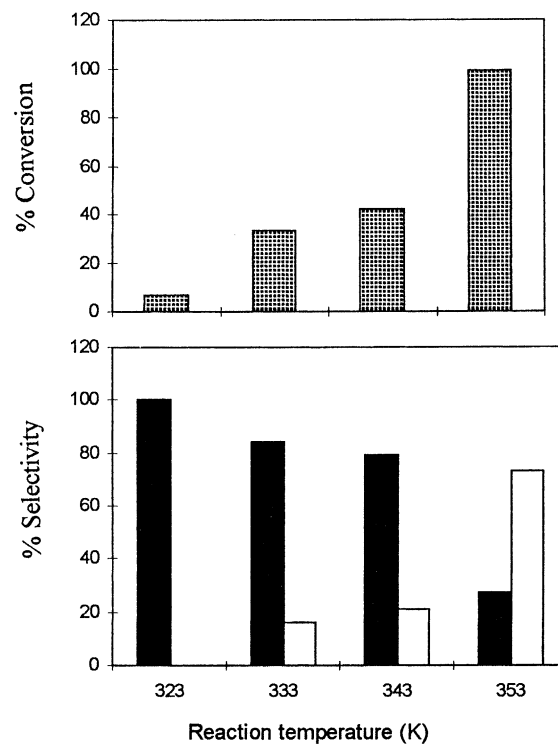
(■) Conversion of resorcinol   (□) 4-tert.butyl resorcinol

(▦) 4,6-di-tert.butyl resorcinol.

Fig. 1. Liquid phase *tert*.-butylation of resorcinol at 353 K; resorcinol/*tert*.-butanol = 1:3 mole/mole; resorcinol/catalyst = 1: 5 wt./wt.

(▦) conversion of resorcinol.   (■) 4-tert.butyl resorcinol

(□) 4,6-di tert.butyl resorcinol

Fig. 2. Effect of reaction temperature on *tert*.-butylation of resorcinol over acidified mont.-K10.

mont.-K10. H_2SO_4 gives a resorcinol conversion higher than all other catalysts except ofcourse acidified mont.-K10. The low conversion behavior over zeolites compared to acidified mont.-K10 might be attributed to the diffusion limitations due to its small pore-structure (Table 1).

The influence of temperature on alkylation of resorcinol with *tert*.-butanol over acidified mont.-K10 is depicted in Fig. 2. The conversion of resorcinol increases from 7 to 99% as the reaction temperature increases from 323 to 353 K. At 323 K, the selectivity to monoalkylation is 100% eventhough the conversion is only 7%. With the increase of reaction temperature the dialkylated resorcinol is also formed and it surpasses the selectivity of the monoalkylated resorcinol at 353 K. This is also an indication that the monoalky-

lation precedes the dialkylation and the high temperature facilitates the formation of dialkylated product.

The changes in conversion and selectivity on the *tert*.-butylation of resorcinol over acidified mont.-K10 is shown in Fig. 3. The conversion varies slightly with time. It can be seen that the selectivity for 4-*tert*.-butyl resorcinol is always higher than the selectivity for 4,6-di-*tert*.-butyl resorcinol. It looks like there is a kind of an equilibrium pattern on conversion and selectivity during the time period studied.

