Selective N-alkylation of aniline with methanol over a heteropolyacid on montmorillonite K10

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ABSTRACT

N-methylaniline is an industrially important product in the manufacture of paper, textile dyes, drugs, perfumes and explosives. The vapour phase alkylation of aniline with methanol forming N-methylaniline is advantageous over liquid phase alkylation. In present study, vapour phase methylation of aniline over dodecatungstophosphoric acid supported on K10 montmorillonite was systematically studied and optimization of process parameters was carried out. The 20% m/m DTPA/K10 was found to be optimum with 79% aniline conversion and 99% N-methylaniline selectivity. The reaction required milder operating conditions than reported for commercial catalysts. We also studied the feasibility of 20% m/m DTPA/K10 as a catalyst for the alkylation of aniline with other alcohols like ethanol, n-propanol, iso-propanol and n-butanol. The activity of 20% m/m DTPA/K10 decreased with increasing carbon number.

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1. Introduction

Alkylation belongs to the most important reactions in organic chemistry. Aniline alkylation is an industrially important reaction due to the fact that alkyl-anilines are basic raw materials for synthesis of organic chemicals, chemical intermediates and/or additives in dyes, synthetic rubbers, explosives, herbicides and pharmaceuticals (Negwer, 1994; Kim et al., 2002; Stauffer and Hartwig, 2003; Sunwanprasop et al., 2004). Vapour phase aniline alkylation over environmentally safe solid catalysts is the answer to the conventional method of liquid phase alkylation using mineral acids and Friedel–Crafts type catalysts (Bhattacharya and Nandi, 1975). Although it provides higher yields (Doraiswamy et al., 1981) than vapor phase alkylation, this process is restricted due to disadvantages such as high capital cost, corrosion problems and formation of byproducts that cannot be recycled. With the increasing awareness of environmental issues, a wide variety of solid acid catalysts and alkylating reagents have been employed in this process. Recently, progress in the application of acid catalysts for aniline alkylation has been reviewed (Narayanan and Deshpande, 2000). Several solid acids have been reported for aniline alkylation with methanol, including zeolites (Narayanan and Sultana, 1998; Ivanova et al., 2001; Anand et al., 2003), modified clay minerals (Narayanan and Deshpande, 1996; Sreekumar and Sugunan, 2002; Yadav and Doshi, 2003), vanadium (Narayanan and Deshpande, 1995; Narayanan and Prasad, 1995) and iron oxides (Sreekumar et al., 2000; Nishamol et al., 2004), leading to N-methylaniline (NMA), N,N-dimethylaniline (DMA) and o-toluidine

(OT). However, there is a selectivity issue between mono-N and N,N-dimethylated products of the existing catalysts, based on zeolite or alumina are successful in stopping or controlling the conversion of mono-N-methylated to N,N-dimethylated aniline products. Such conversion is mainly controlled by the process parameters (Luque et al., 2007).

Demand for the selective synthesis of N-methylanilines has recently grown due to a variety of applications in agrochemical industries, as antioxidants in rubber industries and as dye-stuffs in textile industries (Baustista et al., 1997; Baustista et al., 1998; Ullmann, 1999; Narayanan and Deshpande, 2000; Ivanova et al., 2001; Garces et al., 2003). The selective N-alkylation of aniline with dialkyl carbonates in liquid phase on zeolites with high yields was reported (Selva et al., 2005). However, a very large molar ratio of dialkyl carbonate to aniline (up to 70:1) employed in this study prevents the process from being commercially viable. The products are complex (Scheme 1) and the selectivity depends strongly on the experimental conditions and on the nature of the catalyst. In particular, it is more difficult to control the reaction for obtaining NMA with a high selectivity.

The aim of this study was to develop a new catalyst and to chose the process parameters for selective synthesis of N-methylaniline from aniline and methanol. A heteropolyacid supported on K10 montmorillonite fulfills this condition.

2. Experimental

2.1. Chemicals

Dodecatungstophosphoric acid [$H_3W_{12}O_{40}$ xH_2O] (DTPA), methanol (99%), montmorillonite K10 and aniline (99%) were obtained from

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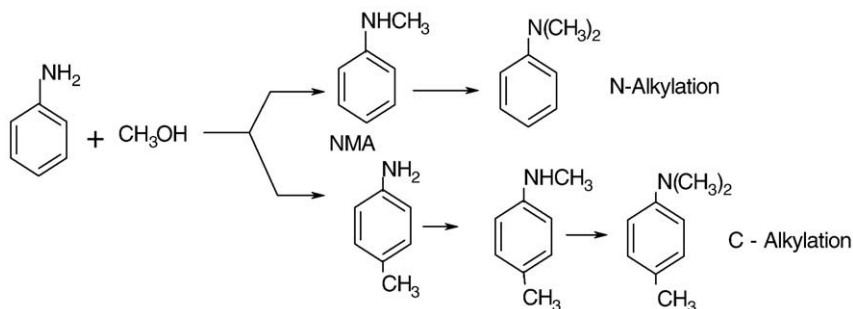
Scheme 1. Reaction scheme.

