Effect of the position of Cl-substituents on the nitrile formation during the ammoxidation of chlorotoluenes

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Received 13 December 1994; accepted 19 April 1995

The conversion of isomeric chlorotoluenes to the corresponding benzonitriles by heterogeneous catalytic ammoxidation was studied. The reaction was 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 $VOHPO_4 \cdot 0.5H_2O$. Activity and selectivity of the ammoxidation of chlorotoluenes are shown to depend on the position of the Cl-substituents causing a changed accessibility of the methyl group and a possible different electronic stabilization of the reaction intermediates.

Keywords: ammoxidation; vanadiumphosphate catalyst; chlorotoluenes; substituted benzonitriles

1. Introduction

The ammoxidation of methyl aromatics and methyl heteroaromatics is a preferred method for the synthesis of aromatic and heteroaromatic nitriles. Usually, V/Ti, V/Mo, V/Sb or V/Sn oxide systems promoted by further transition metals, on carriers (e.g. alumina or silica) or fused, either in a fixed or fluidized catalyst bed, are used as catalysts (refs. [1–6] and references therein). Apart from vanadiumphosphate oxides applied successfully as catalyst in the ammoxidation reaction of aromatics without a more detailed description of their structural properties (e.g. vanadiumphosphates on Al_2O_3 used in the conversion of toluene to benzonitrile

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[7]) defined vanadiumphosphates, well known as catalysts in the *n*-butane oxidation to maleic anhydride (e.g. ref. [8]), are described in the literature in few examples only for the ammoxidation of 4-methylpyridine [9] as well as of 4-methylpyridine and 2-cyanopyridine [10].

Recently, we have investigated the ammoxidation of different substituted toluenes as well as the picolines to the corresponding nitriles using different oxovanadium(V)- and oxovanadium(IV)-monophosphates as well as oxovanadium (IV)-diphosphates as catalyst precursor compounds [11–13]. The goal of these studies was the exposure of precursor/catalyst transformations processing in solid-state reactions under reaction conditions. These transformation reactions resulted mainly in the formation of ammonium-containing oxovanadium(IV)-diphosphates as well as vanadium(III)-diphosphates as observed by XRD. In situ techniques just reveal the interaction of ammonia and vanadiumphosphates proving to be a redox reaction accompanied by the break of V–O–P and/or P–O–P links and the formation of new active sites [14].

The ammoxidation of substituted toluenes and methylheterocycles to the corresponding nitriles is an industrially important reaction. The synthesized nitriles are valuable intermediates in the organic synthesis of different dyestuffs, pesticides and pharmaceuticals (e.g. ref. [1]). The reactivity of the aromatic or heteroaromatic substrate and the selectivity of the formation of the corresponding nitrile are determined by different causes. Thus, the position, size and additionally electronic effects of one or more substituents should influence significantly the chemisorption state of the substrate molecule on the electrophilic catalyst surface, the subsequently processing reaction of the chemisorbed substrate and activated ammonia surface species, the electronic and/or mesomeric stabilization of the intermediate generated in this way and last, but not least, the desorption of the formed nitrile from the catalyst surface. Apart from electronic and steric properties of different substituents of monosubstituted methylaromatics and -heteroaromatics, it would be interesting to investigate the influence of the position of a second substituent on the process, particularly if the substituents located directly neighbouring the methyl group.

This communication reports the ammoxidation reaction of the isomeric dichlorotoluenes (DCT) in comparison to the reaction of the isomeric monochlorotoluenes (MCT) studied more in detail on $(NH_4)_2[(VO)_3(P_2O_7)_2]$ as vanadiumphosphate catalyst to the corresponding dichlorobenzonitriles (DCBN) and monochlorobenzonitriles (MCBN). Moreover, the investigation should clarify the influence of the position of the substituents on the reactivity of the methyl group and on the selectivity of the nitrile formation.

2. Experimental

$VOHPO_4 \cdot 0.5H_2O$ was used as catalyst precursor and synthesized by addition of V_2O_5 (72.8 g) to a hot mixture (ca. 353 K) of phosphoric acid (59.7 ml), oxalic acid (75.6 g) and water (160 ml) under vigorous stirring. The resulting solution was subsequently heated for 18 h, then cooled, filtered and the residue was dried at 423 K overnight. The light-blue crystals were washed with diluted hydrochloric acid (1 : 3) and acetone one after the other and dried at 298 K. Normally, $VOHPO_4 \cdot 0.5H_2O$ is used as catalyst precursor for the generation of $(VO)_2P_2O_7$ applied as catalyst for the *n*-butane oxidation to maleic anhydride [15]. Its solid-state transformation to $(VO)_2P_2O_7$ for use as oxidation catalyst is carried out in a *n*-butane/air atmosphere but also a simple temperature-programmed heating under inert gas yields $(VO)_2P_2O_7$. This transformation process starts noticeable at ca. 623 K [16]. Otherwise, the precursor transformation leads mainly to $(NH_4)_2[(VO)_3(P_2O_7)_2]$ passing the ammoxidation feed over the catalyst precursor already at ca. 613 K [17]. This was indicated by XRD performed by the Guinier technique using Cu K_α radiation.

