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Ammoxidation of 2-picoline catalyzed by modified V₂O₅/TiO₂

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Abstract A vanadium-titanium catalyst was used in the preparation of aromatic nitriles by ammoxidation in a fixed-bed reactor. The catalyst prepared by the mixing method showed high conversion (91 %) and selectivity (95 %) in the ammoxidation of 2-picoline. The effect of varied conditions on the ammoxidation of 2-picoline was also explored, including LHSV, H_2O/NH_3 molar ratio, reaction temperature, and the catalyst calcination temperature. This catalyst was also used in the ammoxidation of 3-picoline, 4-picoline, and toluene derivatives.

Keywords Catalysts · Aromatic nitriles · Fix-bed reactor · Calcination temperature · Mixing method

Introduction

The aromatic nitriles are important reactants in the fine chemical sector [1-3]. In addition, they can be converted to commercially interesting and valuable intermediates for the synthesis of several pharmaceuticals and dyestuffs as well as pesticides and final products [4].

At present, there are a few methods available for the preparation of aromatic nitriles. One of them is cyanation [5-8]. The pyridine nitrogen was activated by using dinitrogen pentoxide or nitric acid to give a corresponding

J. Pan (⊠) · J. Huang · C. Qian · X. Chen State Key Laboratory of Chemical Engineering, Zhejiang University, Hangzhou, People's Republic of China e-mail: 3090103113@zju.edu.cn intermediate; then this intermediate could be reacted with KCN to form the corresponding cyanopyridine. However, this method showed poor yield and used toxic cyanide. Another approach is dehydration of primary amides, although some amides on thermolysis showed some tendency for dehydration to nitriles [9, 10]; the formed water can hydrolyze another molecule of amide to acid. Besides, ammoxidation is a significant reaction for producing aromatic nitriles [11, 12]. In this approach, the by-product is only water, and the yield of product is higher than in the above two methods. In addition, NH₃ used in this method is friendlier to the environment than the cyanide used in cyanation. Many previous researches on the ammoxidation of picoline isomers have been reported. Conversions of 3-picoline and 4-picoline were similarly high as well as the corresponding nitrile yields [1, 4, 13, 14]. While in case of using 2-picoline as material, the yield of 2-cyanopyridine was low, and pyridine was the main by-product. Until now, there have been no reports on the ammoxidation of 2-picoline giving a high yield of the corresponding nitrile.

A V-containing catalyst such as VTi, VMo, VSb, VSn, or VCr oxides is a good catalytic system for ammoxidation [4, 15–18]. The catalytic properties are largely influenced by the composition, character of support, and method of preparation [18–22]. Narayana et al. [14] reported on the influence of V₂O₅ content on the V₂O₅/TiO₂ catalyst for ammoxidation of 3-picoline. Their study revealed that the catalysts show increasing conversion of 3-picoline up to 3.4 mol% V₂O₅ content with close to 100 % selectivity of 3-cyanopyridine. Rao et al. [13] studied the ammoxidation of 3-picoline over ceria-titania catalysts. Their research revealed anatase-supported ceria catalysts exhibited higher ammoxidation activities (68.1 % yield) than rutile-supported ones (37.5 % yield). Besides, the method of preparation is a significant factor of the catalytic

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properties. Most of the vanadium-containing catalysts used in the ammoxidation were prepared by the impregnation method, but the mixing method had been rarely used. Martin et al. [23, 24] reported on the use of vanadium phosphate catalysts for the ammoxidation of 2-picoline, and V–P–O catalyst showed the highest 2-cyanopyridine yield of only 57 %. Verma [25] studied the ammoxidation of 2-picoline on V–Sb catalysts with a 2-cyanopyridine yield of 65 %. Almost all of the ammoxidation catalysts showed poor yield of 2-cyanopyridine.

In this article, we show that the modified vanadiumtitanium catalyst prepared by the mixing method can act as an efficient catalyst for the ammoxidation of 2-picoline. This catalyst also showed good activity and selectivity in the ammoxidation of 3-picoline, 4-picoline, and toluene derivatives. Furthermore, the influence of varied conditions on the ammoxidation of 2-picoline was also studied.

