

Amoxidation of methylaromatics over VPO/SiO₂ catalysts

Xie Guang-yong^{1*} & Huang Chi²

¹Key Laboratory of Catalysis and Materials Science of Hubei Province, College of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan 430074, China

²College of Chemistry & Molecular Sciences, Wuhan University, Wuhan 430072, China
Email: xxgyy@hotmail.com

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Amoxidation of methyl aromatics to their corresponding nitriles over silica-supported vanadium phosphorus oxide (VPO/SiO₂) catalysts has been studied. The effects of carrier silica, the addition of phosphorus, the substituents and the loadings on catalytic performances have been discussed. Compared with unsupported VPO, the VPO/SiO₂ catalysts have higher catalytic activity for amoxidation of substituted toluenes at much lower reaction temperature. XPS shows that vanadium and phosphorus exist mainly in the pentavalent state in the VPO/SiO₂ catalysts. XRD shows that vanadium phosphorus oxides exist as amorphous phase in 10 wt.% catalyst. When the loadings are over 10 wt.%, the crystalline α -VOPO₄ would emerge, which would decrease the yield and selectivity. Additional phosphorus can inhibit the formation of crystalline V₂O₅ and form amorphous composite oxides with vanadia, which play concerted catalytic function and increase the selectivity of nitriles remarkably. The methyl aromatics with different substituents or same substituents on different positions have different catalytic activities because of the variant electronic stability of intermediates, the hindered accessibility of methyl group or the chemisorption state of the substrate molecule on the electrophilic catalyst surface.

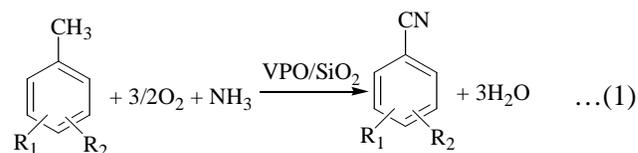
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Amoxidation of methylaromatics is an excellent method to prepare aromatic nitriles which are valuable intermediates for the production of dyestuffs, pesticides, pharmaceuticals and many other fine chemicals¹⁻³. In the last several decades, investigation on the amoxidation reactions was emphasized mostly on developing new catalysts and examining reaction mechanisms^{3,4}.

Vanadium-containing composite oxides are extensively used in the selective oxidation of organic materials⁵⁻¹¹. Vanadium phosphorus oxides (VPO), well-known as catalysts of the *n*-butane conversion to maleic anhydride⁹⁻¹¹, are successfully used in the amoxidation reaction of methylaromatics^{2-5,12-14}. Martin *et al.*^{2-5,12,13} reported the amoxidation of substituted toluenes over unsupported vanadium phosphorus oxide catalysts to the corresponding nitriles, showing attractive use of VPO catalyst. But unsupported catalysts are unsuitable to be used in a fluid-bed for large-scale operations of chemical industry. In the manufacture of *o*-chlorobenzonitrile, silica-supported VPO catalysts in fluid-bed reactors have been used which gave excellent result¹⁵. It has been found that the VPO/SiO₂ catalysts have good

catalytic activity to many other substituted toluenes¹⁶.

The route of amoxidation of substituted toluenes over silica-supported VPO catalysts is shown as Eq. (1).



R₁, R₂ = -H, -CH₃, -Cl, -Br, -I, -OCH₃, -CN

Use of supported oxide has many advantages over an unsupported one, e.g. higher mechanical strength, better thermal stability, larger surface area and longer lifetime. Supports were long believed to be inert in catalytic reactions, however, it is known now that the structure and the composition of the materials used as supports can influence the activity and selectivity of the active phase to a remarked degree¹⁷. After being supported on silica, the vanadium phosphorus oxides showed different structure and catalytic property. In the amoxidation of many methylaromatics, silica-

supported VPO catalysts usually show better catalytic property than unsupported one.

Experimental Procedure

Preparation and characterization of catalysts

V₂O₅ (1.8504 g) was added into a hot mixture of 85% phosphoric acid (2.3452 g), oxalic acid (3.8478 g) and water (25 mL) under rigorous stirring, obtaining a blue solution. The solution was subsequently impregnated on 15 g SiO₂ (φ0.3~0.45 mm). Dried at 383K overnight, the catalyst precursor was calcined at 773K for 5 h, then cooled to store for use. The loading of vanadium-phosphorus is 10 wt.%.