Thus, the in situ prepared $(NH_4)_2[(VO)_3(P_2O_7)_2]$ was used as catalyst ($VOHPO_4 \cdot 0.5H_2O$ as precursor was heated to 678 K [heating rate $\beta = 10$ K/min] under ammoxidation feed and held for 4 h) for the ammoxidation investigations. No catalyst deactivation has been observed, as shown during the reaction with *p*-chlorotoluene (*p*CT) as organic feed every time before changing the ammoxidation substrate.

All catalytic runs were carried out in a bench-scale stainless-steel reactor under atmospheric pressure. 2,3-DCT, 2,4-DCT, 2,5-DCT, 2,6-DCT and 3,4-DCT (all from Aldrich or Fluka) as well as *p*CT, *m*-chlorotoluene (*m*CT) and *o*-chlorotoluene (*o*CT) (all from Merck) were used as aromatic feed. The chlorotoluenes were fed by a micropump, vaporized and mixed in a preheated vessel with ammonia and air after having passed flow controllers. Water was introduced by a tubing pump, vaporized and passed to the mixture vessel. The preheated gas flow was then fed directly into the reactor. The following reaction conditions were applied: molar ratio of DCT or MCT : $O_2 : NH_3 : H_2O = 1 : 5 : 8 : 25$, reaction temperatures 688–728 K, catalyst weight (W) 5 g, and space velocity (W/F) 10 g_{cat} h/mol. The reactor outlet stream was analyzed by gas chromatography at 423 K with flame ionization detector and argon as carrier gas, using benzonitrile as standard and a stainless-steel column packed with Chromosorb W/AW/DMCS (0.16–0.20 mm) (Serva) coated with 10% Carbowax 20M (Serva).

3. Results and discussion

The application of the isomeric MCT as feed reflects a clear dependence of the position of the Cl-substituent on the conversion and yield data as shown in figs. 1 and 2. The reactivity of the substrates shows a $p \gg o \approx m$ ranking reflecting a hindered reaction of such toluenes having the second substituent in *o*- and *m*-position in comparison to the *p*-position. The yield of the nitriles appears in the same order

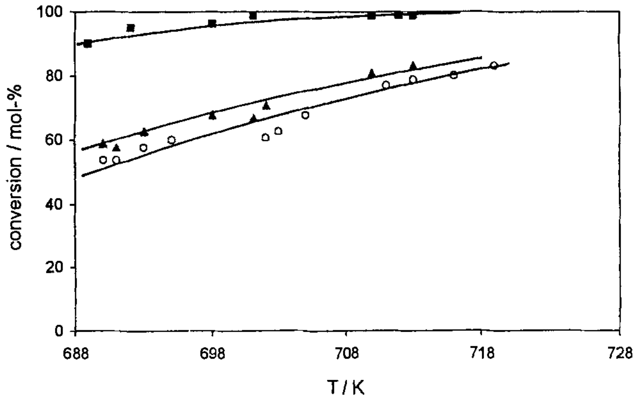

Fig. 1. Conversion of isomeric monochlorotoluenes in dependence on the reaction temperature on $(NH_4)_2[(VO)_3(P_2O_7)_2]$: (■) *p*-chlorotoluene, (○) *m*-chlorotoluene, (▲) *o*-chlorotoluene.

$p >> o \approx m$. This row mirrors on the one hand the different accessibility and reactivity of the methyl group in dependence on the position of the Cl-substituent and, on the other hand, the possibility of a different electronic stabilization of intermediates during the nitrile formation process. The MCBN yields decrease with increasing reaction temperature after passing a maximum and the yield of the carbon oxides as undesired total oxidation products increases. Similar data were obtained taking these results into account using DCT as feed.

Fig. 3 demonstrates the conversion of the DCT under the same reaction conditions. The conversion data for the DCT substrates are significantly graded in the following order: 3,4-DCT ≈ 2,4-DCT > 2,3-DCT > 2,5-DCT ≈ 2,6-DCT. The low conversion rate of such substrates having both substituents nearby the methyl group (2,6-DCT and 2,5-DCT) reflects again the hindered accessibility and possibility of the methyl group either to react with possibly preformed V=NH imido spe-

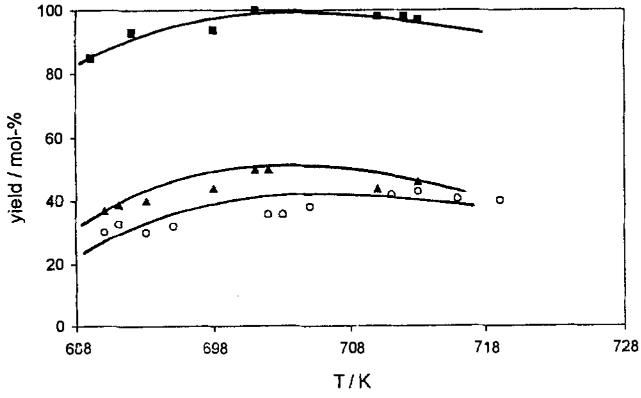

Fig. 2. Yield of isomeric monochlorobenzonitriles in dependence on the reaction temperature: (■) *p*-chlorobenzonitrile, (○) *m*-chlorobenzonitrile, (▲) *o*-chlorobenzonitrile.

