Ammoxidation of Isomeric Picolines on Molybdenum Phosphate Catalyst

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Abstract−Ammoxidation of 2-, 3-, and 4-picolines to their nitrile compounds has been studied on an amorphous molybdenum phosphate (MoPO) catalyst with P/Mo=1.0. The overall catalytic results of this study reveal that the conversion is in the order 2-picoline>4-picoline>3-picoline, which can be rationalized neither by the steric effects nor by the thermodynamic point of view. However, the MoPO catalyst prepared here was found to be very effective for the ammoxidation reaction of picolines. Even at almost 100% conversion levels of all three picoline isomers, selectivities to their nitrile compounds on this MoPO catalyst were higher than 90% or so.

Key words: Amorphous MoPO Catalyst, Ammoxidation of Picoline Isomers, Cyanopyridine

INTRODUCTION

Picolines consist of three structural isomers with methyl group at different positions from the nitrogen atom in their pyridine ring (i.e., 2-, 3-, and 4-methylpyridines). Cyanopyridines obtained by the ammoxidation of methylpyridine isomers are main raw materials in the pharmaceutical and food industries. For example, 4-cyanopyridine, generally produced via the ammoxidation of 4-picoline, is a raw material for the manufacture of isonicotinic acid hydrazide that is widely used for treatment of pulmonary tuberculosis. On the other hand, cyanopyridines are known to be easily transformed to the corresponding acids and amides by simple pH control [Paustian et al., 1981]. Among these products, in particular, nicotinamide is an important chemical compound for the metabolism of humans and animals, and is used as a food additive.

The ammoxidation of picolines to cyanopyridines has been extensively studied on numerous catalysts including vanadium-modified zeolites, vanadium-containing silico-aluminophosphates [Rao et al., 1996], titania-supported ceria [Rao et al., 1997], vanadium-supported zirconia [Chary et al., 1998], etc. [Suvorov et al., 1968; Anderson et al., 1979; Rizayev et al., 1992; Chary et al., 1999, 2000; Narayana et al., 1998]. Recently, we have synthesized various metal phosphates and tested as catalysts for the ammoxidation of 3-picoline or methylpyrazine [Shin et al., 1997a, b, c]. Among these phosphate-based materials, an amorphous molybdenum phosphate (MoPO) was found to be the best catalyst for the ammoxiation of 3-picoline. Here we describe the reactivity of this amorphous MoPO catalyst with an atomic P/Mo ratio in the ammoxidation of 2-, 3-, and 4-picolines and compare the results in an attempt to understand the influence of the methyl group position in the pyridine ring on the conversion of picoline isomers to the corresponding nitrile compounds.

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EXPERIMENTAL

An amorphous MoPO catalyst with P/Mo=1.0 was prepared by reacting ammonium heptamolybdate tetrahydrate ((NH_4)$_6$$Mo_7$$O_{24}$· $4H_2O$, 99%, Aldrich) with the equimolar amount of phosphoric acid (85 wt%, Aldrich) in water at 353 K for 2 h. The slurry obtained was dried overnight at 383 K and then crushed into powders below 60 mesh (230 μm). Finally, the resulting solid was heated under flowing air, N_2, H_2, or NH_3 (4 L h^{-1}) at 673-773 K for 4 h. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku 2155 D6 diffractometer with Cu K$_\alpha$ radiation. The N_2 BET surface areas were measured on a Micromeritics ASAP 2010 analyzer.

The ammoxidation of 2-, 3-, and 4-picolines on the MoPO catalyst prepared here was performed at atmospheric pressure and 563-703 K in a quartz flow reactor system with fritted silica disk on which 0.42 g of catalyst powder was loaded. Liquid 2-picoline (98%, Aldrich), 3-picoline (99%, Aldrich), or 4-picoline (98%, Aldrich) was pumped into a constant temperature vaporizer where it was mixed with NH_3 and O_2 to give a reactant stream having a molar ratio of 1 : 10 : 10. The catalyst was pretreated to 773 K with a heating rate of 4 K min^{-1} and held for 4 h in flowing nitrogen (4 L h^{-1}). Then, the ammoxidation reaction was started at a desired temperature and run over the periods of time on stream up to 500 h. N_2 was used as a diluent, and the partial pressure of the picoline isomer and the total flow rate of reactants were fixed to 0.67 kPa and 4.6 L h^{-1}, respectively. The flow of gases was controlled and mixed with a Matheson Model 8274 mass flow controller. The reaction products were analyzed on-line in a Chrompack CP 9000 gas chromatograph. Picolines, pyridine, cyanopyridine (CP), pyridinecarboxaldehyde (PCA), pyridinecarboxylic acid (PCAcid), pyridinecarboxylic amide (PCAmide), and ethylamine (EA) were separated in a capillary CP-Sil 5 CB column (0.25 mm×10 m) and analyzed in a flame ionization detector. CO, CO_2, NH_3, N_2O, and H_2O were separated in a packed Chromosorb 103 column (1/8"×2 m) and analyzed in a thermal conductivity detector. The conversion was defined as the mole of the picoline isomer reacted to that of the same isomer fed, and the se-

