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Ammoxidation of 2,6-dichloro toluene—From first trials to pilot plant studies

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ABSTRACT

The scaling-up of the gas phase catalytic ammoxidation of 2,6-dichloro toluene (DCT) to 2,6-dichloro benzonitrile (DCBN) over a promoted vanadium phosphate (VPO) catalyst from first lab-scale experiments to pilot plant runs is reported. First experiments in a row of conversions of isomeric dichloro toluenes using simple, non-promoted VPO catalysts only show poor yield and selectivity. In particular, DCT ammoxidation is hindered due to bulky chlorine substituents probably preventing a sufficient interaction of the methyl group and lattice oxygen and/or N-containing surface species. Improved synthesis of VPO catalyst with the addition of promoters and γ-alumina or titania leads to significant increase in DCT conversion and DCBN yield. A Cr containing vanadyl pyrophosphate catalyst admixed with titania (anatase) showed conversion up to 97% with DCBN yields of ca. 80%. The same catalyst was also used for pilot plant runs, usually in the form of 5 mm × 3.5 mm shaped tablets that were prepared from a larger batch of solid synthesis. The scaling-up of the process using 100 ml of catalyst was investigated both by catalytic experiments and reactor simulations. The results showed that the temperature control will be crucial in scaling-up. Validation of simulation results with that of experimental results was also checked and a good agreement between measured and simulated results is observed.

1. Introduction

The transfer of a chemical reaction from lab-scale to commercial dimension is pooled in scale-up studies (e.g. [1]). Such studies are necessary to ensure the establishment of a reliable chemical process for industrial application. This includes the move from the lab-scale test set-up to commercial size equipment and the development of a solid catalyst in a heterogeneously catalyzed reaction. In such a move, a large number of tasks and questions have to be taken into account for example, optimization of reaction conditions, effect of heat and mass transfer, condensation and separation of products, catalyst synthesis and shaping, catalyst deactivation vs. long-term stability and attrition behavior (e.g. [1,2]). A pilot plant with a scale-up factor of ca. 25, if correctly designed, allows detecting the critical aspects of the process and, at the same time, points out solutions that can appreciably decrease various risks in larger size equipment. These studies ensure that the reactor model developed from lab studies can be related and extrapolated to the design and performance of a commercial reactor [3,4].

Ammoxidation is a partial oxidation reaction with selective insertion of nitrogen into a methyl group (also aldehyde or alcoholic groups are able to react) that is located in α-position to double bond of olefinic, aromatic or hetero aromatic hydrocarbons to produce corresponding nitriles in a continuous process (e.g. [5,6]). The heterogeneously catalyzed ammoxidation of various hydrocarbons to synthesize wide range of industrial important nitriles has been the subject of great interest in recent times because the nitriles are very useful basic chemicals (e.g. acrylonitrile by the SOHIO process) and organic intermediates to prepare a good number of value added fine chemicals [5,6]. The reaction runs via H-abstraction from such a methyl group leading to an allylic intermediate that reacts with bulk oxygen to an oxygen-containing intermediate through Mars–van Krevelen mechanism (e.g. [7,8]). In general the industrial reaction is carried out in the gas phase using fixed bed or fluidized bed reactors. Mainly transition metals such as vanadium, antimony, molybdenum, etc. either in supported form or as bulk materials are used as catalysts. Furthermore, ammoxidation is a very "green" reaction because oxygen or air is used as oxidant and in general, water is the only by-product.

The present study was focused on the catalytic ammoxidation of 2,6-dichloro toluene (DCT) to 2,6-dichloro benzonitrile (DCBN) over vanadium phosphate (VPO) catalysts that are well known from large scale conversion of n-butane to maleic anhydride (e.g. [9]). Ammoxidation of DCT to DCBN in a single step is an industrially important reaction as the target product provides an easy access to prepare many effective herbicides and fungicides [10,11]. DCBN is also an interesting intermediate for producing various special kinds of engineering plastics. The results presented

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Table 1
Summary of used vanadium phosphate catalysts.

Catalyst	Precursor	Oxide	Promoter	Shape
VPPaq	VHPaq	–	–	1–1.25 mm sieve fraction
VPPorg	VHPorg	–	–	1–1.25 mm sieve fraction
VPPorg/S	VHPorg	γ-Al_2O_3, TiO_2	–	1–1.25 mm sieve fraction
MVPPorg/S	VHPorg	TiO_2	Mo, Co, Fe, Cr	1–1.25 mm sieve fraction
VPPpp	VHPorg	TiO_2	Cr	5 mm × 3.5 mm tablets (graphite)

in this communication include first lab tests directed to the conversion of isomeric dichloro toluenes over VPO catalysts obtained by an aqueous synthesis route [12]. In addition, some catalyst improvements by means of changed synthesis route using organic reductants, admixture of oxides such as γ-alumina or titania and addition of promoters are reported [13]. Furthermore, details on the assembling of a pilot plant unit and processing of kinetic studies and optimized reaction runs are also given [14,15].

