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NITRATION OF TOLUENE WITH NITRIC ACID IN THE PRESENCE OF AROMATIC SULFONIC ACIDS SUPPORTED ON THE POROUS MATERIALS

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It was found that nitration of toluene with nitric acid catalyzed by aromatic sulfonic acids supported on the porous materials gave mononitrotoluene of the high para-isomer content. Thus, nitration catalyzed by toluene-2,4-disulfonic acid supported on Celite-545 gave higher para:ortho ratio (1.60) than that of mixed acid nitration (0.6).

The classical mononitration of toluene with mixed acid (a mixture of nitric acid and sulfuric acid) gives mononitrotoluene composed of 63% ortho-, 4% meta- and 33% para-isomers.

The great demand for p-nitrotoluene stimulated the elaboration of a variety of methods of toluene nitration that increase the content of p-nitrotoluene in the isomer mixture obtained by nitration. Thus, nitration of toluene with nitric acid in the presence of dehydrated ion-exchange resin (polymeric sulfonic acid)[1] or phosphorus pentoxide[2] increases the para:ortho ratio to 1.1 or 1.16, respectively (usually it is 0.53)[3].

Other suggestion include nitration with dilute nitric acid in the presence of mercuric nitrate[4] and with sodium nitrate in the presence of $AlCl_3$ or $FeCl_3$[5].

However, in order to apply these nitration methods to commercial scale in place of the mixed acid nitration, it seems that these methods have many difficult problems to be solved, e.g. the use of expensive reagents or catalyst, recovery of the catalyst and the low yield of mononitrotoluene etc.

We found that nitration of toluene with nitric acid in the presence of dehydrated aromatic sulfonic acids supported on the porous materials, greatly increase the para:ortho ratio and the yield of mononitrotoluene, compared with nitration without porous supports. Among the aromatic sulfonic acids, toluene-2,4-disulfonic acid was especially effective and in various porous supports, diatomaceous earth (Celite-545) gave the most excellent results.

A nitration procedure is as follows. The concentrated aqueous solution of toluene-2,4-disulfonic acid and porous supports are mixed, and dried at the temperature from 95° to 100°C. Toluene is added in this mixture, and distilled out until any water is not detectable. Fuming nitric acid is slowly added dropwise to the mixture vigorously stirring from 0° to 3°C. The mixture is then stirred for 5 hours at 0°C, and further 5 hours from 20° to 25°C. The catalyst,

toluene-2,4-disulfonic acid supported on porous supports, is filtered off and washed with fresh toluene. The filtrate is washed by aqueous sodium hydroxide solution and is analyzed by means of gas-liquid chromatography.

The results are shown in Table 1.

TABLE 1. NITRATION OF TOLUENE

Supports	Mononitrotoluene					Dinitro-toluene
	ortho	meta	para	p/o	Yield(%)*	
None	50.9	2.3	46.8	0.92	37	Trace
Celite-545	38.5	2.0	61.5	1.60	90	"
Activated clay	49.6	2.1	48.5	0.97	54	"
Silica gel(for chromatography)	45.0	2.3	52.7	1.17	83	"
Porous resin**	41.2	2.2	56.6	1.38	67	"

Toluene-2,4-disulfonic acid(eq.) : Nitric acid(eq.) = 2
Supports(g) : Toluene-2,4-disulfonic acid(g) = 2
Toluene(g) : Supports(g) = 5 to 6

* Yield is based on the used nitric acid.

** Porous styrene-divinylbenzene copolymer.

In order to examine the life of catalyst, the catalyst(toluene-2,4-disulfonic acid supported on Celite-545) was used on the repeated nitration for six times, but the appreciable changes of the catalytic action (isomer ratio and yield of nitrotoluene) were not observed on this repeated runs.

Although the mechanism in which porous supports increase the para:ortho ratio and yield of mononitrotoluene in toluene nitration is not clear at present, it is very interesting that such porous supports play a great role in liquid phase catalytic reaction, and the possibility of many applications to other reactions may be expected.

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