The acidity of the catalyst samples was measured by stepwise temperature programmed desorption of ammonia (STPD). The relative weak, medium and strong acidity of the catalysts namely modified mont.-K10, mont.-K10, HY and HZSM-5 is depicted in Fig. 4. As explained in our earlier paper [10], the desorption of ammonia was done at three predetermined
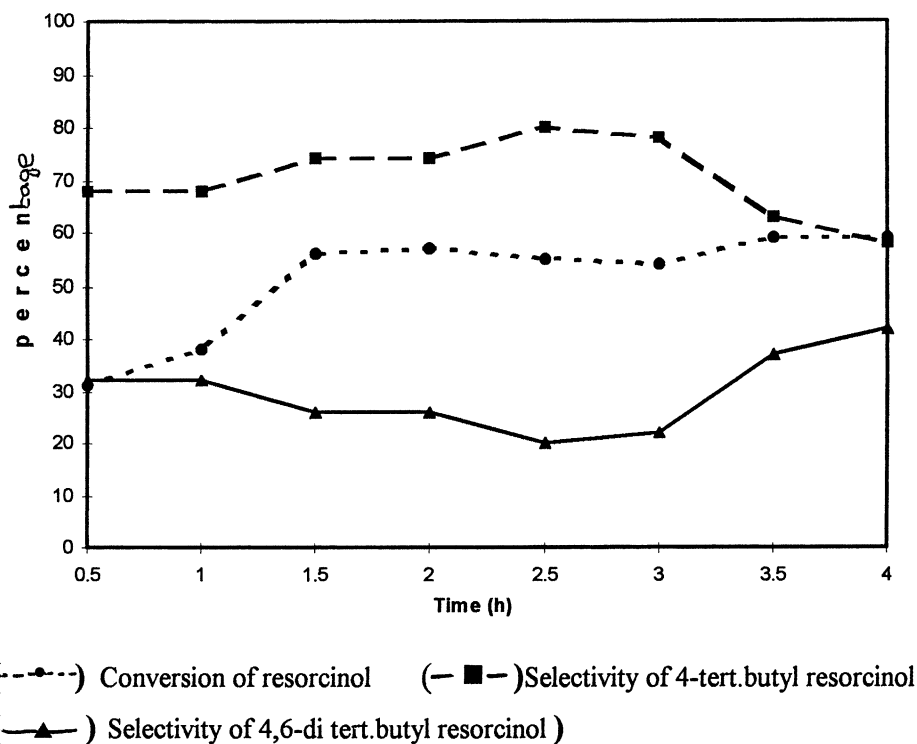
Fig. 3. Alkylation of resorcinol with *tert*.-butyl alcohol: effect of initial reaction time.

temperature regions, by bracketing the lower and upper temperature limits. In this case, for example, A represents the temperature region 353–423 K, B = 423–523 K and C = 523–623 K, respectively. The three relative strength of acidity are measured on the assumption that the strongly held ammonia responsible for strong acidity will be desorbed at higher temperature and the weakly chemisorbed ammonia on a relatively weak acid sites, which will desorb at a low temperature. The total acidity is the sum of all the three acidity as measured by the total ammonia desorbed. The Bronsted and Lewis acid sites present on the surface of the modified clay help in the release of the carbocation, $(CH_3)_3^+$, from *tert*.-butanol and facilitates the reaction [9,13,19–21]. The acidity of the modified mont.-K10 seems to be sufficient to give a good resorcinol conversion of >95%. Eventhough, HY, HZSM-5 catalysts have a relatively strong acidity, only weak to moderate acidity seems to be responsible for the reaction especially if we use *tert*.-butanol

as an alkylating agent. Similar observations have been made by us in the alkylation of aniline using methanol [13]. Very strong and excess acid sites are not beneficial and they only help to crack alcohol and hence it will not be available for the reaction [20]. The mechanism of formation of carbocation over montmorillonite clays and formation of alkyl aniline has been reported by Narayanan et al. [13,21]. Another interesting observation is that, sulfuric acid, a commonly used Friedel-Crafts catalysts, shows only 70% conversion for this reaction under the same experimental conditions. Thus we have a modified mont.-K10 clay which is even superior to conc. Sulfuric acid for alkylating resorcinol