Table 1. N$_2$ BET surface areas of MoPO catalysts pretreated with different gases at 773 K for 4 h before and after the ammoxidation of 4-picoline at 643 K and their activities in the ammoxidation reaction^a

Pretreatment gas	BET surface area (m^2 g^{-1})		Conversion (%)	Selectivity (%)		
	Before reaction	After reaction		Pyridine	4-CP	PCAmide
H$_2$	1.3	1.2	36.7	0.2	70.1	29.4
Air	0.9	1.0	37.8	0.2	81.9	17.4
NH$_3$	1.3	2.2	58.0	0.4	88.1	11.5
N$_2$	1.9	2.7	73.8	0.2	86.9	12.5

^{a}The catalytic data are reported as the values of 24 h time on stream.

lectivity was calculated as the mole of each product to that of the picoline isomer reacted.

RESULTS AND DISCUSSION

It is well known that the catalytic properties of most partial oxidation catalysts can differ highly according to the catalyst pretreatment conditions. Thus, the initial aim of this study was made to find the optimal gas for the pretreatment of MoPO catalyst. First, the catalyst prepared here was heated under flowing air, H$_2$, NH$_3$, or N$_2$ at 773 K for 4 h. Then, the resulting solids were tested as catalysts in the ammoxidation of 4-picoline at atmospheric pressure and 643 K. Table 1 lists 4-picoline conversion and selectivities to pyridine, 4-CP, and 4-PCAmide at 24 h time on stream after pretreatments with different gases. These data reveal that among the catalysts tested here, the highest conversion was observed for the MoPO catalyst pretreated with N$_2$. Therefore, we will henceforth use N$_2$ as the pretreatment gas in the ammoxidation of all picoline isomers. We also note that in all cases, except H$_2$ pretreatment, the 4-picoline conversion, as well as the selectivity to 4-CP, increases steadily with increasing time on stream. When pretreated with N$_2$, for example, the MoPO catalyst yields a 4-picoline conversion of 65% at 5 min time on stream, while it exhibits a higher conversion (74%) at 24 h time on stream (see Table 1). Powder XRD patterns (not shown) of the MoPO catalysts pretreated with different gases show that all the materials still remain amorphous even after the ammoxidation of 4-picoline at 643 K for 24 h. However, the N$_2$ BET surface area data in Table 1 reveal a small but non-negligible increase in surface areas after 4-picoline ammoxidation, especially when the catalyst was pretreated with N$_2$ or NH$_3$. In comparison with the 4-picoline reaction data, therefore, it is clear that the higher surface area of the MoPO catalyst, the higher 4-picoline conversion it exhibits. This
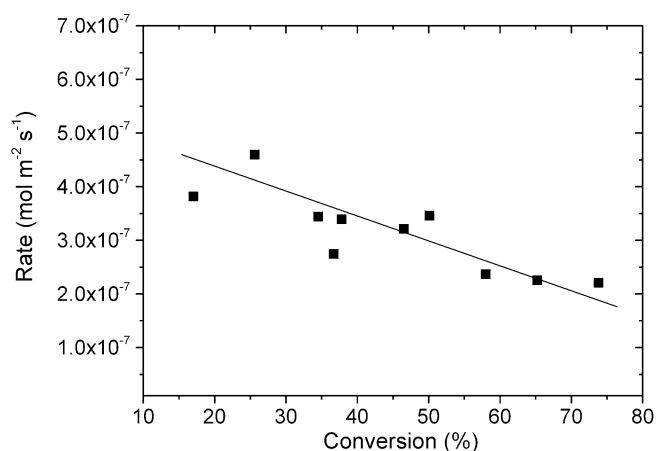
Fig. 1. Conversion versus specific reaction rate expressed per surface area of the MoPO catalyst in the ammoxidation of 4-picoline.