M/s S.D. Fine Chemicals, Mumbai. All reagents were of analytical grade and used without further purification.

2.2. Catalyst preparation

DTPA/montmorillonite was prepared by impregnation. An amount of 2 g DTPA was dissolved in methanol and was added slowly to 20 g K10 with stirring. The paste was dried on a water bath, then at 90 °C to remove methanol completely. Prior to use, the sample was dried at 100 °C to remove moisture. The composition of the catalysts was 5–30% m/m DTPA/K10.

2.3. Catalyst characterization

2.3.1. Powder X-ray diffraction
The crystallinity and the phase purity of the samples were determined by powder X-ray diffraction (XRD) (Rigaku Miniflex, Japan, Cu-Ka) (Fig. 1).

2.3.2. Nitrogen adsorption
The specific surface area was obtained from nitrogen adsorption–desorption isotherms at 787 K measured in an SA 3100, USA analyzer. The surface area was calculated by the BET method (Table 1).

2.3.3. Temperature programmed ammonia desorption (TPAD)
The total amount of acidic sites present in the catalyst was estimated by using temperature-programmed desorption (TPD) of NH_3 on a Micromeritics AutoChem 2910 instrument. 0.1 g of the catalyst was dehydrated at 773 K in dry air for 1 h and then purged with helium for 0.5 h. The temperature was decreased to 398 K under the flow of helium, and then 0.5 ml NH_3 pulses were supplied to the samples until no more NH_3 was uptaken. NH_3 was desorbed in the helium flow by increasing the temperature to 813 K with a heating rate of 10 °C/min NH_3 desorption with a TCD detector (Table 2).

2.4. Catalyst formulation

All catalysts were formulated as pellets by applying 10 ton pressure. The pellets were cut into small pieces of 10–20 mesh (3 mm irregular size).

2.5. Reaction procedure

The vapor phase reaction was carried out in a SS316 (20 ml volume) continuous downflow reactor (Fig. 2). The catalyst (10 g) was activated at 250 °C, under nitrogen (50 ml/min) for 2 h, prior to the experiment. Typically, a mixture of aniline: methanol at a molar ratio of 1:6, at 260 °C at a weight hourly space velocity (WHSV) of 1.1 h^{-1} and atmospheric pressure was used. Each reaction was performed for a period of 6 h during the steady state. The products were cooled in a trap and collected at regular intervals for analysis.

2.6. Analysis

The liquid reaction products were analyzed by gas chromatography (GC-1000) (packed column, liquid phase 5% SE-30, solid support CHW-HP, 1/8' diameter × 8' length) with nitrogen as a carrier gas and programmable temperature between 40 and 200 °C. The reaction
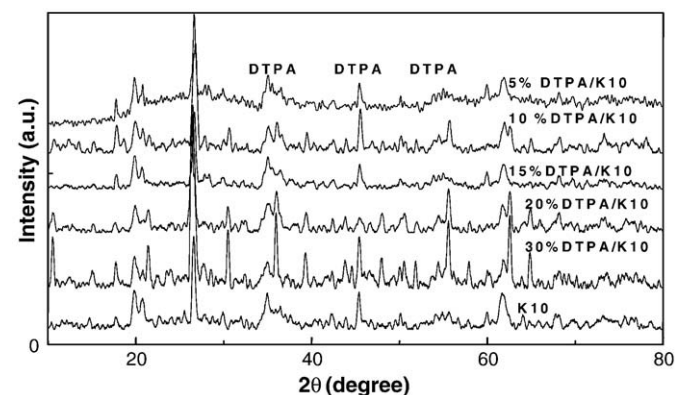

Fig. 1. Powder X-ray diffraction for different percent loading of DTPA on K10 montmorillonite.

Table 1
Nitrogen adsorption by BET method.

No.	Catalyst	Specific BET surface area (m^2/g)
1	K10 montmorillonite	223
2	5% m/m DTPA/K10	217
3	10% m/m DTPA/K10	195
4	15% m/m DTPA/K10	156
5	20% m/m DTPA/K10	135
6	30% m/m DTPA/K10	104

Table 2
Total acidity measured by TPAD.

No.	Catalyst	Total acidity (mmol g^{-1})	Increase of acid site concentration after DTPA loading (%)
1	K10 montmorillonite	0.139	–
2	5% m/m DTPA/K10	0.189	5.00
3	10% m/m DTPA/K10	0.242	10.3
4	15% m/m DTPA/K10	0.328	18.9
5	20% m/m DTPA/K10	0.423	28.4
6	30% m/m DTPA/K10	0.426	28.7