The selectivity of the products based on GC analysis is also shown in Fig. 1. When the conversion is very low (especially below 10%) mont.-K10 and alumina yield mono-*tert*.-butyl resorcinol as the only product. As the conversion increases the second product namely, 4,6-di-*tert*.-butyl resorcinol starts appearing.
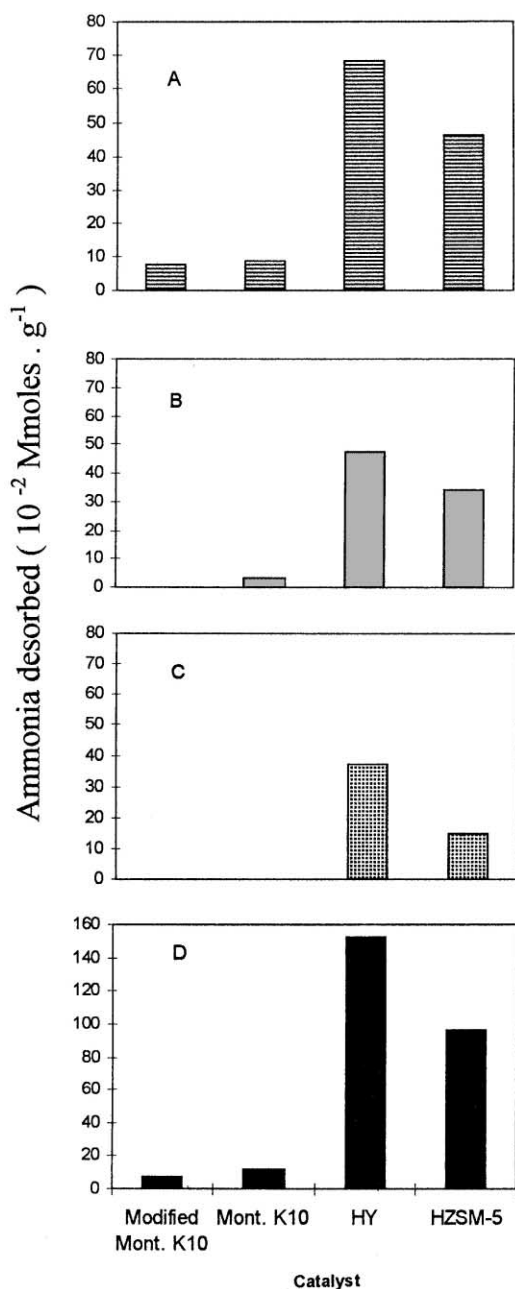
Fig. 4. STPD of ammonia: measured between A = 353–423 K, B = 423-523 K, C = 523–623 K and D = total (353–623 K).

The acidified mont.-K10 with over 95% conversion gives more dialkylated resorcinol than the monoalkylated. The product distribution seems to be dependent on the acidity and pore-size of the catalysts. Acid activation of pristine clay not only affects the acidity, but also enhances the surface area and mesoporosity of the clay [22]. The pore-size of the acidified mont.-K10 is expected to be much larger compared to the pristine clay due to delamination and widening of interlameller spacing. In the case of sulfuric acid, even though the conversion is much higher than zeolites, alumina and unmodified clay, the selectivity of mono and dialkylated products is low indicating that trialkylated products are likely to have been formed due to further alkylation as evidenced by GC analysis. The strong acidic strength of sulfuric acid may be the reason for multiple alkylated products formation. From the conversion and selectivity data, it may be derived that for the formation of monoalkylated resorcinol only weak acid sites are required. The formation of dialkylated product from the monoalkylated product is favored only when the steric hindrance is less, i.e. the catalysts should have large pores to allow the bulky alkylated products to travel out.

The selectivity of the 4,6-di-*tert*.-butyl resorcinol is increased in the order HZSM-5 < HM < HY < acidified mont.-K10. It is likely that some dialkylated product are formed on the external surface of the zeolites, because 4,6-di-*tert*.-butyl resorcinol is too large to penetrate into the zeolites channels. The selectivity of 4-*tert*.-butyl resorcinol is more or less identical for the zeolites, HZSM-5, HY, HM eventhough the conversions of these zeolites vary due to differences in acidity.

The conversion and selectivity patterns of the alkylated products formed over zeolites and clay materials reveal that the temperature, acidity and pore-structure of the catalyst materials influence the reaction. Modified mont.-K10 is a very good candidature for *tert*.-butylation of resorcinol, especially for producing dialkylated resorcinol and much superior over conventional sulfuric acid. Low temperature and weak acid sites seem to favor the monoalkylated resorcinol selectively eventhough the conversion is low. At high temperature, the conversion increases so does the dialkylated product. The strong acidity also favors dialkylation. It appears that the alkylation reaction proceeds via mono to dialkylation in a sequential fashion. The larger pore-size as in the case of modified mont.-K10 having wider interlamellar spacing compared to pristine clay also contribute to the dialkylation.

4. Conclusion

Several solid acid catalysts have been used for *tert.*-butylation of resorcinol. Modified mont.-K10 with wider pore-structure and required acidity seems to be a very good catalyst compared to HY, HZSM-5, HM, pristine mont.-K10 and even H_2SO_4.

Acknowledgements

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