2. Catalysts

Recently, it was shown that VPO derived catalysts are suitable to catalyze ammoxidations of methyl aromatics and hetero aromatics [5,16]. Additionally, these solids again revealed some potential effects in improving their performance in ammoxidations due to some synthesis variations and addition of various promoters and co-components [13].

The layered vanadyl hydrogenphosphate hemihydrate $VOHPO_4 \cdot 0.5\ H_2O$ (VHP) served as precursor for all catalysts; which after calcination (in general 723 K, 3 h, 0.5% O_2 in N_2) gave mainly $(VO)_2P_2O_7$ (VPP) phase. For example, the VHP precursor compound can be obtained according to an aqueous preparation route (aq) using V_2O_5, H_3PO_4 and a reducing agent (e.g. oxalic acid) or an organic synthesis route (org) using benzyl alcohol and 2-butanol as reduction means. Various P:V ratios in the final VPP solid in a range of 0.5–2 were adjusted. Table 1 gives a short summary on the used catalysts. However, VHP compound can also be used directly as catalyst precursor, which is then in situ transformed during ammoxidation reaction into an ammonium ion-containing VPO compound ($(NH_4)_2[(VO)_3(P_2O_7)_2]$ – AVP) that is gradually transformed into VPP, depending on the reaction conditions and time; details on such studies can be found elsewhere [12,13]. The first trials for ammoxidation of DCT described below were conducted using VPPaq and VHPaq that was transformed during reaction first to AVP and then slowly to VPP as well [12].

The preparation of "supported" VPO catalyst (VPPorg/S) was carried out by solid–solid wetting method using the VHPorg precursor (25 wt.%) and γ-alumina or titania (anatase). In this solid–solid wetting procedure, the desired amount of VHPorg and the support powder were mixed thoroughly in a porcelain mortar for about 20 min until the color of the mixture is perfectly uniform. Calcination as described above gives the VPPorg/S solids [13].

The preparation of promoted and "supported" catalyst (MVPPorg/S) was carried out via (i) the addition of suitable promoter to VHPorg precursor and (ii) by solid–solid wetting of the promoted precursor with the support compound [13]. The beneficial behavior of such promoters is recently discovered in n-butane oxidation research [17–20]. The required amount of promoter source (M:V molar ratio = 0.05; Co and Fe as acetates, Cr as nitrate and Mo as ammoniumheptamolybdate) was dissolved in aqueous ethanol (exclusively water was used in case of Mo) and warmed up to ca. 343 K; the calculated amount of VHPorg precursor in powder form was added. Then, the slurry was evaporated to dryness and the resulting solid was oven dried at 393 K for 16 h. Subsequently, the desired amount of carrier (TiO_2 (anatase) or γ-Al_2O_3) was taken for manufacture of MVPPorg/S samples in a solid–solid wetting procedure as described above.

Finally, the catalysts were shaped to larger tablets by hydraulic press and calcined at 723 K for 3 h under weak oxidizing atmosphere (0.5% O_2 in N_2). The resulting promoted and supported VPO final catalyst consists of 25 wt.% VPP(M) with P:V = 0.95 and M:V molar ratio = 0.05 (M = Co, Cr, Fe, and Mo). All catalysts used in lab-scale tube reactor were synthesized in 100 g scale, crushed again after pressing and sieved to the required size fraction (1–1.25 mm).

A MVPPorg/S catalyst (VHPorg precursor (25 wt.%), M = Cr (Cr:V = 0.05), P:V = 0.95, S = titania) was selected for pilot plant tests (VPPpp) and synthesized in an amount of ca. 2.5 kg. After catalyst synthesis, shaping of catalyst powder into the form of tablets for pilot plant runs was conducted. Various trials with graphite and Mg-stearate as auxiliaries were carried out. Catalytic results proved that graphite is the best suited. The catalyst powder was then industrially shaped to 5 mm × 3.5 mm tablets using 5% graphite as pressing auxiliary. The tablets were finally calcined under similar conditions as above (i.e. 723 K, 3 h, 0.5% O_2 in N_2) [10].

