

3,4-Dichlorotoluene Ammoxidation to 3,4-Dichlorobenzonitrile over VPO/SiO₂ Catalyst

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Abstract: Ammoxidation of 3,4-dichlorotoluene (DCT) to prepare 3,4-dichlorobenzonitrile (DCBN) over silica supported vanadium phosphorus oxide catalysts has been studied. On the VPO/SiO₂ catalyst, the influence of the reaction temperature, the molar ratio of air/DCT, the molar ratio of NH₃/DCT in the feed gas and the space velocity (v_s) on the conversion, yield and selectivity was observed. The most appropriate reaction condition is: reaction $T=673$ K, $n(\text{DCT}) : n(\text{NH}_3) : n(\text{air})=1 : 7 : 30$ and $v_s=250$ h⁻¹. At this optimum reaction condition, the conversion of DCT is 97.8%; the molar yield of DCBN is 67.4%. It was found that the addition of element phosphorus can improve the yield of DCBN compared with VO/SiO₂ catalyst.

Key words: ammoxidation; 3,4-dichlorotoluene; 3,4-dichlorobenzonitrile; VPO/SiO₂

CLC number: O 643

0 Introduction

3,4-Dichlorobenzonitrile (DCBN) is an important intermediate which can be used to synthesize 3,4-difluorobenzonitrile, 3-fluoro-4-chlorobenzonitrile, 3-chloro-4-fluorobenzonitrile and their corresponding benzoic acid.^[1-5] 3,4-Dichlorobenzonitrile can be prepared from 3,4-dichlorobenzoic amide, 3,4-dichlorobenzaldehyde or $\alpha,\alpha,\alpha,3,4$ -pentachlorotoluene.^[6-8] But the cost of 3,4-Dichlorobenzonitrile is very high by these methods. Ammoxidation is the most effective method to prepare benzonitrile and substituted benzonitrile. But ammoxidation of cheap 3,4-dichlorotoluene (DCT) for 3,4-dichlorobenzonitrile has only reported by Martin A *et al*^[9] on the unsupported VPO complex oxide catalyst. In this literature, the yield of 3,4-dichlorobenzonitrile was only 52%, the reaction temperature was 713 K and the strength of unsupported VPO complex oxide catalyst is very low, so it cannot use to produce 3,4-dichlorobenzonitrile on commercial scale. We have reported the ammoxidation of 2,4-dichlorotolu-

ene^[10] and 2,6-dichlorotoluene^[11] on silica supported VPO complex oxide catalyst with higher yield of corresponding nitriles than that on the unsupported VPO complex oxide catalyst. In this paper, we will report ammoxidation of 3,4-dichlorotoluene for 3,4-dichlorobenzonitrile with high yield over silica supported VPO complex oxide catalysts.

1 Experimental

The molar ratio of V/P in the catalyst is 1 : 1. V₂O₅ (1.350 g) was added to a hot mixture of phosphoric acid (85%, 1.359 g), oxalic acid (2.564 g) and water (12 mL) under stirring, then the solution was impregnated on SiO₂ (10 g, $\varnothing 300-425$ μm) and the catalyst was calcined in atmosphere at 853 K for 12 h. Other catalysts with the molar ratio of P/V from 0.5 : 1 to 2 : 1 were prepared by same method. The reaction was carried out under atmospheric pressure in a quartz tube with inside diameter 30 mm fixed bed

Received date, 2001-11-19

Foundation item, Supported by Youth Chen-Guang Project of the Committee of Science and Technology of Wuhan (20015005042)
Biography, Huang Chi(1972-), male, Ph D, Lecture, research direction, ammoxidation.

reactor. The conversion of the DCT (c) and the yield of the DCBN (y) were determined by gas chromatography.

2 Results and Discussion

The influence of the reaction temperature, the molar ratio of air/DCT, the molar ratio of NH_3 /DCT in the feed gas and the space velocity (v_s) on the conversion, yield and selectivity (s) is shown in Fig. 1, Fig. 2, Fig. 3 and Fig. 4 respectively.

It can be seen from Fig. 1 that the yield remains 55%–67% in temperature range of 623–683 K, then decreases drastically over 683 K. In

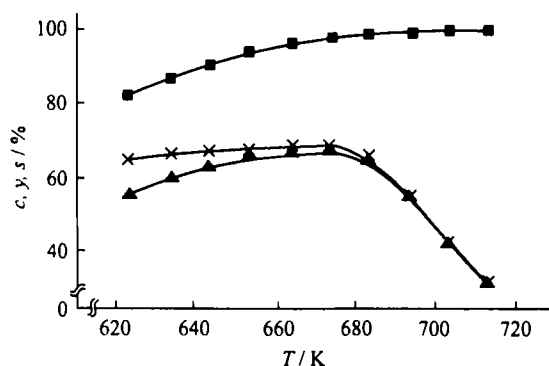


Fig 1 The conversion of DCT(■), yield of DCBN(▲) and DCBN selectivity(×) as the reaction temperature
Reaction condition: catalyst 15 g, $n(\text{DCT}) : n(\text{NH}_3) : n(\text{air}) = 1 : 7 : 30$, $v_s = 250 \text{ h}^{-1}$

Fig. 2, the yield increases from 59% to 65% as the molar ratio of air/DCT from 10 to 15 and the molar ratio of air/DCT is 30 with the highest yield of 67.4%, then the yield is still higher than

