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Heterogeneous Catalysis by Solid Superacids. 5.[1] Methylation of Benzene and Methylbenzenes with Methyl Alcohol over a Perfluorinated Resinsulfonic Acid (Nafion-H) Catalyst

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Nafion-H,[4] a perfluorinated resinsulfonic acid, catalyzes the gas-phase methylation of benzene and methylbenzenes with methyl alcohol under relatively mild experimental conditions (185 °C and atmospheric pressure). Reactions are clean, and water formed as byproduct does not deactivate the catalyst. Dimethyl ether is also formed in the competitive dehydration of methyl alcohol when the extent of methylation is low. Generally, low substrate selectivity is observed, indicating that a highly energetic methylating species is participating in the reaction. Dimethyl ether was also found to be an effective methylating agent, but weaker than methyl alcohol. The catalytic activity was found to drop quickly with onstream time when using dimethyl ether, probably due to esterification of the acidic sites. The catalytic activity can be, however, regenerated by steam treatment of the catalyst. Mechanistic aspects of the reactions are also discussed.

Nafion-H,[4] a perfluorinated resinsulfonic acid, activated in its H form, was found to be an efficient alkylating catalyst for heterogeneous gas-phase reactions.[5] Ethene and propene alkylate benzene to give ethylbenzene and cumene, respectively. Alkylations with ethyl and isopropyl alcohol are also catalyzed by Nafion-H. The observations that propylation of benzene with n-propyl alcohol gave only cumene as the alkylation product and that the alcohols dehydrate to the corresponding alkenes almost quantitatively when passed over Nafion-H raise the question whether the alcohols are merely precursors to the corresponding alkenes (or their protonated form, i.e., the corresponding carbenium ions). In the case of methylations with methyl alcohol no alkene formation is possible, and under the experimental conditions carbene formation is improbable. The high energy of the methyl cation makes its formation in the reactions also questionable.
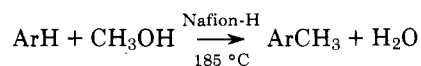
In recent work[1] we found that gas-phase methylation of phenol and cresols with methyl alcohol over Nafion-H catalyst proceeds readily. The reaction involves fast initial O-methylation of the phenol followed by intermolecular rearrangement to ring-methylated phenols. In continuation of our work, we would like to report that the methylation of less activated aromatic hydrocarbons, such as benzene and methylbenzenes, also takes place with methyl alcohol in the gas phase over Nafion-H as catalyst.

Experimental Section

The catalytic reactor and the experimental procedures were previously described.[5c] Dry nitrogen was passed at the rate of 5 mL/min. The liquid feed rate was 0.02 mL/min. Contact time of the catalyst with the gaseous feed was 5–7 s. The temperature was kept at 185 ± 2 °C, except when temperature effects were studied. All compounds used were of commercially available high purity, generally higher than 99.5%. Products were analyzed by gas liquid chromatography using a Perkin-Elmer Model 226 gas chromatograph, equipped with a flame ionization detector. Separation was obtained with a 150 ft × 0.01 in. capillary column coated with m-bis(m-phenoxyphenoxy)benzene + Apiezon L. Peak areas were measured with an electronic integrator and were corrected for differences in detector sensitivity. The accuracy of the determination of the product compositions is considered, based on comparison with mixtures of known composition, as ±0.5%.

Results

Benzene, toluene, and the three isomeric xylenes were methylated with methyl alcohol over Nafion-H catalyst. Polymethylation hardly occurred in the case of reaction of ben-

$$\text{ArH} + \text{CH}_3\text{OH} \xrightarrow[\text{185 °C}]{\text{Nafion-H}} \text{ArCH}_3 + \text{H}_2\text{O}$$

zene and toluene. The increased reactivity of xylenes and trimethylbenzenes toward methylation is reflected in the

Table I. Products of Methylation of Benzene, Toluene, and Xylenes with Methyl Alcohol over Nafion-H Catalyst

aromatic substrate[a]	registry no.	benzene	toluene	dimethylbenzene			trimethylbenzene			tetramethylbenzene		
				1,2	1,3	1,4	1,2,3[e]	1,2,4[f]	1,3,5[g]	1,2,3,4[h]	1,2,3,5[i]	1,2,4,5[j]
benzene[b]		95.9	4.1									
benzene[c]		95.5	4.5									
benzene[d]	71-43-2	99.0	1.0									
toluene[b]	108-88-3		90.8	4.5	1.6	2.5	0.2	0.4				
toluene		0.2	89.3	4.7	1.7	2.3	0.4	0.8				
o-xylene	95-47-6	1.0	57.2	6.2	0.3	7.6	17.9	0.8	2.5	3.5	3.0	
m-xylene	108-38-3		0.6	1.1	68.2	2.5	2.8	14.4	2.3		4.1	4.0
p-xylene	106-42-3		3.4	1.3	2.5	59.5	0.8	18.0	1.1	0.7	5.3	7.4

