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Catalysis Communications 8 (2007) 845–849

CATALYSIS COMMUNICATIONS

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Vapor phase nitration of toluene over $CuFe_{0.8}Al_{1.2}O_4$

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Received 29 May 2006; received in revised form 4 August 2006; accepted 28 August 2006
Available online 6 September 2006

Abstract

Vapor phase nitration of toluene by using $CuFe_{0.8}Al_{1.2}O_4$ as a catalyst was studied by varying strength of nitric acid (10–69%) as a nitrating agent. Water vapor generated during the reaction acts as a diluent for the exothermic process. Varying the reaction temperature in the range of 100–200 °C revealed that below 125 °C lower conversion of toluene to mono-nitro toluene was obtained while above 125 °C dinitro and oxidation byproducts were obtained. The maximum conversion of toluene to mono nitro toluene was 58% with 77% selectivity towards *para* nitro toluene.

Keywords: Vapor phase nitration; Toluene; Nitric acid; Exothermic

1. Introduction

Nitrotoluenes (NTs) find applications as intermediate products in the production of pharmaceutical compounds, dyes, perfumes, explosives, polymers, pesticides and fertilizers. The *para*-isomer has better commercial value as the pharmaceutical intermediate. Industrial-scale nitration of toluene is usually carried out in liquid phase with mixed acids containing nitric and sulfuric acids for reasons of practicability and economics, where sulphuric acid serves as a water binder and heat sink for the nitration as these reactions are exothermic [1,2]. The typical product distribution of *ortho*-, *meta*- and *para*-isomers in the conventional nitration is about 58:4:38, thus the process suffers. Another main drawback of this reaction is the production of large amounts of spent acid, which have to be regenerated because a simple neutralization is uneconomical [3]. Replacement of the above hazardous processes by alternative clean process is the demand today for the nitration hence utilization of solid acid catalyzed vapor phase nitration of toluene appears to be attractive and clean methodology. McKee and Wilhelm [4] studied the vapor phase nitration of benzene and toluene for the first time using nitrogen dioxide as the nitrating agent and silica gel as catalyst. Thus the vapor phase nitration of aromatic compounds either with nitrogen dioxide or with nitric acid and different solid acid catalysts was further studied by many-concerned scientist [5–28].

In earlier work, we have studied the nitration of toluene and other aromatic hydrocarbons in the liquid phase at ambient temperature using $CuFe_{0.8}Al_{1.2}O_4$ and 69 wt% nitric acid. The preparation procedure and characterization like acidity measurements, BET surface area measurement, XRD and SEM of the $CuFe_{0.8}Al_{1.2}O_4$, have been reported [29]. Nitration depends on high acidity and the structure of the catalyst, therefore to maintain the catalyst activity during the reaction it was essential to effectively remove water generated in the reaction. In acidic media the catalyst was leached away, so to overcome above difficulties we have studied nitration of toluene in vapor phase.

2. Experimental

Vapor phase nitration experiments were performed in a fixed-bed continuous down flow glass reactor at atmospheric pressure. One gram of the $CuFe_{0.8}Al_{1.2}O_4$ catalyst was loaded in a tubular glass reactor of 6 cm diameter and 35 cm in length. Then the reactions were carried out

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1566-7367/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.catcom.2006.08.031

Nomenclature

NT	nitro toluene	*p*-NT	*para*-nitro toluene
MNT	mono nitro toluene	OP	oxidation products
o-NT	*ortho*-nitro toluene	DNT	dinitro toluene
m-NT	*meta*-nitro toluene		

by passing toluene and nitric acid (10–69%) in the ratio 1:0.5–1.5 using syringe pump (sage feed pump), in the temperature range of 100–200 °C with nitrogen as a carrier gas. The reaction product was condensed by circulating cold water. The product was treated with urea to separate any traces of nitric acid and analyzed by GC. Total yield of 58.0% mono nitro toluene (MNT) and 37% of unreacted toluene was obtained. Traces of dinitro toluene, benzaldehyde, benzoic acid and nitro benzoic acid were obtained as shown in Scheme 1.

