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Catalysis Today 32 (1996) 279–283

CATALYSIS TODAY

Ammoxidation of methylaromatics over vanadium phosphate catalysts. I. Effect of the size, position and electronic properties of substituents on the catalytic conversion of methylaromatics to the corresponding nitriles

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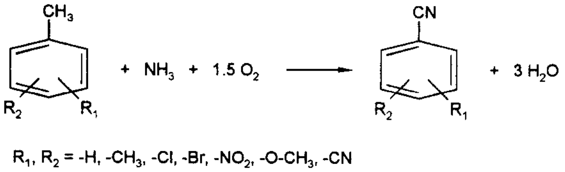
Abstract

The heterogeneous-catalytic ammoxidation of several mono- and disubstituted methylaromatics and heteroaromatics to their corresponding nitriles was studied. The reaction was carried out on an ammonium oxovanadium pyrophosphate ($(NH_4)_2[(VO)_3(P_2O_7)_2]$) generated during the catalytic process. The study shows that the catalytic activity and the nitrile selectivity depend mainly on the position and the electronic nature of the particular substituent due to a changed accessibility of the methyl group as well as a possible different electronic stabilization.

Keywords: Ammoxidation; Methylaromatics; Vanadium phosphate catalysts; Nitriles

1. Introduction

The ammoxidation of substituted toluenes and methylheterocycles to the corresponding nitriles [see Eq. (1)] is an industrially important reaction. Usually, V/Ti, V/Mo, V/Sb or V/Sn oxides promoted by further transition metal components, on carriers (e.g. alumina or silica) or as bulk systems, either in a fixed or fluidized bed, are used as catalysts ([1–4] and references therein). The reaction is carried out at normal pressure and temperatures up to 753 K. Apart from the application of the cited catalyst compositions vanadium phosphorus oxides (VPO), well known as catalysts of the *n*-butane conversion to maleic anhydride (e.g. [5]), are successfully used in the ammoxidation reaction of substituted methylaromatics and heterocycles [6–9].



R_1, R_2 = -H, $-CH_3$, -Cl, -Br, $-NO_2$, $-O-CH_3$, -CN

(1)

The synthesized nitriles are valuable intermediates in the organic synthesis of various dyestuffs, pesticides and pharmaceuticals. The reactivity of the aromatic or heteroaromatic substrate and the nitrile selectivity are determined by several causes in spite of using the same catalytic system. Thus, the position, the size and additionally electronic effects of one or more

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PII S0920-5861(96)00080-6

substituents should influence significantly the chemisorption state of the substrate molecule on the electrophilic catalyst surface, the subsequently processing reaction with activated ammonia surface species, the electronic and/or mesomeric stabilization of the intermediate and finally the desorption of the formed nitrile from the catalyst surface. Furthermore, it would be interesting to investigate the influence of the position of a second substituent, particularly, if the substituents directly located in neighbour to the methyl group. Therefore, the choice of the applied substrates is characterized by (i) a varying size of the substituent (*p*-substituted F-, Cl-, Br- and I-toluene), (ii) a changed position of the same substituent (isomeric chlorotoluenes), (iii) a variable electronic nature of the substituents such as electron-donating groups (methoxytoluenes) or rather electron-withdrawing groups (chlorotoluenes), (iv) an additional second substituent (dichlorotoluenes and dimethoxytoluenes) and (v) a different electronic nature of the ring due to the introduction of an heteroatom (isomeric picolines).

This paper presents a survey on investigations on the heterogeneous-catalytic ammoxidation of the substrates described above and assesses substituent effects, influencing the activity and selectivity of the ammoxidation reaction. The article considers recently obtained results [10,11] as well as newly gained data and tries an extensive description of the problem, also in comparison to mechanistic ideas.

2. Experimental

The conversion of the substituted toluenes as well as picolines to the corresponding nitriles was studied for all the substrates in the temperature region of 673 to 733 K using fixed bed reactors under normal pressure. Ammonia and air were mixed with vaporized organic substrate and water vapor, passing the catalyst bed. The reactor outlet flow was analyzed by on-line gas chromatography with flame ionization detection. The catalytic runs were carried out over $(NH_4)_2[(VO)_3(P_2O_7)_2]$ as catalyst generated under the applied ammoxidation conditions by a solid-state reaction of the precursor compound $VOHPO_4 \cdot 0.5H_2O$ [12]. Other VPO precursor compounds, such as α-$VOPO_4$ or β-$VOPO_4$, are useful as well. They pass through a similar transformation as described in [7,8].