[a] Methanol:aromatic = 1:2 unless otherwise stated. [b] Methanol:aromatic = 1:5. [c] Methanol:aromatic = 1:1. [d] Methanol:aromatic = 5:1. [e] Registry no. 526-73-8. [f] Registry no. 95-63-6. [g] Registry no. 108-67-8. [h] Registry no. 488-23-3. [i] Registry no. 527-53-7. [j] Registry no. 95-93-2.

Table II. Methylation of Toluene with Methyl Alcohol over Nafion-H Catalyst at Different Temperatures

temp, °C	% xylene yield	% o:m:p ratio
145	0.82	56:18:26
155	2.21	56:18:26
171	6.26	55:17:28
185	11.7	53:18:29
209	14.3	32:29:39

appearance of tri- and tetramethylbenzenes, respectively, in the products. The product compositions obtained at 185 °C are summarized in Table I. The reaction of toluene with methyl alcohol was studied at several temperatures. The results are given in Table II.

Dimethyl ether was also studied as a methylating agent with Nafion-H catalysis. When a mixture of dimethyl ether and benzene (molar ratio 1:2.7) was passed over the catalyst at 185 °C, a 1.2% yield of toluene was obtained during the first 30 min of onstream time. The reactivity of the catalyst thereafter quickly diminished and after 90 min only traces of toluene were observed. No alkylating activity was found after 120 min. Steam was then passed through the catalyst at 185 °C for 1 h and the reaction continued. Catalytic reactivity was found to be regenerated to its initial value. The use of moist benzene (saturated with water) slowed the deactivation of the catalyst considerably.

Several competitive methylations of aromatics with methyl alcohol were also conducted. Benzene with an isomeric xylene and methyl alcohol (in 1:1:1 molar ratio) gave the products listed in Table III. The isomeric composition of the tri- and tetramethylbenzenes obtained is similar, but not identical with those observed in the noncompetitive methylation of xylenes. The reason is probably that secondary processes, especially isomerization, are more suppressed in the competition experiments with benzene present (vide infra). Results

of competitive methylation of phenol and benzene, aromatics of significantly different reactivity, and competitive alkylation of toluene with methyl and ethyl alcohol are also listed in Table III.

Discussion

The results summarized show that methylation of benzene and methylbenzenes with methyl alcohol is readily accomplished over Nafion-H catalyst in the gas phase. The yields differ markedly and depend upon the aromatic compound being methylated. Methylation is enhanced going from benzene to toluene to xylenes. An equimolar mixture of benzene and methyl alcohol gave 4% of toluene at 185 °C. The use of a fivefold excess of benzene hardly changed the toluene/benzene ratio in the products, but the conversion of methyl alcohol increased to 23%. From the data in Table II, activation energy for the Nafion-H catalyzed methylation of toluene can be calculated as 28 kcal mol, assuming that the rate constants are proportional to the xylene yield, as at low conversions secondary processes are negligible, and using these values in the Arrhenius equation.

Methylbenzenes gave a higher utilization of methyl alcohol in their methylation than is the case with benzene. With a 2:1 molar toluene to methyl alcohol ratio 21% of the latter was used in the methylation process. Venuto et al.,[6] using a rare earth exchanged zeolite X catalyst, obtained, with a molar feed composition of benzene:methyl alcohol of 3:1, a 17.3% conversion to toluene, based on methyl alcohol, at 200 °C. Yashima et al.[7] found about 18% methyl alcohol conversion over the H form of a zeolite Y catalyst at 185 °C. Ni- and Co-exchanged catalysts were as effective as the H form, while Ce- and La-exchanged catalysts were ca. 50% more active. It is apparent that Nafion-H due to its enhanced acidity is comparable or somewhat superior to zeolite type catalysts. The special geometric arrangement of the zeolite catalysts increases markedly their catalytic activity. The lack of three-dimensional lattice in Nafion-H is compensated by its high

Table III. Competitive Alkylation Experiments over Nafion-H Catalyst

			% product composition						
arenes	alcohols	reagents ratio	toluene	xylenes	ethyl toluenes	trimethyl-benzenes[a]	tetra-methyl-benzenes[a]	cresols	dimethyl-phenols
o-xylene + benzene	methyl	1:1:1	14.7			59.7	25.6		
m-xylene + benzene	methyl	1:1:1	17.6			54.4	28.0		
p-xylene + benzene	methyl	1:1:1	15.0			61.5	23.5		
phenol + benzene	methyl	2:6:1	2.3					75.2[b]	22.5[c]
toluene	methyl + ethyl	4:1:1		20.3	79.7[d]				