3. Results and discussion

At 125 °C using 1:1 mol of toluene and nitric acid the concentration of the nitric acid was varied from 10 to 69%. From Fig. 1 it is seen that nitric acid with strength 25% was the most effective in the nitration of toluene (80% *para*-nitro toluene [*p*-NT]). The yield of mono nitro toluene is optimum nitric acid with strength 25% with further increase in the strength of nitric acid, the yield of mono nitro toluene decreases and also the percentage of *para* isomer decreases. Strength of nitric acid more than 30% generate nitrous oxide, which oxidizes side chain of toluene consequently deactivating the catalyst [30]. Pore blockage of the catalyst surface due to deposition of oxidation products makes the active sites inaccessible for the nitration reaction. Nitration is an exothermic reaction; use of dilute nitric acid provides water vapors, which dissipates the heat of reaction so that the formation of oxidation side products is minimized. The cost of the process operated using dilute nitric acid would be certainly low compared to concentrated nitric acid. This cost factor adds advantage for the commercialization of the vapor phase nitration. All further experiments were done with dilute nitric acid with strength 25%.

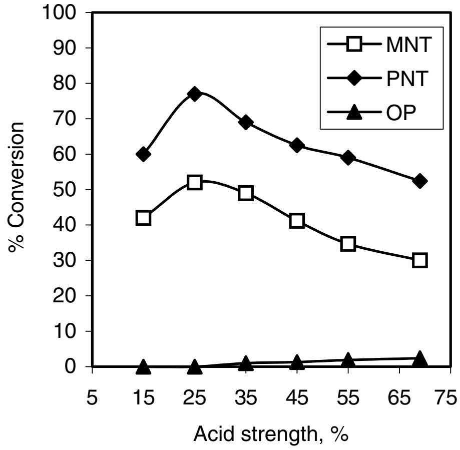
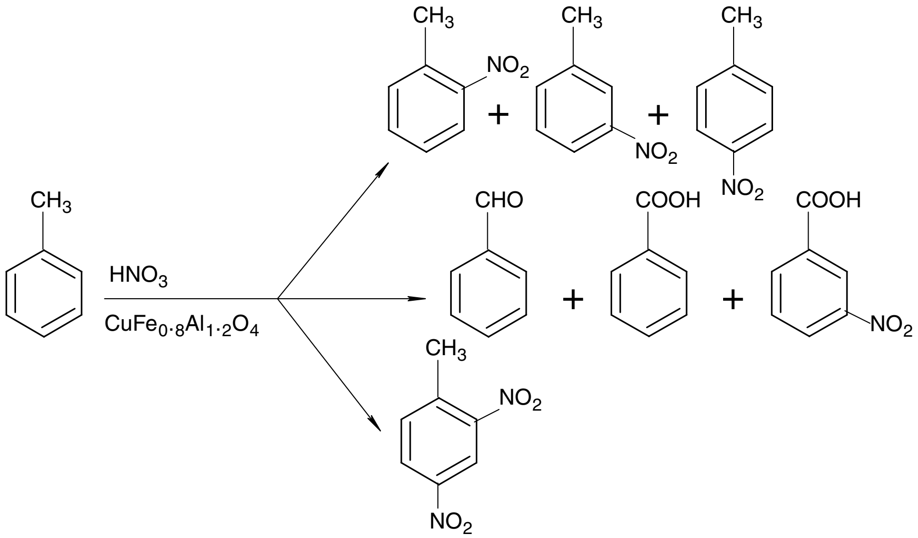


Fig. 1. Influence of the concentration of nitric acid. Toluene (1 mol):HNO_3 (10–69%) = 1:0.7, WHSV = 0.05 h^{-1}, $T = 125$ °C.



Scheme 1. Reaction of toluene with nitric acid in presence of solid acid catalyst.