Other VPO/SiO₂ catalysts of different loadings and 10 wt.% VO/SiO₂ catalyst were prepared by the same method, except for the weight of reagents.

XPS spectra were recorded on KRATOS XSAM 800 spectrometer with Mg Kα; all binding energies were referred to the C_{1s} line at 284.6 eV. XRD patterns were recorded using D/MAX-RB diffractometer with Cu Kα (λ=1.5818Å) radiation from 2θ = 4 to 90.

Catalytic tests

All catalytic runs were carried out in a 30 mm-inside-diameter quartz tube fixed-bed reactor loaded with 10 g catalyst prepared as above under atmospheric pressure^{18,19}. The substituted toluenes 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 outlet stream was cooled. The nitriles were condensed and analyzed by gas chromatography with flame ionization detector and nitrogen as carrier gas.

Results and Discussion

The results of ammoxidation of substituted toluenes on silica-supported vanadium phosphorus oxides are shown as Table 1.

Effect of silica carrier

From Table 1 it can be seen that VPO/SiO₂ catalysts have good catalytic activity for ammoxidation of substituted toluenes. Supported on

silica, the activity of VPO catalysts was usually increased compared with the results reported by Martin *et al.*². The suitable reaction temperatures were decreased remarkably for *ca.* 50 K. In case of ammoxidation of dichlorotoluenes, VPO/SiO₂ catalysts show more evident advancement of activity. On unsupported VPO catalysts, the yields of 2,6-, 2,4- and 3,4-dichlorobenzonitriles as reported by Martin *et al.*^{2,5} are only *ca.* 15, 46, 44%, respectively. The yields of dichlorobenzonitriles have been enhanced *ca.* 20~40% on silica-supported VPO catalysts. The XRD of 10 wt.% VPO/SiO₂ shows that vanadium phosphorus oxides exist as amorphous phase (Fig. 1), which is different from the unsupported VPO catalysts¹³. The carrier silica can interact with vanadium phosphorus oxide and delay the formation

Table 1—Ammoxidation of different substituted toluenes on 10 wt.% VPO/SiO₂ catalyst

Ar-	Conversion	Yield	Selectivity [*]	Purity
			(%)	
<i>o</i> -Cl-	85.0	72.8	85.6	96.9
<i>m</i> -Cl-	79.1	53.6	67.8	95.0
<i>p</i> -Cl-	97.8	90.9	92.9	99.0
<i>P</i> -Br-	98.0	87.7	89.5	98.8
<i>P</i> -I-	98.1	72.3	73.7	98.6
<i>P</i> -CH ₃ O-	96.0	63.0	65.6	97.0
2,6-Cl ₂ -	87.0	57.0	65.5	96.5
2,4-Cl ₂ -	94.0	70.2	74.7	97.8
3,4-Cl ₂ -	92.0	66.0	71.7	98.0
<i>o</i> -xylene	72.5	51.7	71.3	94.0
<i>m</i> -xylene	89.9	48.5	53.9	97.3
<i>p</i> -xylene	98.8	73.6	74.5	99.0

*Selectivity=Yield/Conversion

Reaction conditions: Catalyst wt. = 10 g; T = 653 K;

Methylaromatics: NH₃: Air = 1:7:30(mole)

of crystalline phase.

Influence of substituents

It can be observed from Table 1 that the yield and selectivity of substituted toluenes are different with different size, position or electronic properties of substituents.

From Table 1 it can also be seen that the positions of substituents influence the activity of ammoxidation reaction. For *p*-isomers the processes get the highest yield and selectivity to form nitriles; for *m*-isomers the yields are lowest. Usually the order of reactivity is: *p*->*o*->*m*-. The *p*- and *o*-isomers have the electronic similarity of reaction intermediates, but *o*-isomer has more steric hindrance. The gradation shows that steric hindrance is the major reason of the decrease of activity for *o*-isomer. On the other hand, *m*-isomers show lower activity and selectivity than *p*- and *o*-isomers because of lack of resonance stability of intermediate during the nitriles formation.