Results and discussion

Initially, the ammoxidation of 2-picoline was carried out in the presence of vanadium-titanium catalyst prepared by the mixing method. This catalyst was calcined at 500 °C and marked as V-O-Ti-a. The reaction was carried out at 370 °C and 0.18 h⁻¹ LHSV (2-picoline); the 2-picoline:NH₃:H₂O:air molar ratio was 1:6:3.3:22. The V-O-Tia catalyst showed 97 % conversion of 2-picoline but only 30 % selectivity of 2-cyanopyridine. According to the mechanism of 3-picoline ammoxidation, which was reported by Rao et al. [26], we can guess the possible routes of 2-picoline ammoxidation as Fig. 1 shows. As the corresponding amide and a large number of pyridines were observed in the product, route 3 in Fig. 1 is recommended. The 2-picoline was probably first oxidized to the corresponding carboxylic acid, and the corresponding carboxylic acid decarboxylated to pyridine easily. This reaction behavior was probably because of the involvement of the lone electron pair of the nitrogen ring in the chemisorption process of the 2-picoline molecule, and the methyl group is too near to the surface. Hence, the C-C bond is more easily ruptured [1], so we tried to reduce the catalytic activity to increase the selectivity of 2-cyanopyridine. In the preparation of the catalyst, a high catalyst calcination temperature could reduce the specific surface area and surface activity. Hence, we guess the selectivity of 2-cyanopyridine could be increased by the higher catalyst calcination temperature. To verify whether the catalytic selectivity would be improved by the increase in calcination temperature, V-O-Ti-b, V-O-Ti-c, and V-O-Ti-d were prepared by the V-O-Ti-a catalysts being calcined at 600, 700, and 800 °C, respectively. These three catalysts were used as the catalysts in the ammoxidation of 2-picoline at the same condition as the reaction using the V–O–Ti-a catalyst. As the results show in Fig. 2, the V–O–Ti catalytic activity decreased with increasing calcination temperature, but the catalytic selectivity of V–O–Ti first increased and then slightly decreased. The 2-picoline reacting in the presence of V–O–Ti-c catalyst gave the highest 2-cyanopyridine yield (86 %). The results reveal that the vanadium–titanium catalysts prepared by the mixed method could efficiently catalyze the ammoxidation of 2-picoline, and the catalytic selectivity could be improved by properly increasing the catalyst calcination temperature.

Next, the V-O-Ti-c catalyst was used in the ammoxidation of 3-picoline, 4-picoline, and toluene derivatives. The reactions were carried out at 370 °C and 0.18 h^{-1} LHSV (2-picoline). As shown in Table 1, 3-picoline, 4-picoline, and several kinds of structurally diverse toluene derivatives could be converted into the corresponding nitriles. Both 3-picoline and 4-picoline gave high conversions and high selectivities. In general, good conversions of toluene derivatives and high selectivities of products were obtained. In the case of toluene (entry 4), the conversion of substrate and the selectivity of benzonitrile were considerably high. Xylenes (entry 5-7) gave tolunitriles in high conversions and moderate to high selectivities. In the case of o-xylene, the selectivity of o-tolunitrile was high because of hardly any ammoxidation of o-tolunitrile owing to the space steric effect of the ortho methyl group. In the ammoxidation of *m*-xylene and *p*-xylene, *m*-phthalodinitrile and terephthalonitrile were formed, respectively, as the main products because of the easy ammoxidation of the mtolunitrile and p-tolunitrile. The electronic effect of substituent was not significant in the ammoxidation of toluene derivatives. The conversion of 4-chlorotoluene and the selectivity of 4-chlorobenzonitrile were high. When the substrate was 4-methylanisole, the result was slightly worse than the reaction using 4-chlorotoluene. These results show that the V-O-Ti-c catalyst also had a good activity and selectivity in the ammoxidation of 3-picoline, 4-picoline, and toluene derivatives.