[a] Isomeric composition similar to that obtained with xylenes alone. [b] Isomer ratio o:m:p = 47:10:43. [c] Isomer composition: 2,3 7%, 2,4 27%, 2,5 20%, 2,6 32%, 3,4 7%, 3,5 7%. [d] Isomer ratio o:m:p = 39:36:25.

acidity. Xylenes are methylated more easily than toluene. *m*-Xylene under similar conditions to toluene gave 43% methyl alcohol conversion, while the ortho and para isomers gave 86 and 84% conversions, respectively.

As discussed, an activation energy of 28 kcal/mol was estimated for the methylation of toluene. As the same composition of xylenes was obtained in the temperature range of 145–185 °C, they seem to be formed in the methylation process and do not undergo further isomerization. Indeed, xylenes were found to isomerize and transfer methyl groups only to a limited extent when reacted over Nafion-H at 193 °C.[8] Their isomerizing ability increased at higher temperatures and more prolonged contact time. At 209 °C, methylation of toluene gave a xylene fraction much richer in the meta isomer indicating substantial isomerization of the formed xylenes.[8,9] The overall yield at 209 °C is, however, lower than that expected from extrapolation and data obtained at lower temperatures. This may be due to the increasing thermal instability of Nafion-H above 200 °C reducing its activity.

Methylation of toluene under the regular reaction conditions gave an isomeric xylene composition of about 54% *o*-, 19% *m*-, and 27% *p*-xylene. The high ortho–para ratio of 2 is characteristic of an electrophilic substitution with a reactive alkylating agent. Such cases are usually accompanied by low substrate selectivity, generally measured by the toluene/benzene rate ratio.[10,11] Since the competitive methylation of toluene and benzene could be followed only with the use of labeled compounds, instead, in the present study we carried out the competitive methylation of an equimolar mixture of benzene and an isomeric xylene. According to the data in Table III, *m*-xylene is 4.7 times more reactive in methylation than benzene, and the corresponding value for the other isomeric xylenes is 5.6. We did not consider toluene formation by transmethylation of benzene with xylene, as this reaction is insignificant under the reaction conditions.[5] Methyl transfer from trimethylbenzenes is more significant, but such a process can occur only after methylation and the limited contact time of the reagents over the catalyst in the flow system will minimize this process.

Another way to estimate the reactivity of the different methylbenzenes is to compare the methyl alcohol conversion under the same conditions. From the values of Table I, toluene seems to be 2.5 times more reactive than benzene, while xylenes react 5–10 times faster. The differences found between the results obtained from comparative conversions and competitive methylations may be due to competing dehydration of methyl alcohol and to some differences in the surface activity of the catalytic resin. Such changes are known to change the reactivities in solid acid catalysis.[12]

The lack of regioselectivity and of steric restraints of the methylating agent is again seen in the methylation products of xylenes. Analysis of the products in this case is more complex. The enhanced reactivity of trimethylbenzenes toward methylation gives tetramethylbenzenes in considerable yield. In addition, isomerization of higher methylbenzenes is not insignificant, although the much slower transmethylation is still negligible.[8] The trimethylbenzene composition gives a fair estimate of the positional selectivity in xylenes. Methylation of *p*-xylene should, of course, give only one product, i.e., pseudocumene. In fact this isomer was observed as 90% of the trimethylbenzene fraction, showing that the secondary isomerization process is only of limited importance (10%). Methylation of *o*-xylene gives a trimethylbenzene fraction comprised of 29% hemimellitene, 68% pseudocumene, and 3% mesitylene. The high amount of 1,2,3-isomer again reflects the lack of steric hindrance toward methylation of the activated ortho position. Due to possible isomerization the initial amount of this isomer is probably higher, as being the least stable isomer[9] it isomerizes faster than the other trimethyl-

benzenes.[8] Indeed, in competitive methylation where individual compounds experience shorter contact times, a somewhat higher (37%) amount of hemimellitene was found.

All three possible isomeric trimethylbenzenes were found in the methylation of *m*-xylene, including 12% mesitylene. This amount is much higher than those obtained from secondary isomerization of trimethylbenzenes in the course of the methylation of other xylenes. Direct methylation of the 5 position meta to both methyl groups may be questionable, but formation of 1,3,5-trialkylbenzene from the 1,3-dialkyl precursor has precedents in transmethylation[13] and transethylation[5,14] reactions. The high amount of hemimellitene obtained shows lack of steric hindrance even in a position ortho to two methyl groups.