3. Results and discussion

The results of the investigations that will be presented in course of the following sections are summarized from the viewpoint of a sole substituent property although the effects of all properties can be overlapped and the 'substituent effect' is the sum of several characteristics, respectively.

3.1. Effect of substituent size

Fig. 1 depicts the conversion of several *p*-substituted halotoluenes and the selectivity of the formed nitriles. The results showed a high conversion of all educts (95–99 mol%), but the nitrile selectivity passed through a maximum and decreased from *p*-Cl to *p*-I substituent, respectively. The selectivity data (*p*-Cl > *p*-Br ≫ *p*-I) reflected the higher reactivity of the C–X bond, rising with an increased polarization from C–Cl to C–I. The fluorine compound was omitted from these considerations due to a sometimes different behaviour. Apart from these results, a direct effect of the substituent size in

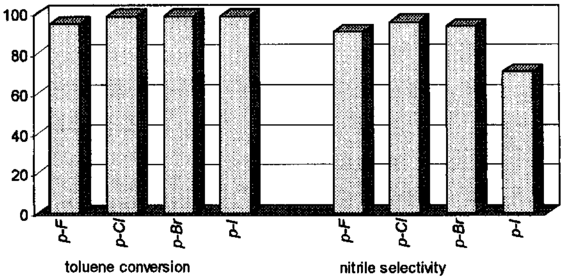

Fig. 1. Conversion of *p*-substituted halotoluenes (mol%) and nitrile selectivity (%) ($VOHPO_4 \cdot 0.5H_2O$ precursor; precursor weight, 5.8 g; $T = 703$ K; halotoluene: O_2:NH_3:H_2O = 1:8:5:25; $W/F = 9.7$ g h mol^{-1}).

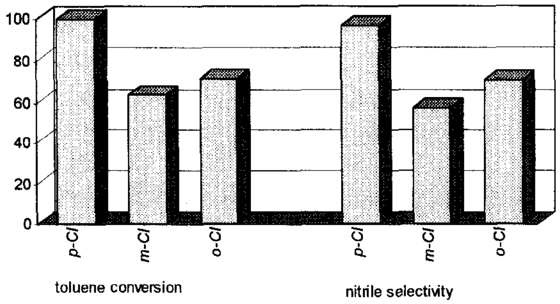

Fig. 2. Conversion of isomeric chlorotoluenes (mol%) and nitrile selectivity (%) ($VOHPO_4 \cdot 0.5H_2O$ precursor; precursor weight, 5.8 g; $T = 703$ K; Cl-toluene: O_2:NH_3:H_2O = 1:8:5:25; W/F = 9.8 g h mol^{-1}).

p-position could not be observed. However, this finding could be alter if substituents located closer to the methyl group as shown below.

3.2. *Influence of a different substituent position*

The results of the ammoxidation of isomeric compounds, i.e. the effect of the position of a Cl-substituent are demonstrated in Fig. 2. Evidently, the p-isomer showed highest conversion and selectivity whereas these data are significantly decreased for the o- and m-isomer. This gradation ($p \gg o > m$) mirrors on the one hand the different accessibility and reactivity of the methyl group in dependence on the position of the substituent despite the electronic similarity of reaction intermediates, having substituents at the o- and p-position. On the other hand, this row reflects the possibility of a different electronic stabilization of intermediates (p-/o- vs. m-isomer), appearing during the nitrile formation. Thus, activity and selectivity are influenced by the position of the substituent, but this effect is overlapped by a different electronic stabilization of reaction intermediates.

3.3. *Effect of electron-withdrawing and electron-donating groups*

Fig. 3 depicts conversion and nitrile selectivity of the ammoxidation of isomeric chlorotoluenes (electron-withdrawing) and methoxytoluenes (electron-donating). The results demonstrated that toluenes, having electron-acceptor substituents (e.g. –Cl) were converted with higher activity and selectivity to their nitriles compared to that, having electron-donor groups (e.g. –O–Me). Moreover, the results of the methoxytoluene conversion confirm the conclusion drawn from the investigation of the effect of the substituent position as described above.