To determine how the varied reaction conditions affect the ammoxidation of 2-picoline, several related experiments were done in the model reaction, and the results are depicted in Table 2. The effect of liquid hourly space velocity (2-picoline) on the ammoxidation of 2-picoline was studied. The conversion and selectivity of product are highly influenced by the LHSV, because it determines the contact time between the reactant and the catalyst. The conversion of 2-picoline increased from 79 to 99 % with the decrease of LHSV from 0.3 to 0.15 h⁻¹ (entry 1–3). In addition, the effect of reaction temperature on the ammoxidation of 2-picoline was studied. On the one hand, low temperature led to a low conversion of 2-picoline. On



Fig. 1 The possible routes of ammoxidation. [O] represents lattice oxygen



Fig. 2 The results of ammoxidation of 2-picoline in the presence of V–O–Ti-a, V–O–Ti-b, V–O–Ti-c, and V–O–Ti-d

the other hand, too high temperature gave a low selectivity of 2-cyanopyridine (entries 2, 4, 5) due to the separation of the methyl group with the increase of temperature. The influence of the mole ratio of 2-picoline to ammonia and the mole ratio of 2-picoline to H₂O were also explored (entries 2, 6, 7). The decrease in the mole ratio of 2-picoline to ammonia and the increase in the mole ratio of 2-picoline to H₂O both raised the selectivity of 2-cyanopyridine. According to route 3 in Fig. 1, the increased amount of ammonia could restrain the generation of pyridine, and the decreased amount of H₂O could promote the yield of 2-cyanopyridine, consistent with the results.

Catalyst characterization

The XRD analyses (D/max-rA; Rigaku Co., Ltd., Japan) of V–O–Ti-a, V–O–Ti-b, V–O–Ti-c, and V–O–Ti-d catalysts

Table 1 Ammoxidation of picoline isomers and toluene derivatives

Entry	Substrate	Product	Conversion/%	Yield/%
1	2-Picoline	2-Cyanopyridine	91	86
2	3-Picoline	3-Cyanopyridine	92	88 ^a
3	4-Picoline	4-Cyanopyridine	95	92 ^a
4	C ₆ H ₅ CH ₃	C ₆ H ₅ CN	93	91
5	$m-C_6H_4(CH_3)_2$	$m-C_6H_4(CN)_2$	96	77
6	o-C ₆ H ₄ (CH ₃) ₂	o-CH3-C6H4CN	98	97
7	$p-C_{6}H_{4}(CH_{3})_{2}$	$p-C_6H_4(CN)_2$	90	77
8	p-Cl-C ₆ H ₄ CH ₃	p-Cl-C ₆ H ₄ CN	95	91
9	<i>p</i> -CH ₃ O- C ₆ H ₄ CH ₃	<i>p</i> -CH ₃ O- C ₆ H ₄ CN	92	88

Reaction temperature 370 °C; feed: substrate + H₂O + ammonia + air; LHSV = 0.18 h⁻¹; substrate:NH₃:H₂O:air = 1:6:3.3:22 ^a Reaction temperature 380 °C

after catalyst preparation are shown in Fig. 3, and the crystallite diameter was estimated by the Scherrer formula diameters = $K\lambda/B\cos\theta$, (D = crystallite)K = 0.89, $\lambda = 0.154$ nm, B = FWHM, $\theta = diffraction$ angle). The BET surface area and the pore size were determined by nitrogen adsorption at 77 K (ASAP 2020; Micromeritics Co., Ltd., USA). The crystallite diameter of the catalyst, BET surface area, and pore size results are shown in Table 3. The catalyst characterization results reveal that the vanadium-titanium catalyst calcined at higher temperature obtained a larger crystallite diameter of the catalyst, smaller surface area, and larger pore size, which cause the decrease of the catalyst activity but increased the catalyst selectivity to some extent. The BET surface areas of V-O-Ti-a, V-O-Ti-b, V-O-Ti-c, and V-O-Ti-d