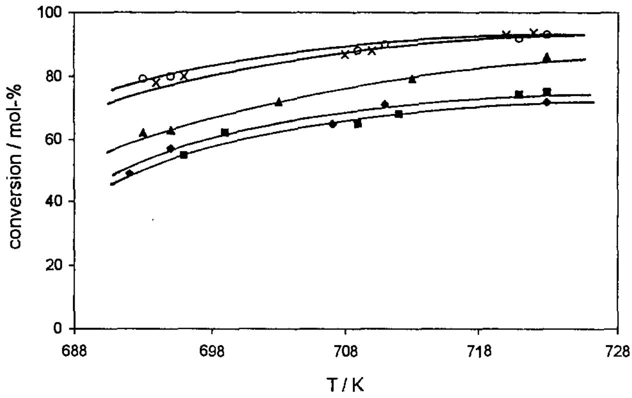

Fig. 3. Conversion of isomeric dichlorotoluenes in dependence on the reaction temperature during the ammoxidation on $(NH_4)_2[(VO)_3(P_2O_7)_2]$: (○) 3,4-dichlorotoluene, (×) 2,4-dichlorotoluene, (▲) 2,3-dichlorotoluene, (■) 2,5-dichlorotoluene, (◆) 2,6-dichlorotoluene.

cies [18] or ammonia adsorbed on coordinatively unsaturated P-ions as proposed in ref. [9], especially at lower reaction temperatures. The same order is obtained concerning the yield of the formed nitriles as depicted in fig. 4. Apart from carbon oxides, only minor amounts of monochlorobenzonitriles and traces of chlorobenzenes are found, especially at higher reaction temperatures.

The investigations demonstrate a strong dependence of the catalytic results on the position of the Cl-substituents and a possible superposition of steric and electronic stabilization effects of the intermediates. A separation of steric and electronic effects can usually be achieved by the application of a Hammett equation. The fitting of kinetic or equilibrium data to free energy relationships is practicable only for meta- and para-substituents, whereas aromatics containing ortho-substituents

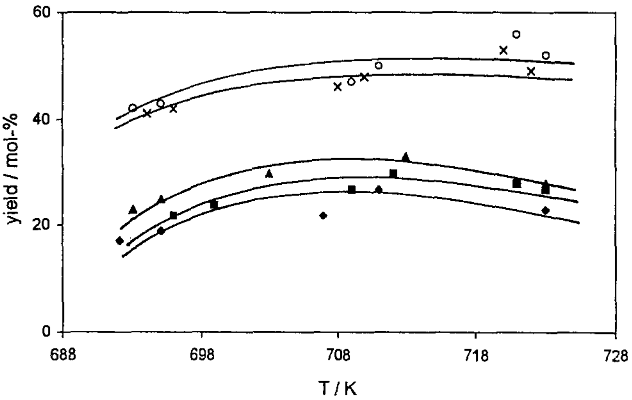

Fig. 4. Yield of isomeric dichlorobenzonitriles in dependence on the reaction temperature: (○) 3,4-dichlorobenzonitrile, (×) 2,4-dichlorobenzonitrile, (▲) 2,3-dichlorobenzonitrile, (■) 2,5-dichlorobenzonitrile, (◆) 2,6-dichlorobenzonitrile.

cannot be considered due to their steric influences. The most organic feed compounds used in our investigation have one of the Cl-substituents in ortho-position and therefore the application of a Hammett plot is not reasonable. Nevertheless, the observed conversion data show clearly that substrates with two Cl-substituents located nearby the methyl group and additionally on both sides of it (2,5- and 2,6-DCT) reveal a lower conversion compared to such feeds having only one Cl-substituent or two substituents located more remotely and only on one side of the methyl group (2,4- and 3,4-DCT), respectively. Thus, the steric effect of the position of the substituents during the catalytic reaction come to the fore. Furthermore, the different position of the substituents influences also the chemisorption step of the substrate because the chemisorption of the π-electron system of the aromatic substrate on the electrophilic catalyst surface should not proceed more or less planar as conceivable using toluene as feed. This also results in the first reaction step of the H-abstraction from the methyl group [19] and in further steps including surface bound species as =NH or NH_4-cations. The decreased DCBN yields could be also due to a more difficult electronic stabilization of the aromatic intermediates compared to the intermediates formed during the MCBN generation.

In conclusion, we have shown that the activity and selectivity of the ammoxidation of isomeric monochloro- and dichlorotoluenes depend on the position of the Cl-substituents effecting a possible reduced accessibility of the methyl group during the first reaction steps and a different electronic stabilization of the reaction intermediates.

Acknowledgement

We thank Mrs. H. Rusche and Mrs. H. French for experimental assistance. Financial support by the Bundesminister für Forschung und Technologie (BMFT 423-4003-03D0001B0) and the WIP programme (project #018506) is gratefully acknowledged.

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