For the substrates having different substituents with same substitute position in the ring and similar electronic property, the sizes of substituents affect the reactivity and selectivity. From Table 1 it can be seen that the reactivities of *p*-halotoluenes are in the order: *p*-chloro- > *p*-bromo- > *p*-iodo-. The C-X bond energies decreased from Cl to I, so the iodotoluene is easier to be overoxidized. It may be the main cause for the decrease of selectivity from chlorotoluene to iodotoluene.

The data in Table 1 also show that the activity and selectivity are influenced by electronic properties of substituents. The order is *p*-Cl- C₆H₄CH₃ > *p*-CH₃-C₆H₄CH₃ > *p*-CH₃O-C₆H₄CH₃. This order demonstrates that substituted toluenes owning electron-acceptor substituents are converted to their nitriles with higher activity and selectivity than those owning electron-donor groups. This fact could be explained by the chemisorption state of the substrate molecule on the electrophilic catalyst surface². In the ammoxidation of methylaromatics, the first step is the H-abstraction from the methyl group and the intermediate of a methylene-like species is formed. The substrates with electron-donating groups could be chemisorbed stronger on the surface because of higher density of electron cloud. The intermediates could be overoxidized more easily, so the yield and selectivity are lower.

Effect of loadings

The VPO/SiO₂ catalysts with the different loading contents of vanadium-phosphorus show different catalytic activity and selectivity. The results in Table 2 show the influences of loadings over the yield and selectivity of anisonitrile by ammoxidation of *p*-methoxytoluene on VPO/SiO₂ catalysts.

From Table 2 it can be found that the yield at

Table 2—Influences of loadings of VPO over the yields of anisonitrile

Loadings (%)	5	10	15	20	25
Conversion (%)	92.5	96.0	95.0	94.3	94.5
Yield (%)	61.0	63.0	61.6	58.1	53.8
Selectivity (%)	65.9	65.6	64.8	61.6	56.9

Reaction conditions: Catalyst wt. = 10 g; T = 653 K; *p*-Methoxytoluene: NH₃: Air = 1:7:30

10 wt.% loading catalyst is highest. The yields decrease with the addition of contents when loadings are over 10 wt.%. From Fig. 1 the XRD characterization of different loadings of VPO catalysts shows that the vanadium phosphorus oxides exit as amorphous phase when loadings are less than 10 wt.%. When contents are over 10 wt.%, the crystalline phase emerged, which has been proved to be α -VOPO₄ mostly. At very low loadings, the amount of active components is less, which would lower the catalytic activity. So the ammoxidation reaction on 5 wt.% loading catalyst has a little lower conversion and yield than on 10 wt.% catalyst. When loadings exceed 10 wt.%, the crystalline α -VOPO₄ emerged, which would decrease the catalytic activity and selectivity. Martine-Lara *et al.*¹⁰ found similar situation in the oxidation of *n*-butane to maleic anhydride.

VPO/SiO₂ catalysts with different loadings were also characterized by XPS. The B.E. of V_{2p} in VPO/SiO₂ was found to be 517.3~517.5 eV and that of P_{2p} 134.1 eV (Table 3). According to literature, the B.E. of V_{2p} in V₂O₅/SiO₂ is *ca.* 517.4 eV¹⁷ and that of P_{2p} in (VO)₂P₂O₇ is 134.0 eV²⁰. Hence, it can be inferred that vanadium and phosphorus exist mainly in the pentavalent state in the VPO/SiO₂ catalysts. From Table 3 it can also be seen that only a little

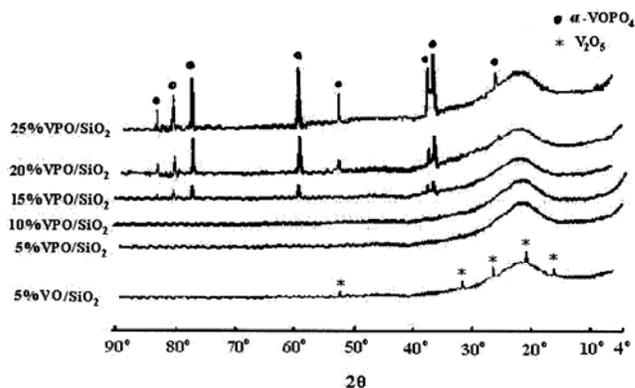


Fig.1—XRD patterns of different loading VPO/SiO₂ and 5% VO/SiO₂ catalysts

Table 3—Binding energies and surface atom ratios on different loading VPO/SiO₂ catalysts