Entry	T/°C	$LHSV/h^{-1}$	2-Picoline:NH ₃ ^a	2-Picoline:H ₂ O ^a	Conversion/%	Selectivity/%
1	370	0.15	1:6	1:3.3	99	78
2	370	0.18	1:6	1:3.3	91	95
3	370	0.3	1:6	1:3.3	79	96
4	350	0.18	1:6	1:3.3	71	89
5	390	0.18	1:6	1:3.3	98	60
6	370	0.18	1:3	1:3.3	85	84
7	370	0.18	1:6	1:7	90	75

Table 2 The effect of varied conditions on the ammoxidation of 2-picoline

The reactions were carried out at 150 cm³ s⁻¹ air in the presence of V–O–Ti-c catalyst

^a Mole ratio



Fig. 3 XRD patterns of V–O–Ti-a, V–O–Ti-b, V–O–Ti-c, and V–O–Ti-d catalyst

 Table 3
 BET surface area, pore size, and crystallite diameter of the catalyst

Catalysts	BET surface area/m ² g^{-1}	Pore size/nm	D/nm
V–O–Ti-a	0.9	14.3	55
V–O–Ti-b	0.8	15.5	62
V-O-Ti-c	0.7	17.0	68
V–O–Ti-d	0.7	17.7	72

catalysts are from 0.7 to 0.9 m² g⁻¹, but Narayana et al. [14] observed an 18.6 m² g⁻¹ BET surface area in a 7.2 mol% V₂O₅/TiO₂ catalyst. These two different results are due to the different methods of preparing the catalyst. The catalyst prepared by the impregnation method had a larger BET surface area because of the supporter. However, the surface area of the catalyst prepared by the mixing method was mainly obtained from the porous structure that was generated during the decomposition of ammonium vanadate.



Fig. 4 The process of preparing the V–O–Ti catalyst by the mixing method

Experimental

Catalyst preparation

The V–O–Ti catalyst was prepared by using the mixing method (Fig. 4). Solid TiO₂ (150 g) and 20 g NH₄VO₃ crystals were added to 50 cm³ distilled water. The mixture was formed into a cylindrical catalyst of 7 mm length and 4 mm diameter. The cylindrical catalyst was dried for 1 h at 60 °C, then calcined for 2 h at 250 °C and for 5 h at 500 °C (V–O–Ti-a) in a muffle furnace. The V–O–Ti-b, V–O–Ti-c, and V–O–Ti-d catalysts were prepared by the calcination of V–O–Ti-a catalysts for 4 h at 600, 700, and 800 °C, respectively. The V₂O₅ loading of the V–O–Ti catalyst was 8.3 mol%. Compared to the impregnation method [14], this mixing method is simpler for preparation of V₂O₅/TiO₂ catalyst, and the V–O–Ti catalyst had comparative catalytic activity.

Reaction procedure

The synthesis was carried out in a stainless-steel fixed-bed reactor. The reactants were fed from the top of the reactor. Three calibrated flow meters were used for ammonia, air, and the mixture of picoline and water. The reactor was



Fig. 5 The fixed-bed reactor

surrounded by a heating jacket to control the temperature of the fixed bed. The mixture was reacted in a 40-cm catalyst bed, and the effective radius of the reactor was 15 mm. The amount of catalysts packed was 260 cm^3 . The products were cooled using a condenser. The figure of the fixed-bed reactor is shown in Fig. 5.

The product analysis was checked by GC (Agilent 1790F and SE-30 column; Nan-jing Xuxi Apparatus Co., Ltd., China) and GC-MS (TRACEGC2000/TRACEMS; Thermo Quest, USA). The conversion and selectivity were determined by an external standard method, the steps of which were as follows:

- 1. First, seven standard samples of different concentrations were prepared and then analyzed by GC at the same injection.
- 2. Second, a scatter diagram with a regression line was made, for which the abscissa was the concentration of the standard sample and the ordinate was the peak area.
- 3. Finally, the reaction mixture was analyzed by GC at the same injection volume as the standard samples, and then the expected product's concentration was obtained.

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