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A novel synthesis of tolunitriles by selective ammoxidation

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Abstract A new approach to synthesize tolunitriles is reported. Tolunitriles can be prepared by selective ammoxidation of methylbenzyl chlorides prepared by chloromethylation of toluene. The total yields can reach 83% and the selectivity of tolunitriles is almost 100%. This approach provides a new path for preparing alkylbenzonitriles and other aromatic nitriles.

Keywords Selective ammoxidation · Tolunitriles · Methylbenzyl chlorides · Chloromethylation

Introduction

Aromatic nitriles are important industrial chemicals and valuable synthetic intermediates; the nitrile function can easily be converted into a large variety of other functional groups such as amides, acids, esters, amines, etc., and can also be used for further synthesis of many useful products [1–3]. Tolunitriles are an important type of aromatic nitriles, from which many pharmaceuticals, dyes, fluorescence whitener and other fine chemicals can be produced [4, 5].

Tolunitriles are traditionally synthesized from the dehydration of amide [6] or aldoxime [7], cyanation of aryl chloride [8, 9] or of toluic acid [10, 11] and diazotization of toluidine [12], etc. However, these methods usually require

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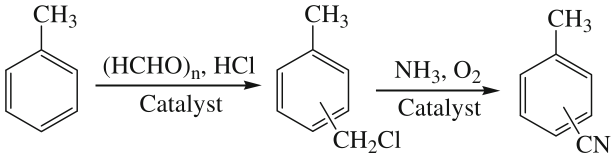
expensive starting materials or lead to serious pollution and are not suitable for industrial production on a large scale. The heterogeneous catalytic ammoxidation of methyl aromatics is a preferred method for the synthesis of some aromatic nitriles [1–3, 13]. Tolunitriles can also be prepared by catalytic gas phase ammoxidation of xylenes, but the yield and selectivity of tolunitriles are very low [14–17]. Angstadt [14, 15] developed a type of new catalyst for the ammoxidation of *p*-xylene over 400 °C with an improved selectivity of *p*-tolunitrile to 64%; however, the conversion of *p*-xylene was only 42% and the portion of dinitrile in the products could reach 31%. In addition, the mononitrile and dinitrile are difficult to separate. Tolunitriles can also be synthesized from liquid phase ammoxidation of xylenes. The selectivity of tolunitriles was increased with a lower reaction temperature, but the yields are very low and do not satisfy the required application [4, 5, 18].

It is well known that, in gas-phase ammoxidation of methylaromatics, the first step, i.e., proton extraction from the methyl group to generate the benzyl species, is the rate-determining step of the reaction. Because two methyl groups in xylenes are identical, it is difficult for only one methyl to be converted to the cyano group at ca. 400 °C temperature. Alkylaromatics can also be ammoxidized to aromatic nitriles, and two different alkyl groups existing on one benzene ring would have different reactivity. For example, in the ammoxidation of cymene, the methyl and isopropyl groups are all ammoxidized to the cyano groups generally, but due to the lower dissociation energy of the hydrogen in α-C of the isopropyl group, the isopropyl group is more active and would thus be more easily ammoxidized to the cyano group first. So except for dinitriles, considerable tolunitriles would exist in products [19]. We now report a new route to prepare tolunitriles from inexpensive toluene by chloromethylation to methylbenzyl chlorides, which could then be ammoxidized selectively to tolunitriles at a relatively low temperature, as shown in Scheme 1.

Chloromethylation of toluene gave *o*-methylbenzyl chloride and *p*-methylbenzyl chloride (gas chromatography), which, because of the very close boiling point and similar reactivity under the ammoxidation conditions, could not be separated, but reacted as a mixture to afford the tolunitrile isomers, which can be separated by fractional distillation. The higher reactivity of the chloromethyl group made it easier to cleave [20] at relatively low temperatures leading to the high selectivity of tolunitriles. The ammoxidation temperature of methylbenzyl chlorides is more than 100 °C lower compared with xylenes, and the selectivity for mononitriles can be increased remarkably.

The most active and selective catalysts used for ammoxidation of methylaromatics and propane or propene are generally based on vanadium-containing mixed oxides; for example, vanadium–phosphorus oxides (V–P–O) [21],



Scheme 1 Synthesis of tolunitriles by selective ammoxidation

Table 1 The results of ammoxidation of methylbenzyl chlorides on different catalysts

Entry	Catalysts	Molar ratio of metal atoms	Conversion (%)	Yield of tolunitriles (%)	Selectivity (%)
1	VO/SiO_2		97	82	85
2	VPO/SiO_2	V:P = 1:0.5	96	86	90
3		V:P = 1:1	94	89	95
4		V:P = 1:2	86	76	88
5	$VCrO/SiO_2$	V:Cr = 1:0.5	98	90	92
6		V:Cr = 1:1	98	97	99
7		V:Cr = 1:2	96	76	79