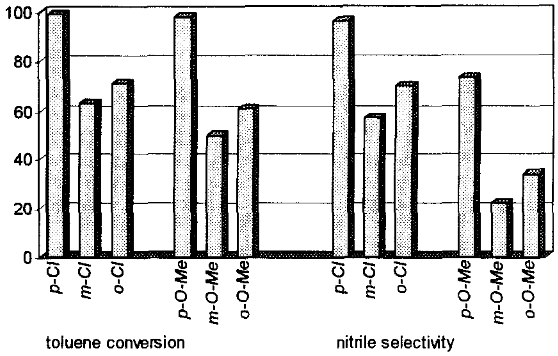

Fig. 3. Conversion of isomeric chloro- and methoxytoluenes (mol%) and nitrile selectivity (%) ($VOHPO_4 \cdot 0.5H_2O$ precursor; precursor weight, 5.8 g; T = 703 K; Cl-/Me-O-toluene: O_2:NH_3:H_2O = 1:8:5:25; W/F = 9.8 g h mol^{-1}).

3.4. *Action of an additional second substituent*

Fig. 4 shows the conversion data of some dichlorotoluenes used in the ammoxidation as well as the obtained nitrile selectivity. The data are significantly graded in the following order

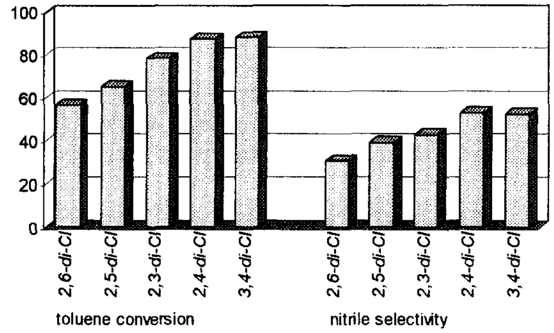

Fig. 4. Conversion of isomeric dichlorotoluenes (mol%) and nitrile selectivity (%) ($VOHPO_4 \cdot 0.5H_2O$ precursor; precursor weight, 10.5 g; $T = 688$ K; di-Cl-toluene: O_2:NH_3:H_2O = 1: 9:5:29; W/F = 10.2 g h mol^{-1}).

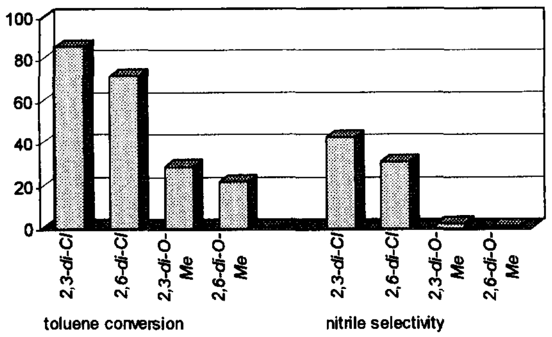

Fig. 5. Conversion of dichloro-/dimethoxytoluenes (mol%) and nitrile selectivity (%) ($VOHPO_4 \cdot 0.5H_2O$ precursor; precursor weight, 10.5 g; $T = 688$ K; di-Cl-toluene: O_2:NH_3:H_2O = 1:9:5:29; $W/F = 10.2$ g h mol^{-1}).

2,6-di-Cl < 2,5-di-Cl < 2,3-di-Cl < 2,4-di-Cl ~ 3,4-di-Cl, showing a low conversion rate of such substrates, having both substituents nearby the methyl group in comparison to suchlike feeds, having the two substituents more remotely from the reaction centre. Thus, the steric effect of the position of the substituents come to the fore. Apart from the steric influence, a more difficult electronic stabilization of reaction intermediates could cause the decreased nitrile selectivities proportionally compared to substrates, having only one substituent.

A comparison of the ammoxidation results of 2,3-di-Cl- and 2,6-di-Cl-toluene as well as the corresponding methoxy-substituted compounds is given in Fig. 5. The data revealed a decreased conversion and a drastically declined selectivity compared to the monosubstituted substrates as explained for dichlorotoluenes above. Moreover, dimethoxybenzonitriles were obtained in traces only, reflecting more unstable reaction intermediates due to electron-donating of two methoxy substituents, probably.