The methylating agent clearly has electrophilic character. However, it is not considered to be a free methyl cation, an unfavorable, highly energetic species, but a polarized methyl alcohol entity which methylates the aromatic rings. We suggest that methyl alcohol is preferentially adsorbed on the acidic sites of Nafion-H. Its high polarization occurs upon adsorption. The partially positively charged methyl group then reacts with an aromatic hydrocarbon absorbed on an adjacent site. Desorption of the products, water and the methylated arene, completes the reaction.

It is further reasonable to assume that methyl alcohol, being a stronger nucleophile than benzene or toluene, will be more easily adsorbed. In addition, we found that the same percentage of benzene was methylated with methyl alcohol when their mole ratio was 5:1 or 1:1. The same observation was made with toluene (5:1 and 2:1 molar ratios). Higher excess of the aromatics causes a proportional increase in acidic sites containing adsorbed arene (which represents, however, only a small fraction of all the sites) adjacent to sites with adsorbed methyl alcohol, the essential condition for the methylation process. The higher yields in the methylation of toluene are the result of the higher susceptibility of toluene toward methylation and not of increased adsorption. Once a toluene molecule is adsorbed on a site adjacent to one containing an adsorbed methyl alcohol molecule, the chance of methylation to take place is higher in comparison with an adsorbed benzene molecule. *m*-Xylene, which has a much higher basicity than all the other compounds investigated, does compete efficiently with methyl alcohol for adsorption. As a result less methyl alcohol is adsorbed. The decrease in the amount of available methylating agent is reflected in the lower yields of methylation of *m*-xylene in comparison with other xylenes. This suggested reaction path is, however, speculative and detailed kinetic studies[15] would be required in order to verify it.

When methyl alcohol is in excess to benzene, the toluene yield drops appreciably. Polarized methyl alcohol molecules adsorbed on the catalyst can also readily methylate a second molecule of methyl alcohol. Dimethyl ether and water are the products of this reaction, which always take place to some extent. As a result, less toluene and more dimethyl ether are formed. The dehydration of methyl alcohol probably involves an electrophilic attack of the partially positively charged methyl group, rather than the nucleophilic attack of methoxide ion on a second molecule of methyl alcohol, as suggested for the dehydration of alcohols over alumina.[16] The latter mechanism requires the existence of both acidic and basic sites on the catalysis which is not the case with Nafion-H. The perfluorinated ether oxygen atoms seem to lack significant nucleophilicity.

Dimethyl ether itself is a known methylating agent. Using methyl alcohol and benzene over alumina[17] dehydration to dimethyl ether took place first, followed by methylation of benzene by the ether. With Nafion-H catalysis dimethyl ether was found to be an inferior methylating agent relative to

methyl alcohol, thus ruling out the intermediacy of the former in methylation reactions with methyl alcohol. Apart from its reduced methylating ability, dimethyl ether deactivates the catalyst by esterifying the sulfonic acid groups of Nafion-H, thus reducing its acidity. Water vapor hydrolyzes the ester and regenerates the catalytic activity. Using moist benzene and dimethyl ether, the deactivation was slowed down appreciably, but the low concentration of water due to its limited solubility did not supress the esterification completely. When methyl alcohol is the methylating agent, water formed in the methylation process as the by-product is present in high enough concentration to prevent esterification.

Methyl alcohol and phenol, as reported, react smoothly over Nafion-H to give a mixture of anisoles and methylphenols.[1] Competitive methylation between phenol and benzene showed methylation of phenol to be preferred by a factor of ca. 250. Comparison of the yields in noncompetitive direct methylation of phenol and benzene gives a reactivity ratio of 15–20. Gas-phase ethylation of phenol and benzene with ethene using a rare earth exchanged zeolite X catalyst gave a selectivity value of 7 in favor of phenol.[18] Homogeneous gas-phase *tert*-butylation showed phenol to be only 4–5 times more active than toluene.[19] The tenfold difference in the selectivity obtained in the present work compared with the literature values indicates a marked difference in the adsorption over Nafion-H in the competition experiment. The presence of phenol prevents adsorption of benzene as they compete for the same sites. Similar phenomenon in liquid phase catalysis was reported.[12b]

We also found ethyl alcohol to be a better alkylating agent than methyl alcohol. An equimolar mixture of these alcohols reacted with toluene gave four times more ethyltoluenes than xylenes. As these alcohols do not differ much in the basicity, we assume simlar adsorption ability for both on Nafion-H. The higher amounts of ethyltoluenes formed are due to the easier formation of the ethylating agent (ethyl cation or protonated ethyl alcohol) than the methylating species, i.e., easier polarization of the alcohol upon adsorption.

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