Bull. Chem. Soc. Jpn., 61, 1379—1381 (1988)

Alkylation of Phenol by C_9 and C_{12} Olefins

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(Received November 17, 1986)

Alkylation of phenol by 1-dodecene, propylene tetramer and trimer is investigated using a variety of acid catalysts. The catalytic activity of perfluorinated sulfonic acid resin Nafion-H, the recently described 'sulfate treated' zirconia and trifluoromethanesulfonic acid is compared with that of cation exchange resin (CER) catalyst which is commonly employed in industrial practice. The activity of zirconia is observed to be comparable to CER and Nafion-H. In view of its low cost and higher thermal and structural stability, this catalyst shows considerable promise for practical application.

Alkylation of phenol with higher olefins in C_8 to C_{15} range does not take place as readily as with the lower olefins.[1] Among these alkylated phenols, nonyl- and dodecylphenol are of considerable commercial importance, especially in the manufacture of surfactants and lube oil additives.[2] Propylene oligomers have branched chain structure and the resultant alkylphenols are nonbiodegradable. Hence, for use in biodegradable surfactants linear α-olefins such as 1-dodecene, 1-nonene, or linear olefins with internal double bond are preferred.

These alkylation reactions have been studied on a variety of acid catalysts such as *p*-toluenesulfonic acid, boron trifluoride, boron trifluoride etherate, hydrofluoric acid, aluminium chloride-sulfuric acid,[3] hydrofluoric acid-carbon dioxide,[4] cation exchange resin,[5] bentonite clay,[6] zinc chloride-hydrochloric acid,[7] and silica-alumina.[8] Most of the literature is in the form of patents and hence provides limited information. Most of the catalysts mentioned above suffer from various drawbacks such as problems of separation from reaction products, corrosion and nonreusability. Boron trifluoride and CER catalysts seem to be preferred in industrial practice. Use of solid catalysts has clear advantage due to the ease of separation from the products and noncorrosive nature of reaction medium. In the present work, catalytic activity of a variety of solid acid catalysts is investigated for alkylation of phenol with 1-dodecene, propylene tetramer and trimer. The catalysts include the perfluorinated sulfonic acid resin Nafion-H, and the 'sulfate treated' zirconia recently described by Arata and Hino.[9—11] The catalytic activity of these catalysts is compared with that of CER catalysts. Trifluoromethanesulfonic acid (triflic acid) is one of the strongest acids known and unlike many other super acids, it is stable in a variety of reaction media and is also reusable.[1,2] The catalytic activity of this acid was also investigated.

Experimental

Materials. Phenol, 1-dodecene Fluka, zirconium dichloride oxide of A.R. grade, while propylene trimer (135—137 °C, ρ=0.739 g cm^{-3}) and propylene tetramer (187—188 °C, ρ=0.770 g cm^{-3}) were used in the present study.

Catalysts. The superacid catalysts Nafion-H and triflic acid [≥98%] were obtained from Du Pont and Fluka respectively. The 'sulfate treated' zirconia was prepared by treating zirconium hydroxide with 0.5 M sulfuric acid (1 M=1 mol dm^{-3}) followed by drying and calcination at 650 °C for 3 h. This zirconium hydroxide was prepared from zirconium dichloride oxide by hydrolysis with aq ammonia.[9] 98% Sulfuric acid of A.R. grade was used. The CER [Polystyrene-DVB crosslinked resin sulfonic acid, Indion-130] was procured from Ion Exchange India. The solid catalysts were dried at 110 °C for 1 h just before use.

General Reaction Procedure and Analysis. The reactor consisted of a flat bottom glass vessel of 5.0 cm i.d. and 200 ml volume. The reactor was equipped with baffles and was stirred by a glass turbine stirrer at 1000 rpm. The reactor was kept in a constant temperature bath. In a typical run, 29 g of phenol (0.31 mol) was brought to the required temperature under agitation and 0.73 g of catalyst [2.5% (w/w) of phenol] and 34.7 g of 1-dodecene [0.207 mol] were added. This was considered as zero time. Samples of the reaction mixture (0.5 ml) were withdrawn from time to time. Samples were analyzed by gas chromatography using a s.s. column containing 5% SE-30 on Chromosorb-W [HP] as stationary phase and flame ionization detector.

Results and Discussion

In all experiments, the alkylated product consisted of the para isomer exclusively.