led us to tentatively speculate that the steady increase in 4-picoline conversion with time on stream is attributed mainly to the textural change such as particle size or surface roughness in the MoPO catalyst during the ammoxidation reaction rather than to its phase change. If such an increase in conversion is entirely due to an increase in catalyst surface area, on the other hand, the specific reaction rate expressed per catalyst surface area should be constant in the full conversion range studied here. As seen in Fig. 1, however, there is a continuous decrease in specific reaction rate with respect to the 4-picoline conversion, suggesting that the observed increase in conversion cannot be explained solely by the textural change in the used MoPO catalyst. Therefore, we cannot rule out the possibility of the partial transformation of this amorphous MoPO catalyst into another

Table 2. N$_2$ BET surface areas of MoPO catalysts pretreated under flowing N$_2$ at different temperatures and their reactivities in the ammoxidation of 3-picoline at 643 K^a

Pretreatment temp. (K)	BET surface area (m^2 g^{-1})	Conversion (%)	Selectivity (%)			
			Pyridine	3-PCA	3-CP	PCAmide+PCAcid
673	1.1	6.2	7.8	2.0	18.0	72.3
723	1.6	19.2	2.5	2.0	18.9	76.5
773	2.6	21.2	2.6	2.3	27.8	67.2
823	2.5	27.0	2.0	2.3	28.1	67.6
873	1.3	13.8	3.5	2.2	19.9	74.4

^{a}The catalytic data are reported as the values of 24 h time on stream.

phase during the ammoxidation, which must be very difficult to ascertain by powder XRD.

To investigate the effects of the pretreatment temperature on the picoline activity of the MoPO catalyst, then, we have carried out the ammoxidation of 3-picoline under flowing N_2 at 643 K. Table 2 lists the conversion and selectivities to pyridine, 3-PCA, 3-CP, 3-PCAmide, and 3-PCAcid in the ammoxidation of 3-picoline as a function of pretreatment temperature. The highest conversion and selectivity to 3-CP were obtained after pretreatment at 823 K. However, we should note here that there is also a continuous increase in the conversion and selectivity to 3-CP on the MoPO catalyst with increasing time on stream, regardless of the pretreatment temperature, which is quite similar to the trend observed for the Sb-V-SAPO-5 molecular sieve catalyst [Srinvias et al., 2000]. For example, our MoPO catalyst gives a 3-picoline conversion of 27% at 24 h time on stream, when pretreated at 823 K. However, its conversion at the steady state, which was measured after the 250 h time on stream, is ca. 60% (*vide infra*). Again, this can be attributed mainly to textural changes in the MoPO catalyst during the ammoxidation reaction. As seen in Table 2, however, its BET surface area becomes decreased when the pretreatment temperature is higher than 773 K. We believe that this may be due to the agglomeration of MoPO particles at elevated temperatures. Table 2 also shows that the highest surface area can be achieved when the MoPO catalyst is pretreated under flowing N_2 at 773 or 823 K. However, recall that the maximum 3-picoline conversion on this catalyst is 27% at 823 K. This led us to pretreat our MoPO catalyst at 823 K prior to the ammoxidation of isomeric picolines.

Table 3 compares the conversions and product distributions from the ammoxidation of 2-, 3-, and 4-picolines on the MoPO catalyst measured at 623 K and 24 h time on stream. Little formation of pyridine on this amorphous catalyst, regardless of the type of the picoline isomers employed, suggests that the activity of dealkylation is negligible. The catalytic data in Table 3 reveal that the conversion is in the order 2-picoline>4-picoline>3-picoline, which is against our expectations from differences in the distance between the methyl group and the nitrogen in the pyridine ring of each isomer. We should note here that this trend is substantially different than that observed for the other phosphate-based catalysts. For example, the conversions of three isomeric picolines on the vanadium phosphate catalyst are reported to be in the order 4-picoline>2-picoline>3-picoline [Martin et al., 1989, 1996]. As seen in Table 3, on the other hand, the apparent activation energy (14.9 kcal mol^{-1}) of 3-picoline determined from the catalytic data measured at different temperatures was found to be considerably lower than that (26-27 kcal mol^{-1})