Loadings (%)		5	10	15	20	25
O _{1s}	B.E./eV	532.4	532.4	532.4	532.4	532.4
	Atom ratio (%)	68.2	67.5	67.1	66.8	66.7
Si _{2p}	B.E./eV	103.4	103.4	103.5	103.4	103.4
	Atom ratio (%)	30.0	29.6	29.4	29.3	29.3
V _{2p}	B.E./eV	517.4	517.5	517.4	517.5	517.3
	Atom ratio (%)	0.3	0.5	0.6	0.7	0.7
P _{2p}	B.E./eV	134.1	134.1	134.1	134.1	134.0
	Atom ratio (%)	1.5	2.4	2.9	3.2	3.4

Table 4—Amoxidation of different substituted toluenes on 10 wt.% V-O/SiO₂ catalyst

Ar-	Conversion	Yield	Selectivity	Purity
		(%)		
<i>o</i> -Cl-	87.3	47.8	54.8	94.0
<i>m</i> -Cl-	83.0	44.4	53.5	94.6
<i>p</i> -Cl-	96.0	70.1	73.0	97.2
<i>p</i> -Br-	97.5	68.0	69.7	97.0
<i>p</i> -I-	97.6	56.9	58.3	96.5
<i>p</i> -CH ₃ O-	95.0	22.0	23.2	95.6
2,6-Cl ₂ -	86.2	32.0	37.1	96.0
2,4-Cl ₂ -	92.0	46.0	50.0	97.3
3,4-Cl ₂ -	93.0	45.0	48.4	97.0
<i>o</i> -xylene	65.0	38.1	58.6	92.0
<i>m</i> -xylene	91.8	36.6	39.9	95.0
<i>p</i> -xylene	94.3	59.5	63.1	97.8

Reaction conditions: Catalyst wt. = 10 g; T = 653 K; Ar- : NH₃ : Air = 1:7:30

vanadium and phosphorus atoms cover the surface of silica. Vanadium-phosphorus composite oxides are likely to be present mostly in the pores of silica. Similar phenomena have been observed in VCrO/SiO₂ catalysts²¹.

Influence of addition of phosphorus

The results of ammoxidation of methylaromatics on silica-supported vanadium oxides are shown in Table 4.

The data in Tables 1 and 4 show that the ammoxidation reaction with V-O/SiO₂ and VPO/SiO₂ catalysts has similar conversions, but the yields with V-O/SiO₂ catalysts are much lower than that with VPO/SiO₂ catalysts. It can be seen from Fig. 1 that the crystalline V₂O₅ emerged on the surface of VO/SiO₂ catalysts, even if the loadings of vanadia are very low (~5%)²¹, would make raw material be overoxidated²² and lower the selectivity of reaction. The additive

phosphorus can inhibit the formation of crystalline V₂O₅ and form amorphous composite oxides with vanadia, which play concerted catalytic function and increase the selectivity of ammoxidation reaction of methylaromatics to their corresponding nitriles remarkably.

The results derived from V-O/SiO₂ catalyst also confirm the conclusion drawn from VPO/SiO₂ catalyst about the influence of substituents.

Conclusions

Aromatic nitriles can be prepared by ammoxidation of methylaromatics on VPO/SiO₂ catalysts. Supported on silica, the vanadium phosphorus oxides exist as amorphous phase. The VPO/SiO₂ catalysts show higher catalytic activity than unsupported VPC catalysts for ammoxidation of substituted toluenes, especially for dichlorotoluenes and the reaction temperature decreased markedly. Different size, position or electronic properties of substituents can affect the yield and selectivity of aromatic nitriles depending on the hindered accessibility of methyl group and the stability of reaction intermediates. The loadings can also influence the yield. The VPO/SiO₂ catalyst with 10 wt.% loading has highest catalytic activity. When the loadings are over 10 wt.%, the crystalline α -VOPO₄ would emerge, which would decrease the catalytic activity and selectivity. XPS shows that vanadium and phosphorus exist mainly in the pentavalent state in the VPO/SiO₂ catalysts. The additional phosphorus constraints the formation of crystalline V₂O₅ and forms amorphous composite oxides with vanadia, which increase the selectivity of aromatic nitriles evidently.

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