Alkylation of Phenol with 1-Dodecene. Alkylation of phenol with 1-dodecene was studied in the temperature range of 100—145 °C using zirconia catalyst. The conversions observed at different reaction time are given in Table 1. The data could be fitted to a simple

Table 1. Alkylation of Phenol with 1-Dodecene
Effect of Temperature on Activity

Time	% Conversion of 1-dodecene at temp			
min	100 °C	115 °C	130 °C	145 °C
15	8	23	30	35
30	13	33	49	51
60	27	48	62	65
90	37	55	75	77
120	45	68	77	79

Mole ratio, phenol: 1-dodecene=1.5: 1.
Loading of zirconia=2.5% (w/w) of phenol.

Table 2. Alkylation of Phenol with 1-Dodecene Effect of Mole Ratio on Activity

Mole ratio phenol: 1-dodecene	% Conversion of 1-dodecene at time in min					
	15	30	45	60	120	180
1 : 1	10	25	32	38	60	70
1.5 : 1	35	49	53	64	78	
1 : 1.5	2	11	17	20	27	31

Temperature 130 °C. Loading of zirconia 2.5% (w/w) of phenol.

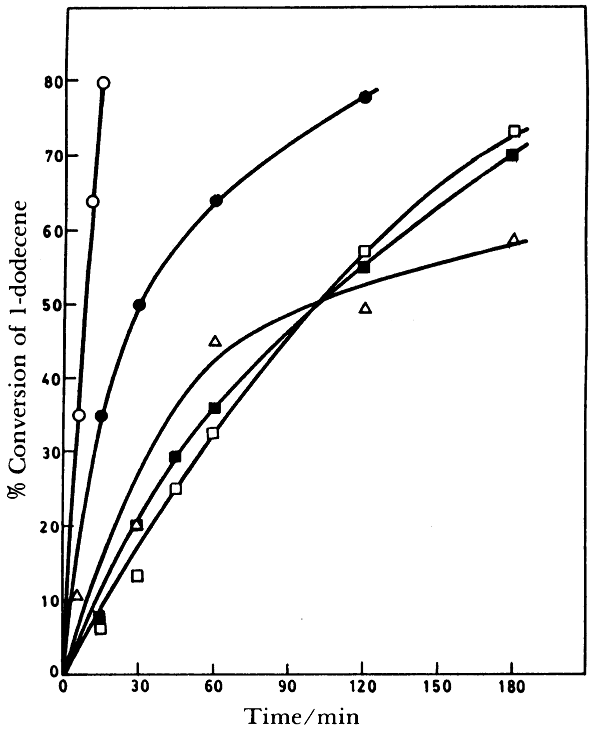

Fig. 1. Alkylation of phenol with 1-dodecene; comparison of activity of different catalysts. Mole ratio of phenol:1-dodecene 1.5:1, 130 °C, catalyst 2.5% (w/w) of phenol: ● zirconia, ■ Nafion-H, ○ triflic acid, □ CER, △ 98% sulfuric acid.

second-order kinetic expression. The activation energy was found to be 7.5 kcal mol^{-1}. The reaction was also carried out using different initial mole ratio of reactants. The results are give in Table 2.

Figure 1 compares the catalytic activities of Nafion-H, triflic acid, CER, 98% sulfuric acid, and zirconia. Equal weights of all the catalysts were employed in these experiments. Triflic acid exhibited highest activity while sulfuric acid showed lowest activity. The product was deeply colored when these two homogeneous acids were used. The three solid acid catalysts showed comparable activity. Repetitive experiments were carried out to investigate the reusability of these catalysts. No change of activity could be observed after two recycles.

Alkylation of Phenol with Propylene Tetramer. Alkylation of phenol with propylene tetramer was observed to be considerably slower than that with 1-dodecene and hence much higher loading of the catalysts had to be employed. The tetramer has branched skeletal structure and the double bond is located anywhere in the skeleton. This probably results in steric hindrance in the reaction between the tetramer and phenol. Table 3 shows the progress of the reaction at different temperatures. The data were fitted to a simple second-order kinetic expression. The variation of the rate constants with temperature gave an activation energy of 8.0 kcal mol^{-1}.

Table 3. Alkylation of Phenol by Propylene Tetramer: Effect of Temperature on Activity

Time	% Conversion of propylene tetramer at temp			
min	100 °C	115 °C	130 °C	145 °C
15	8	19	27	30
30	20	25	48	50
60	32	41	60	67
90	43	52	70	78
120	48	61	78	80

Mole ratio: phenol, propylene tetramer=1.5: 1. Loading of zirconia: 15% (w/w) of phenol.