of 2- or 4-picoline. Therefore, it appears that the ammoxidation of isomeric picolines on the MoPO catalyst can be rationalized neither by the steric effects nor by the thermodynamic point of view, although the precise reason for the observed reactivity is not known at this time. The catalytic data in Table 3 also show that the MoPO catalyst produces no noticeable amounts of n-PCAcids in the ammoxidation of 2- and 4-picolines, while it gives a significant amount of 3-PCAcid together with 3-PCAmide when reacted with 3-picoline. In general, the ammoxidation of isomeric picolines to the corresponding CPs is known to proceed in three different pathways including n-PCAmides, n-PCAcids, and n-picolylamines, respectively [Suvorov et al., 2000; Prasad and Kar, 1976; Anderson and Lundin, 1979]. While n-PCAmides are produced via the reaction of n-PCAs with both NH_3 and O_2, the formation of n-PCAcids may be a result of the subsequent oxidation of n-PCAs. On the other hand, it is well-established that the dehydrogenation of n-picolylamines to n-CPs occurs at high rates in a selective manner, due to their high reactivities [Suvorov et al., 1968]. Significant production of 3-PCAcid in the ammoxidation of 3-picoline strongly suggests that the conversion of 3-PCAcid to 3-CP under the conditions studied here may be much more lower than that of 2-PCAcid to 2-CP or of 4-PCAacid to 4-CP, because the selectivity to 3-CP is much lower than that to 2-CP or 4-CP. We believe that this is the reason 3-PCAcid is produced in a significant amount during the ammoxidation of 3-picoline, although detailed information concerning the reaction pathways to the ammoxidation of the three picoline isomers cannot be drawn from the catalytic data in Table 3.

Figs. 2-4 show the conversions of n-picolines and selectivities to the representative products from each isomer as a function of reaction temperature in the ammoxidation of n-picolines on the MoPO catalyst. Due to the high dependence of n-picoline conversion and selectivities to each product on time on stream, as described above, all these catalytic data were obtained after ca. 250 h time on stream where no detectable change in n-picoline activities on our MoPO catalyst was observed. It can be seen from Fig. 2 that the 2-picoline

Table 3. Results from the ammoxidation of three different isomeric picolines on the MoPO catalyst at 623 K.

Isomer	Conversion (%)	Selectivity (%)			E_a^{*a} (kcal mol^{-1})
		Pyridine	n-CP	n-PCAmide	
2-picoline	80.6	0.3	96.0	2.9	26.7
3-picoline	42.8	1.2	43.4	53.1^b	14.9
4-picoline	48.4	0.3	75.0	23.4	26.0

^{a}Apparent activation energy.

^{b}Sum of 3-PCAcid plus 3-PCAmide with almost equal quantities.
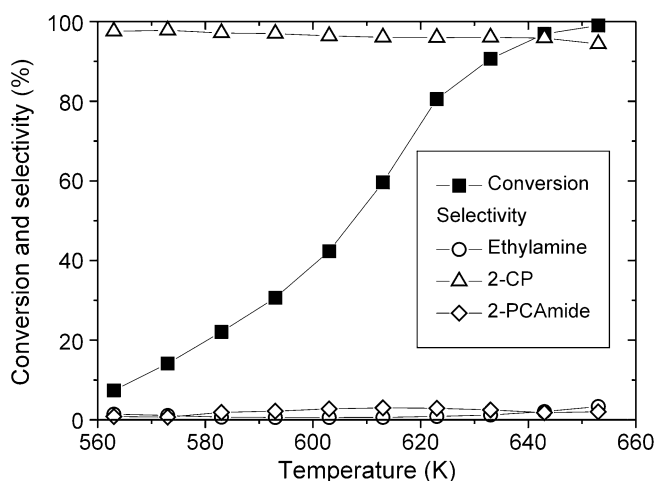
Fig. 2. 2-Picoline conversion and selectivities to pyridine, 2-CP, ethylamine, and 2-PCAmide as a function of reaction temperature in the ammoxidation of 2-picoline on the MoPO catalyst. The data were taken after the catalyst arrived at steady state (after *ca.* 250 h time on stream).

conversion increases dramatically with increasing the reaction temperature from 563 to 653 K. As a result, the conversion was found to reach a value close to 100% at 653 K. Fig. 2 also shows that the selectivity to 2-CP, the main product, always maintains above 95% over the temperature range studied here. Also, no significant changes in the selectivities to pyridine, ethylamine, and 2-PCAmide appearing as minor products during this ammoxidation reaction are observed. Therefore, it is clear that the MoPO catalyst is very active for the ammoxidation of 2-picoline. Like the case of 2-picoline, the conversion of 3-picoline on MoPO increases significantly with increasing reaction temperature. As seen in Fig. 3, however, the selectivity to 3-CP was found to highly depend on the reaction temperature. For example, the selectivity to 3-CP at 583 K is 23%, which is quite low as compared to that to 2-CP measured at the same temperature in the ammoxidation of 2-picoline. With increasing to 703 K,