Reaction conditions: temperature 220 °C, $MBCs/Air/NH_3 = 1/20/5$(mol)

vanadium–titanium oxides (V–Ti–O) [22], vanadium–chromium oxides (V–Cr–O) [23, 24], vanadium–molybdenum oxides (V–Mo–O) [25], vanadium–antimony oxides (V–Sb–O) [26], vanadium–zirconium oxides (V–Zr–O) [27] or multi-component mixed oxides [28]. We found that silica-supported vanadium–phosphorus [29] and vanadium–chromium [23, 24] mixed oxides show higher catalytic activity and selectivity at a lower reaction temperature than the corresponding unsupported vanadium-containing oxides for ammoxidation of methylaromatics. They could also be used for ammoxidation of methylbenzyl chlorides at very low temperatures as shown in Table 1. The silica-supported vanadium-containing oxides were prepared according to our previous reports [23, 24, 29]. The loading contents of V–P or V–Cr in catalysts are 10 wt%, in which the catalytic activity and selectivity for ammoxidation of methylaromatics are highest [23, 29]. Different catalysts have different catalytic behaviors. $VCrO/SiO_2$ catalysts have better catalytic performances than VPO/SiO_2 or VO/SiO_2 catalysts. When the molar ratio of V and Cr is 1, the $VCrO/SiO_2$ catalyst shows the best catalytic performance with 97% yield and 99% selectivity, respectively. By XPS, it was found that vanadium exists mainly as pentavalent and chromium as trivalent in the $V–Cr–O/SiO_2$ catalysts, and the X-ray diffraction (XRD) characterization showed that vanadium and chromium form composite oxides and exist as amorphous phase in 10 wt.% loadings.

Experimental

General

Reagents from which catalysts were prepared and toluene were analytically or chemically pure. Products were characterized by ^1H NMR and IR spectra. The ^1H NMR spectra were recorded on a Bruker AM-300 MHz spectrometer with tetramethylsilane as an internal standard. The IR spectrum was measured on a Nicolet Nexus 470 FT-IR spectrometer. The melting points were determined on a X6 microscopic warming apparatus and are uncorrected. The purity of products was determined with Shimadzu GC-17A gas chromatograph.

Preparation of catalysts

The catalysts, vanadium-containing oxides supported on silica (φ0.3–0.45 mm, S_{BET} 210 m^2/g), were prepared according to the literature [23, 29]. First, the support was impregnated with an aqueous solution of mixed metal salts or oxides, and then, after drying overnight, the precursors were heated at 280 °C for 2 h and calcinated at 500 °C for 5 h to afford the catalysts. The loading of metals is 10 wt % and the mole ratios of metal atoms are listed in Table 1.

Chloromethylation of toluene [30]

A mixture of toluene, paraformaldehyde, concentrated hydrochloric acid and anhydrous zinc chloride in athree-necked flask was stirred at 60 °C, with hydrogen chloride gas being introduced for 6 h. The mixture was cooled to room temperature. The organic layer was washed twice with 10% sodium carbonate aqueous solution and three times with water, then dried over Na_2SO_4, filtered, and concentrated to remove excess toluene under reduced pressure. The mixture of products was obtained by vacuum distillation in 86% yields, bp. 74–77 °C/10 mm Hg.

Selective ammoxidation of methylbenzyl chlorides

The selective ammoxidation of methylbenzyl chlorides was carried out in a 30-mm inside-diameter quartz tube fixed-bed reactor [23, 29] loaded with 10 g catalyst. The methylbenzyl chlorides were fed by a micropump, vaporized and mixed in a preheated vessel with ammonia and air after having passed gas flowmeters with suitable molar ratios. The preheated gas flow was then fed directly into the reactor. The temperature was maintained at 210 ± 2 °C. Methylbenzyl chlorides (MBCs) were entered 0.6 ml/h, and the molar ratios of air/MBCs and NH_3/MBCs were 20 and 5, respectively. After the reaction, the outlet stream was cooled and the products were condensed in a condensing apparatus in 97% yields. The reaction can be carried out continuously. The condensing apparatus was replaced by another one every 8 h, and the test lasted nearly 80 h. Pure *o*-tolunitrile and *p*-tolunitrile could be obtained by fractional distillation with 47% (bp. 80–82 °C/10 mm Hg) and 50% (bp. 91–93 °C/10 mm Hg) yields, respectively, and the purities were 97 and 98% by GC. The structures of the products were confirmed by IR and ^{1}H NMR compared with the Sadtler Standard Spectra.

Conclusions

In conclusion, tolunitriles were synthesized by selective ammoxidation of methylbenzyl chlorides prepared by chloromethylation of toluene in high yields and nearly 100% selectivity at low temperature. This approach provides a new path to alkylbenzonitriles and other aromatic nitriles.

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