3. Catalytic tests and scale-up of DCBN synthesis

3.1. First trials – ammoxidation of isomeric dichloro toluenes at lab-scale

In an early stage of the investigations various isomeric dichloro toluenes were converted to their corresponding nitriles mainly to discover the effect of the position of the bulky chlorine substituents on the activity and selectivity, details can be found elsewhere [12]. VPPaq and VHPaq (transformed into AVP phase on-stream) were used as catalysts and precursor, respectively. Fig. 1 shows a nitrile yield vs. dichloro toluenes conversion plot. It is clear from the figure that the conversions and nitrile yields achieved are higher in case of reactants, where the substituents are located more remote from the reaction center, i.e. from the methyl group. For instance, in case of 3,4-dichloro benzonitrile, a yield of ca. 55% was reached at conversions close to 90–95%. On the other hand, DCT, having substituents close to the reaction centre, the conversion obtained was considerably low (between 50% and

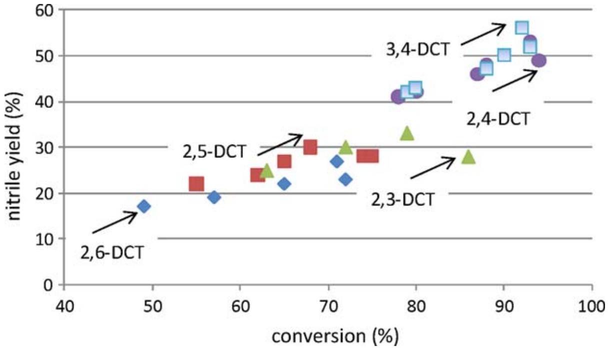

Fig. 1. Nitrile yield vs. isomeric dichloro toluenes conversion: $(NH_4)_2(VO)_3(P_2O_7)_2$ and $(VO)_2P_2O_7$ used as catalysts (both aqueous route), dichloro toluene: O_2:NH_3:H_2O = 1:5:8:25, reaction temperatures of 688–728 K, 2,6-, 2,5-, 2,4-, 2,3-, 3,4-DCT.

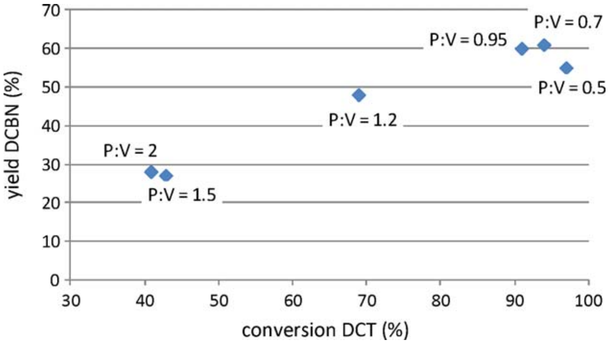

Fig. 2. DCBN yield vs. DCT conversion: over vanadyl pyrophosphate catalysts (VPPorg) with varying P:V ratio: DCT:H_2O:NH_3:air = 1:15:6:50, T = 713 K.

70%) compared to others and at the same time, DCBN yield was also rather poor (around 20%). Mainly destruction products such as carbon oxides were detected as reaction products in this case.

3.2. Lab-scale progresses – catalyst improvements and optimization of reaction conditions

In a next step, catalyst performance had to be improved and reaction conditions need to be optimized for obtaining enhanced conversion of DCT with good selectivity towards DCBN. To achieve such objective, the BET surface area rich VPPorg catalysts were prepared and used for the target reaction. In the first step, bulk VPPorg samples showing a wide range of P:V ratios from 0.5 to 2 were checked. Fig. 2 illustrates DCBN yield vs. DCT conversion depending on the P:V ratio. It can be seen from the figure that the solids with a P:V ratio of 0.7 and 0.95, respectively, reveal the highest conversion and product yield around 90–95% and 60%, respectively. This corresponds to ca. 65% selectivity of DCBN. For further development, catalyst with P:V ratio of 0.95 was selected; in particular due to its larger P content compared to the P:V = 0.7 sample. Interestingly, the yield obtained from VPPorg solids is almost double compared to the one obtained with VPPaq or AVP catalyst. The reason for such a dramatic increase in performance is mainly due to the increased BET surface area of the VPPorg catalyst and its morphology (e.g. [21]). Additionally, the preparation of present VPO catalysts from V_2O_5, organic alcohols and o-H_3PO_4 leads to initial formation of VHP precursor phase with organic alcohols trapped between the layers of phosphate structures, which provoke some kind of disorderness in the catalyst structure. During the successive calcination, VHP transforms into vanadyl-pyrophosphate phase with the corresponding disorder in the plane of layer stacking [18,21–23]. This disorder in the catalysts in turn influence (i) the catalytic activity, (ii) redox properties and (iii) the reducibility of the catalysts. Due to all these effects, the catalysts prepared through organic route exhibited better performance compared to the ones prepared by an aqueous route.

