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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

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To cite this article: Yuan Liu , Min Zhong , Wei Yu & Yu-Long Ma (2005) One-Step Synthesis of Tolunitriles by Heterogeneously Catalyzed Liquid-Phase Ammoxidation, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 35:23, 2951-2954

To link to this article: http://dx.doi.org/10.1080/00397910500278214

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One-Step Synthesis of Tolunitriles by Heterogeneously Catalyzed Liquid-Phase Ammoxidation

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Abstract: Tolunitriles have been efficiently synthesized by selective ammoxidation of corresponding xylene over silica-supported Co-Mn-Mg-Ni catalysts, without solvent for the first time in a one-pot procedure. The selectivity for mono-nitriles is almost 100%.

Keywords: Ammoxidation, liquid-phase ammoxidation, tolunitrile, xylene

INTRODUCTION

Mononitriles are of widespread use in fine chemical production. They can be converted into commercially interesting and valuable intermediates for the synthesis of pharmaceuticals, plastics, resins, fibers, dyestuffs, and so on.^[1,2]

Traditionally, tolunitrile was mainly synthesized from diazotization of methylbenzamine,^[3] catalysis of benzoate ions in the presence of ammonia,^[4] dehydration of methylbenzamide^[5] or aldoxime,^[6] and cyanation of aryl chloride^[7] or toluic acid.^[8] These methods usually employ expensive feedstock or cause serious pollution and are not suitable for large-scale production. The vapor-phase ammoxidation of xylenes based on vanadium-containing catalysts has considerable importance as the commercial method for producing tolunitrile and dicyanobenzenes.^[9,10] However, the temperature is usually greater than 673 K, and the yield and selectivity for tolunitriles are very low, because two methyl groups in xylene are identical.

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Scheme 1. One-step synthesis of tolunitriles.

Another method for the synthesis of tolunitriles is the selective ammoxidation of methylbenzyl chlorides.^[11] However, the drawbacks of this process are the use of a large amount of chlorine and the generation of large amounts of poisonous effluents.

To the best of our knowledge, there are no reports about heterogeneously catalysed ammoxidation of xylene to tolunitrile. By comparison, cobalt oxides possess an extremely high oxidative reactivity, and manganese and magnesium oxides have a lower, although still high, activation ability in the liquid-phase ammoxidation. After being used five times, the catalyst still demonstrates good activity. The main by-products of this reaction are tolualdehyde and toluic acid, and their content increases with the time. Taking into account the optimal selectivity, we choose 5 h as the reaction time.

In conclusion, we have showed an efficient synthesis of mono-nitriles from xylene (Scheme 1). The mild reaction conditions coupled with high selectivity makes this methodology a valuable tool to generate tolunitrile. The absence of solvent and the recyclability of the catalyst make this an environmentally friendly methodology amenable to scaling.

The position of the second substituent (methyl) on the toluene molecule greatly influenced the yield and the selectivity of the reactivity under comparable conditions. As shown in Table 1, the 4-isomer revealed the highest conversion and selectivity to the desired nitrile, whereas the data significantly declined for the 3- and 2-isomers (4 > 3 > 2). This row mirrors the different accessibility and reactivity depending on the position of the substituent methyl. It may be attributed to an electronic effect on the aromatic ring

Isomer	Catalyst	Molar ratio	Metal weight (wt%)	Selectivity (%)	Yield (%)
0-	Co/Mn/Mg/Ni	1:0.946:1.188:0.056	6.9	99.6	14.0
m-	Co/Mn/Mg/Ni	1:1.397:1.527:0.016	9.3	99.3	18.3
p-	Co/Mn/Mg/Ni	1:1.012:1.224:0.081	9.9	99.7	28.7

Table 1. Result of liquid-phase ammoxidation of xylene

One-Step Tolunitrile Synthesis

related to the addition of Me groups, although steric hindrance also appeared to be responsible for the consistently low rates of o-xylene ammoxidation.^[12,13] We also prepared p-tertbutyl benzonitrile by p-tertbutyl toluene under the same conditions.^[14] In the case of p-tertbutyl toluene, a 35.92 mol% conversion with 99.8 mol% selectivity to p-tertbutyl benzonitrile was obtained, which exhibits higher activity and selectivity than xylene. Possibly due to the electron effect, tertbutyl is more electron-donating compared with methyl group, thus stimulating H-extraction of methyl, which is the control step of the reaction.^[15]

EXPERIMENTAL

Xylenes and reagents from which catalysts were prepared were analytically or chemically pure. Products were characterized by ¹H NMR and IR spectra. The IR spectrum was recorded on an Avatar 360 infrared spectrophotometer. The ¹H NMR spectra were measured on a Varian Mercury VX-300 ¹H NMR spectra with $(CH_3)_4Si$ as internal standard. The purity of products was tested with a 102G gas chromatograph.

Catalyst Preparation

The catalyst was prepared by using a commercially available silica (grain diameter $125-425 \,\mu$ m) as support. The support was impregnated with an aqueous solution of mixed cobalt, manganese acetates, magnesium, and nickel chloride. The mole ratio of metal salts and their wt% on silica were demonstrated in Table 1. After being impregnated, the mixture was first calcined 2 h at 573 K and then 5 h at 773 K in a muffle to afford the oxides. Compared to the three-component catalyst we reported before,^[15] the catalyst composed of magnesium chloride performed a more efficient catalytic activity.

Preparation of Tolunitrile by Liquid Ammoxidation

The catalytic ammoxidation reactions were carried out in an 300-ml autoclave that was equipped with a magnetic-type stirrer (Dalian Instrument, China). In the typical experiment, xylene (150 g) and catalyst (1.0 g) were added, and the mixture was stirred at a constant speed of 500 rpm. After the mixture was heated to 363 K, the oxygen and ammonia were injected into the reactor and the reaction pressure was maintained at 0.5 MPa. The ratio of oxygen and ammonia was modulated to 5:1 by rotor flowmeter. The reaction was terminated by charging the cool water through the cooling coil inside. When the reaction was finished, the catalyst was filtered and the residue mixture was distilled under the condition of decompression. Product samples were

collected and analyzed by gas chromatography (Shanghai 102G gas chromatograph). Only a trace amount of tolualdehyde was detected, because when tolualdehyde was contacted with ammonia on the surface of catalyst, the corresponding tolunitrile was produced.

Now, a detailed investigation is under way to prepare the optimized catalyst and to increase the yield of tolunitrile.

Spectral Data of the Products

Benzonitrile, 4-methyl-: FT-IR γ_{max} (KBr, cm⁻¹): 2229, 1609, 1509, 1178, 817, 64; ¹H NMR δ H (CDCl₃, 300 MHz): 7.23–7.47 (m, 4H, PhH), 2.41 (S, 3H, CH₃).

Benzonitrile, 3-methyl-: FT-IR γ_{max} (KBr, cm⁻¹): 2230, 1585, 1485, 789, 667; ¹H NMR δ H (CDCl₃, 300 MHz): 7.34–7.47 (m, 4H, PhH), 2.39 (S, 3H, CH₃).

Benzonitrile, 2-methyl-: FT-IR γ_{max} (KBr, cm⁻¹): 2226, 1487, 761, 712, 469; ¹H NMR δ H (CDCl₃, 300 MHz): 7.26–7.53 (m, 4H, PhH), 2.54 (S, 3H, CH₃).

ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (Project 20376064) is gratefully acknowledged.

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