Eco-friendly Synthesis of *m*-Tolunitrile by Heterogeneously Catalysed Liquid Phase Ammoxidation

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The ammoxidation of *m*-xylene to *m*-tolunitrile over silica-supported Co–Mn–Ni catalyst was conducted for the first time in liquid phase without solvent in one-step procedure.

Aromatic nitriles are valuable intermediates and reactants in the fine chemical sector used for the synthesis of several pharmaceuticals, dyestuffs and pesticides,[1,2] However, their synthesis can be problematic, hazardous or environmentally damaging. For example: the yield of *m*-tolunitrile are sometimes high with traditional synthetic methods but a number of hazardous reagents, expensive feed components and solvents are used. Another process for the preparation of *m*-tolunitrile in a single step reaction is the vapour phase ammoxidation, which is ecologically and economically profitable route,[1,2] but the selectivity for *m*-tolunitrile is very low.[3–6] Therefore, in terms of simplicity, safety, and waste-minimization, the development of new and practical methodologies on the production of *m*-tolunitrile is welcome.

Vanadium and molybdenum oxides are well known as catalysts for the oxidation of propane to acrylic acid.[7] They can also be successfully employed as highly active catalysts in the heterogeneously catalysed ammoxidation of propane,[8] and other substituted methyl aromatics.[9,10] But it is diffcult for only one methyl to be converted to cyano group, because two methyl groups in *m*-xylene are identical. By comparison, cobalt oxides posses an extremely high oxidative reactivity and manganese oxides has a lower, although still high activation ability in the liquid phase oxidation.[11,12] They have similar redox properties to those of Vanadium, molybdenum oxides. Then we chose silica-supported Co–Mn–Ni oxides catalysts to improve the selectivity for *m*-tolunitrile. To the best of our knowledge, there are no reports on the heterogeneously catalyzed liquid phase ammoxidation of *m*-xylene to *m*-tolunitrile.

The catalyst was prepared using a commercial silica (grain diameter 125–425 µm) as support. The support was impregnated with an aqueous solution of cobalt, manganese acetates and nickel chloride (n(Co):n(Mn):n(Ni) $= 1{:}1.397{:}0.016$) and the mixture was dried at 393 K. The as-prepared precursor was calcined for 3 h at 573 K and kept for 5 h at 773 K in a muffle to afford the oxides. Weight per cent of Co + Mn + Ni are 9.32% on SiO_2.

The catalytic ammoxidation reactions were carried out in a 300-mL capacity autoclave equipped with a magnetic-type stirrer (Dalian Instruments, china). *m*-xylene (180 g) and the catalyst (0.5 g) were added to the rector; the mixture was stirred at a constant speed of 500 rpm; it was heated to 363 K; and then oxygen and ammonia with the ratio of 5:1 was injected into the reactor and maintaining the reaction-system pressure of 0.5 MPa; finally the O_2 concentration of tail gas was measured by an automatic oxygen-measuring instrument on line. After the reaction was finished, the catalyst was filtered and the residual mixture was distilled under the condition of decompression. Products were analyzed by a Shanghai 102G type gas chromatography. Authenticated standard samples were used to determine the identity of the products. The total conversion and product distribution were evaluated with calibration curves, which were obtained by injecting known amount of authenticated standard.

The performance of catalysts for *m*-xylene ammoxidation was studied under the same reaction conditions. For silica-supported Co–Mn–Ni catalyst, the selectivity is 99.3%, and the yield is 16.3%. Two blank reactions were studied so as to dismiss questions of support-catalyzed ammoxidation of *m*-xylene to *m*-tolunitrile. In one blank reaction, no catalyst was used. In the other blank reaction, only silica was used. Subsequent GC analysis of the solutions indicated that no products were presented. Catalyst without support exhibited lower activity and selectivity than supported catalysts.

The powder X-ray diffraction (XRD) patterns of the samples were recorded by a Shimadzu XRD-6000 diffractometer in a scanning rate of 2°/min from 10 to 80° using Cu Kα_1 radiation ($\lambda = 1.54056$ Å). Figure 1 shows the XRD patterns of different catalysts. For sample a, four sharp peaks, centered at about 29.2, 32.8, 36.3, and 60.7° are attributed to spinel-type composite oxide (Co, Mn)(Co, Mn)$_2$O$_4$, which is corresponding with the JCPDS card (number 18-408). For sample b and c, a broad peak assigned to amorphous silica is observed at about 22.2°, which indicates that the oxides are well dispersed on the surface of silica support within and without in the amorphous or microcrystal ($<$4 nm) and small amount of spinel composite oxide emerged on the surface of silica support. Furthermore, the intensity of the peak at 36.3, 44.1, 57.2, and 64.5° in (c) increased compared with (b), which is attributed to the better crystallized oxide after the first run and enriched on the surface of silica. Hence, the sinter was occured on the surface of catalyst.