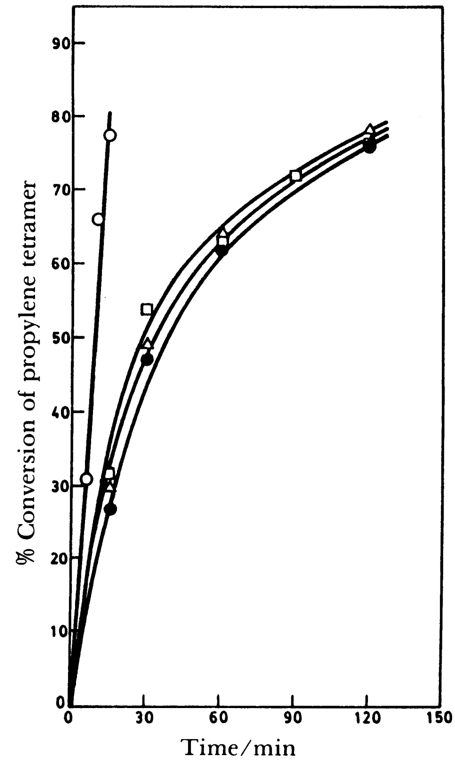

Fig. 2. Alkylation of phenol with propylene tetramer. Comparison of activity of different catalysts. Mole ratio of phenol: propylene tetramer, 1.5:1, 130 °C. Catalyst [%(w/w) of phenol]: ● Zirconia [15%], □ Nafion-H [15%], ○ triflic acid [2.5%], △ CER [15%].

The activity of different catalysts is compared in Fig.

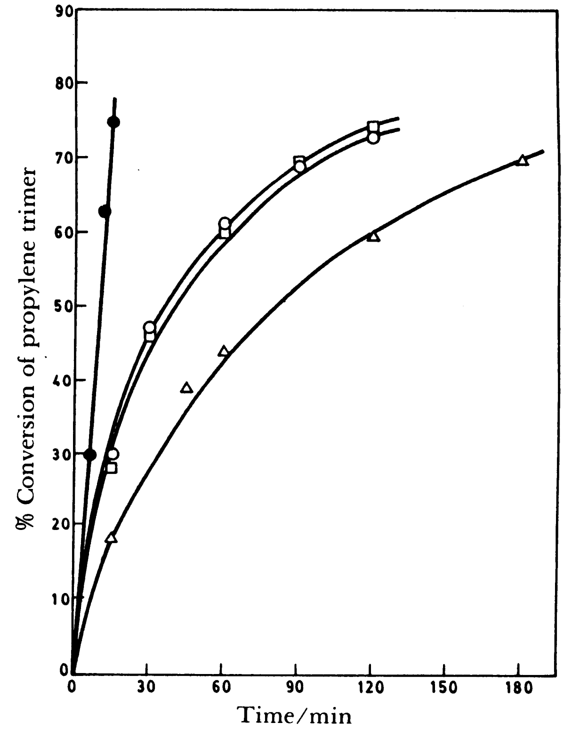

Fig. 3. Alkylation of phenol with propylene trimer. Comparison of activity of different catalysts. Molar ratio of phenol: propylene trimer 1.5:1, 130°C. Catalyst [%(w/w) of phenol]: △ Zirconia [20%], ○ Nafion-H [20%], ● triflic acid [2.5%], □ CER [20%].

2. The order of activity for the different catalysts is similar to that observed in alkylation with 1-dodecene.

Alkylation of Phenol with Propylene Trimer. The reaction was observed to be slower than that in the case of propylene tetramer. Comparable conversions were obtained at 20% [(w/w) of phenol] loading of zirconia and hence subsequent experiments were carried out at this loading. In the temperature range of 100—130 °C, the activation energy was found to be 10.3 kcal mol^{-1}.

The comparison of the activities of the different catalysts is shown in Fig. 3. Once again the order of activity is similar to that observed with the previous systems. Among the solid acid catalysts, zirconia showed somewhat lower activity than Nafion-H and CER.

Conclusion

Triflic acid exhibits the highest activity for the reactions, however, its use always results in deeply colored products and hence this catalyst appears unsuitable for practical use. Nafion-H is considerably more expensive as compared to CER and zirconia and exhibits similar activity. The zirconia catalyst, on the other hand, can be relatively inexpensive as compared to the polymer resin catalyst and at the same time has higher thermal and structural stability. Thus the present work demonstrates the promise of this novel catalyst for an industrially useful class of reactions.

One of us (DDC) wishes to thank CSIR, New Delhi, for the award of a Senior Research Feffowship.

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