the selectivity to 3-CP increases remarkably and eventually reaches about 85%. By contrast, the opposite is observed for selectivities to 3-PCAcid and 3-PCAmide. This suggests that 3-PCAcid and 3-PCAmide may be as intermediates to finally form 3-CP. The 4-picoline conversion and selectivities to pyridine, 4-CP, and 4-PCAmide as a function of reaction temperature in the ammoxidation of 4-picoline on the MoPO catalyst prepared in this study are shown in Fig. 4. Both the 4-picoline conversion and the selectivity to 4-CP on this amorphous catalyst were found to notably increase with increasing reaction temperature. Thus, the general trend observed for the ammoxidation of this picoline is essentially identical to that from the ammoxidation of 3-picoline. Unlike the case of 3-picoline, however, the selectivity to 4-CP is higher than 50% over the temperature range 583-673 K. According to the catalytic studies reported thus far, finally, it has been speculated that changes in the textural properties such as surface area of the catalyst during the ammoxidation of isomeric picolines have little effect on the *n*-picoline conversions and selectivity to the corresponding CP's [Srinvias et al., 2000]. However, it is clear to us that this is not the case of the MoPO catalyst system, since its textural properties play a significant role in achieving high ammoxidation reactivity.

In conclusion, the overall results of this study demonstrate that an amorphous MoPO phase is an active catalyst for the ammoxidation of 2-, 3-, and 4-picolines to the corresponding cyanopyridines. Even at almost 100% conversion levels of all three picoline isomers, selectivities to their nitrile compounds on this MoPO catalyst were found to be higher than 90% or so.
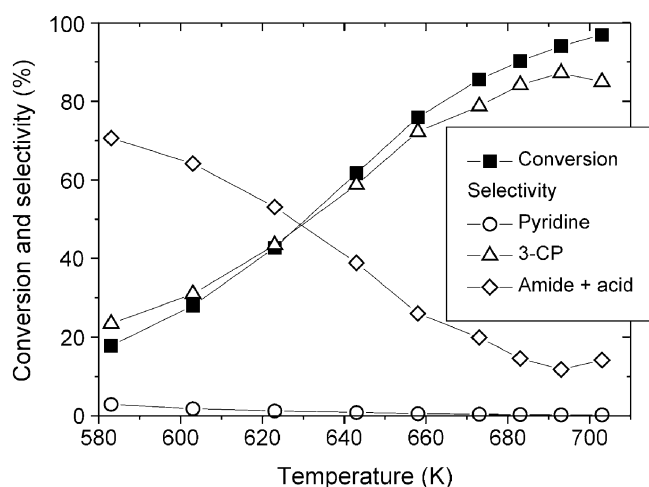

Fig. 3. 3-Picoline conversion and selectivities to pyridine, 3-CP, and 3-PCAmide plus 3-PCAcid as a function of reaction temperature in the ammoxidation of 3-picoline on the MoPO catalyst. The data were taken after the catalyst arrived at steady state.
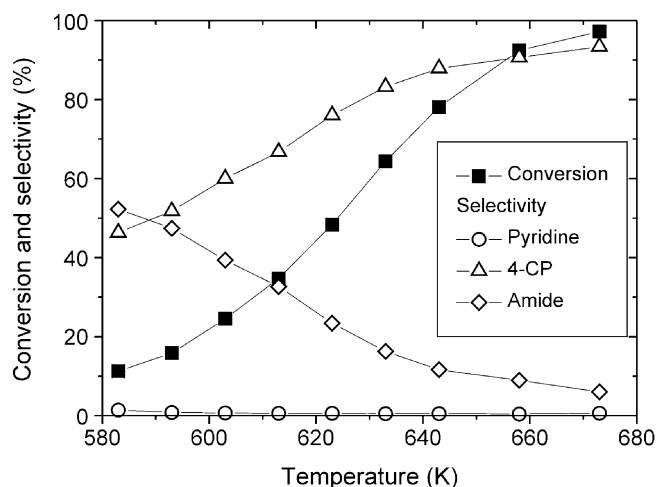

Fig. 4. 4-Picoline conversion and selectivities to pyridine, 4-CP, and 4-PCAmide as a function of reaction temperature in the ammoxidation of 4-picoline on the MoPO catalyst. The data were taken after the catalyst arrived at steady state.

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