Figure 2 exhibits scanning electron micrographs of the fresh catalyst and its sample after first run. As seen from the morphol-

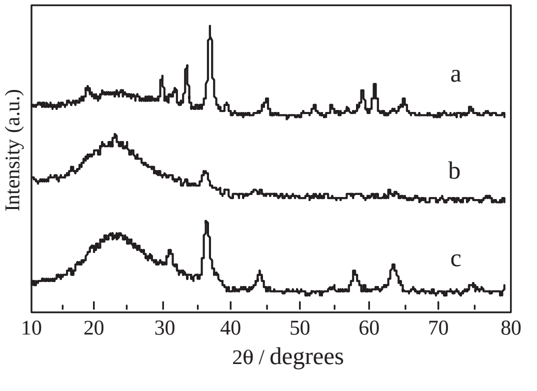


Figure 1. XRD patterns of the samples: (a). catalyst without support; (b). fresh supported catalyst; (c). first run.

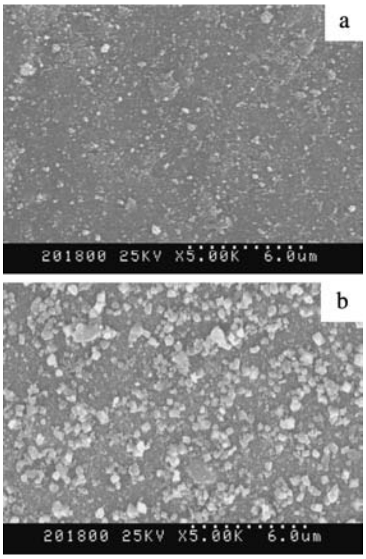
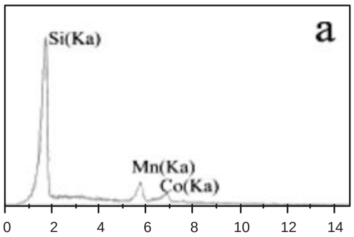
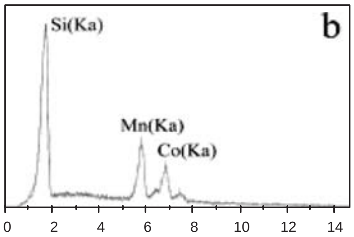


Figure 2. SEM image of fresh catalyst (a) and used (b) catalyst after first run.



	Weight%	Atomic%	Rel.	Error
Si	83.42	91.09	0.98	
Mn	7.35	4.10	3.74	
Co	9.23	4.80	3.67	



	Weight%	Atomic%	Rel.	Error
Si	62.36	76.95	1.22	
Mn	21.48	13.55	2.10	
Co	16.15	9.50	2.73	

Figure 3. Superficial distribution of (a) fresh and (b) used catalysts after first run.

ogy, particles were well distributed on porous silica in both (a) and (b). The presence of loosely stacked grains (average size 250 nm) with a porous state is notable for a sample to be employed as a catalyst to provide the aisle of reactants and selectivity, which average size is less than 80 nm estimated in (a) from SEM data. The particles in (b) demonstrated crystal phase well and particle size grew larger after ammoxidation, which is coincided with the XRD results.

Moreover, as superficial distribution of fresh (a) and used (b) catalyst are shown in Figure 3, it is seen that the used catalyst have higher superficial content of Mn, Co than the fresh one, which indicated that the active components of catalyst are enriched on the surface, in good agreement with the micrographs of the used catalyst.

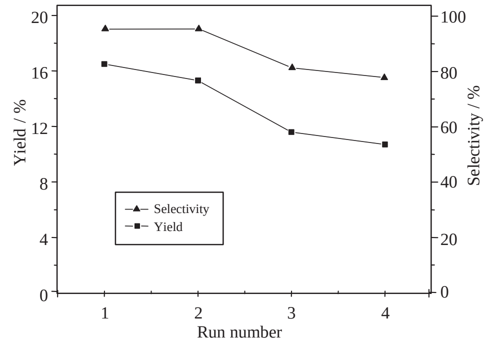


Figure 4. Reusage of CoMnNi/SiO$_2$ catalyst.

Finally, the catalyst was recycled for four times in order to check the activity and stability. After reaction of each cycle, the catalyst was filtered off without any processing. Figure 4 lists the results of these experiments. However, after successive recycling (cycles 2 to 4) of the catalyst, a minor decrease in the catalytic activity was noticed, and by-product detected in the reaction was *m*-tolualdehyde, but its content was small. when *m*-tolualdehyde was contacted with ammonia on surface of catalyst, *m*-tolunitrile was formed.[13] No more runs were carried out because of the decrease recovered each time. The silica was splitted to pieces under solution-reaction conditions with high-speed stirring. Future studies will concentrate on improving the mechanical strength of catalyst by changing preparation method toward large-scale applications.

In summary, the preparation of *m*-tolunitrile from *m*-xylene was carried out directly by a heterogeneously catalytic method over CoMnNi/SiO$_2$ catalyst for the first time. Compared to organometallic catalysts[11] and Cerium complexes with acetato-acyl-bis(pyrazolinone)ligands,[14] CoMnNi/SiO$_2$ catalyst is less demanding, economical in preparation, and suitable for large-scale production. Moreover, the route is environmentally friendly, so it has a potential industrial application. Further, the catalyst can be recycled and reused for four times. Now, a detailed investigation is under progress to prepare the optimized catalysts and to increase the yield of *m*-tolunitrile.

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