3.5. Ammoxidation of isomeric picolines

The application of N-heterocyclic compounds as ammoxidation feed changes the adsorption state of the substrate in comparison to methylaromatics due to the inclusion of the additional electron pair of the ring nitrogen in the adsorbate complex. Furthermore, the pyridine molecule can be considered to be similar to nitrobenzene in the substitution effects (electron-withdrawing effect). The consequence of these changes is shown in Fig. 6, depicting the reaction data. Catalyst activity and nitrile selectivity reflected a 4- > 3- > 2-picoline gradation. The row shows the expected results if only steric factors would influence the reaction, i.e. in this case the steric conditions between the catalyst surface and the methyl group determine activity and nitrile selectivity.

3.6. Influence of the substituent properties on the ammoxidation reaction mechanism

The ammoxidation of methylaromatics on vanadium-containing catalysts could usually proceed by substrate chemisorption via π-complex on a coordinatively unsaturated vanadium (Lewis centre). Heteroaromatics should be analogously chemisorbed, taking free electron pairs into account (e.g. picolines or methylpyrazines) that probably lead to additional steric influences. The first H-abstraction from the methyl group is carried out in a following step, proceeding on an adjacent vanadyl site. A methylene-like species is formed (e.g. [13,14]) similar to the generation of allyl species during reaction of olefins. An aldehyde surface species is the first partial oxidation product, i.e. benzaldehyde was found as intermediate during toluene ammoxidation on $(VO)_2P_2O_7$ by IR spectroscopy

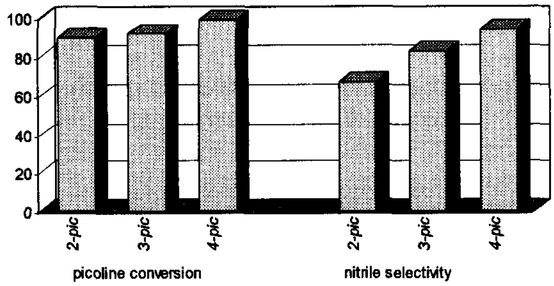

Fig. 6. Conversion of isomeric picolines (mol%) and nitrile selectivity (%) (α-$VOPO_4$ precursor; precursor weight, 28 g; $T = 703$ K; picoline: O_2:NH_3:H_2O = 1:5:3:21; $W/F = 10$ g h mol^{-1}).

[14] as well as by transient experiments (TAP technique) [15]. The next reaction step results in the formation of benzylimine [14] by reaction of the aldehyde with chemisorbed and activated ammonia species; the presence and/or generation of ammonium ions probably plays a crucial role on vanadium phosphates at least [16]. Finally, benzonitrile is formed by a subsequent oxidative dehydrogenation step. The main route of total oxidation seems to be the formation of cyclic anhydrides by overoxidation [14], probably occurring on V^V sites.

It seems that the observed differences in activity and selectivity reflect parts of these mechanistic suggestions. This should be illustrated by some examples. Different substituents could change the chemisorption state of the substrate in comparison to toluene. Thus, substrates with electron-donating groups (e.g. O–Me) could be chemisorbed stronger on the surface, i.e. intermediates could be overoxidized more easily and/or final products are desorbed slower. Furthermore, *o*-substituents (e.g. *o*-O–Me or *o*-Cl) restrict the spatial accessibility of the methyl group; the result is a decreased conversion compared to the *p*-isomers. Additionally, two larger substituents (di-O–Me or di-Cl) in several position could hinder a more or less planar substrate chemisorption, probably leading to an impeded reactivity of the methyl group.

4. Conclusions

The investigations have shown that activity and nitrile selectivity of the ammoxidation reaction of methylaromatics/heteroaromatics depend strongly on the one hand on the position of the substituent, effecting a more hindered accessibility of the methyl group in the following order ($p < m < o$). A second substituent of the same kind could strengthen the steric hindrance (e.g. 2,6-dichlorotoluene). On the other hand, the electronic properties of the substituent influence the stability of reaction intermediates, i.e. electron-withdrawing substituents stabilize intermediates whereas electron-donating substituents cause an increased total oxidation. Additionally, a different electronic stabilization of reaction intermediates due to a different position of the substituent as well as possible mesomerism effects (e.g. methoxytoluenes) must be taken into account.

Acknowledgements

The authors thank Mrs. H. French for experimental assistance. Financial support by the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (grant no. 03D0001B0) is gratefully acknowledged.

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