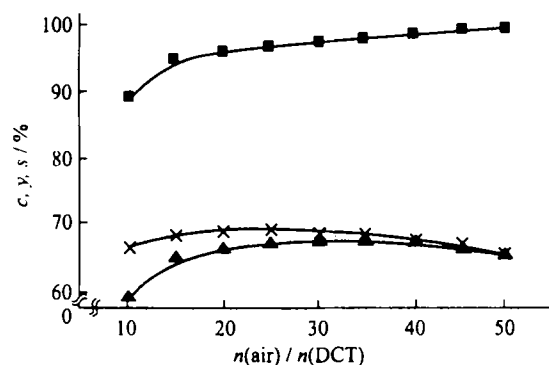


Fig 2 The conversion of DCT(■), yield of DCBN(▲) and DCBN selectivity(×) as the molar ratio of air/DCT
Reaction condition: catalyst 15 g, $T = 673 \text{ K}$, $n(\text{DCT}) : n(\text{NH}_3) = 1 : 7$, $v_s = 250 \text{ h}^{-1}$

65% as the molar ratio of air/DCT from 30 to 50. As shown in Fig. 3 and Fig. 4, the yield and selectivity of DCBN are not sensitive to the change of molar ratio of NH_3 /DCT and v_s . The most appropriate reaction condition is: reaction temperature = 673 K, $n(\text{DCT}) : n(\text{NH}_3) : n(\text{air}) = 1 : 7 : 30$ and $v_s = 250 \text{ h}^{-1}$. At this optimum reaction condition, the conversion of DCT is 97.8%; the molar yield of DCBN is 67.4%. Compared with the unsupported VPO catalyst, the highest yield increases ca. 15% and the optimum reaction temperature goes down 40–50 K over the VPO/ SiO_2 catalyst. This suggests that the structure of the catalysts is different with the unsupported VPO complex oxide because of the

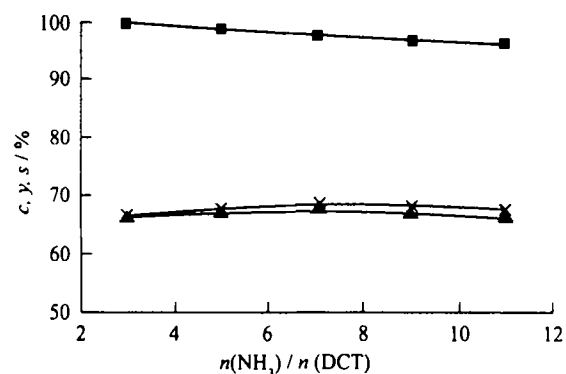


Fig 3 The conversion of DCT(■), yield of DCBN(▲) and DCBN selectivity(×) as the molar ratio of NH_3 /DCT
Reaction condition: catalyst 15 g, $T = 673 \text{ K}$, $n(\text{DCT}) : n(\text{air}) = 1 : 30$, $v_s = 250 \text{ h}^{-1}$

interaction of the vanadium and phosphorus oxides with SiO_2 oxide support. The fresh-calcined VPO/ SiO_2 catalyst and the VPO/ SiO_2 catalyst subjected to reaction medium for 10 h

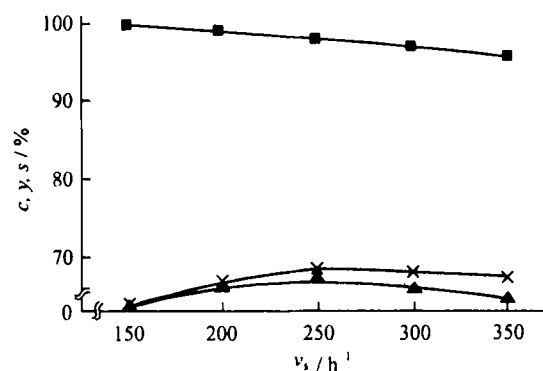


Fig 4 The conversion of DCT(■), yield of DCBN(▲) and DCBN selectivity(×) as the v_s
Reaction condition: catalyst 15 g, $T = 673 \text{ K}$, $n(\text{DCT}) : n(\text{NH}_3) : n(\text{air}) = 1 : 7 : 30$

were investigated by XRD analysis respectively, but no diffraction of crystalline phase was detected in both cases. It may be concluded that SiO₂ support can promote high dispersion of the applied phase to be amorphous. In addition, support SiO₂ can improve the mechanical strength, thermal stability and lifetime of the catalyst.

The conversion of DCT, yield and selection of DCBN upon the catalysts with different molar ratio of P/V are shown in Table 1. It can be seen that the addition of element phosphorus can improve the yield of DCBN and there is little effect on the conversion of DCT, yield and selection of DCBN as the molar ratio of P/V of the catalysts from 0.5 to 2.

Table 1 Effect of molar ratio of P/V of the catalysts on the conversion of DCT, yield and selection of DCBN (reaction condition: catalyst 15 g, reaction temperature 673 K, $n(\text{DCT}) : n(\text{NH}_3) : n(\text{air}) = 1 : 7 : 30$, $v_r = 250 \text{ h}^{-1}$)

$n(\text{P}) : n(\text{V})$	Conversion of DCT/%	Yield of DCBN/%	Selection of DCBN/%
0 : 1	100	43.2	43.2
0.5 : 1	98.1	66.9	68.2
0.8 : 1	98.5	67.3	68.3
1 : 1	97.8	67.4	68.9
1.2 : 1	97.6	66.8	68.4
1.4 : 1	98.3	67.6	68.8
1.7 : 1	97.2	66.7	68.6
2 : 1	96.9	66.1	68.2

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