A further improvement was reached by mixing VPO and oxidic "supports" in a solid–solid wetting procedure. Titania (anatase) and γ-alumina were used for the preparation of those catalysts containing 25 wt.% VPO proportion, in general. The results showed that a conversion of DCT around 90% and a DCBN yield up to ca. 70% could be obtained using supported catalysts. This result clearly indicates that a further increase in DCBN selectivity of ca. 20% is successfully achieved compared to the performance of bulk VPOs. The improvement of the catalytic performance seems to be caused by acidic properties of the admixed oxides; acidic properties (Lewis and Brønsted sites) of aluminas are well known but also the applied titania showed acidic properties due to remaining sulfate stemming from the use of titanyl sulfate as a precursor for the titania synthesis. Such additional acidity (acidic sites) can supply additional sorption sites for ammonia but also for Lewis bound aromatic reactant molecules helping to speed up the reaction.

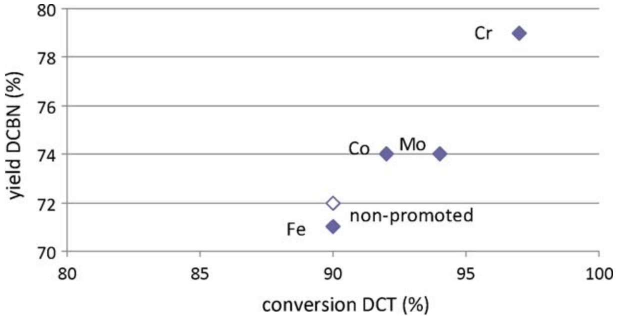

Fig. 3. DCBN yield vs. DCT conversion: over transition metal promoter containing vanadyl pyrophosphate catalysts (MVPPorg/TiO_2) with M = Fe, Co, Mo, and Cr (M:V = 0.05); DCT:H_2O:NH_3:air = 1:15:4:21, T = 673 K (open symbol marks performance on non-promoted supported catalyst (VPPorg/TiO_2) for comparison).

In a last stage of the catalyst development, additional transition metal promoters such as Cr, Co, Fe or Mo were added during catalyst synthesis in a M:V ratio of 0.05. The admixture of such promoters revealed a further beneficial effect both on catalyst activity and selectivity. As a result, the yield of DCBN increased considerably, the results are plotted in Fig. 3. The catalytic tests were carried out under comparable conditions and the use of Cr as promoter revealed the highest conversion of DCT of 97% and a yield of DCBN of 79%, which is in accordance with a DCBN selectivity of ca. 81%. These results revealed that incorporation of promoters play a key role in enhancing the performance. Most of the promoted catalysts of this study displayed good potentiality giving high yields of DCBN (70–80%) at high conversion levels (90–97%) compared to their parent bulk VPO solids. After successful achievement of DCBN yields close to 80%, the further investigations were focussed on scale-up studies, which are described below in more detail.

3.3. Scale-up – pilot plant set up and catalytic test runs

The pilot plant experiments were carried out in a flow apparatus equipped with a stainless steel fixed bed reactor (i.d.: 0.016 m, length: 1 m; catalyst amount up to 100 ml), feeding section, cooling and product separation units (for separating liquid and solid products from gaseous mixture) including online-GC. Gases and liquids were fed using mass flow controllers and HPLC pumps, respectively. The gaseous stream was preheated and then introduced to the reactor along with vaporized liquid feed (DCT and water). The reactor outlet was heated to 623–673 K to avoid the condensation of product components (DCBN, melting point: 416–419 K), and also to prevent deposition of by-products (e.g. $(NH_4)_2CO_3$ or NH_4Cl formed by DCT total oxidation, (NH_4Cl sublimation point is ca. 613 K!)) that can easily block the reactor outlet. In general, catalyst was used in pure form or diluted with glass beads (1:5) in order to study heat transfer effects and hot-spot behavior. The volumetric flow rate was set to 34–68 m^3/h (STP) resulting in a residence time of 700–4600 kg_{cat} s/m^3 (STP) depending upon catalyst amount used. The reaction conditions also determined the fluid dynamics in the reactor depending on volume flow rate and composition of the feed. Based on that the dimensionless numbers can be derived (e.g. Re, Nu).

The product stream from the catalytic reactor consisted of unconverted feed components (i.e. DCT, oxygen, and ammonia), diluting agent (e.g. neon that was used sometimes to determine undesired N_2 formation caused by NH_3 oxidation) and the reaction products such as DCBN, $(NH_4)_2CO_3$, NH_4Cl, CO, CO_2, water and minor amounts of other trace products. Analytically detected concentration (GC) of those components (including NO_x) was lower than 1 mass% and can be neglected in further discussion. C-balance was always above 95% and close to 100% in most runs. The gaseous product mixture from the reactor outlet is subsequently cooled both externally and internally by quenching from reaction temperature 623–673 K to 303–313 K depending upon the product composition using an internal water spray tower (mainly for dissolving salts and preventing blockages). The gas outlet from the quenching column was connected to online-GC equipped with two capillary columns such as PoraPlot Q & molecular sieve and TCD and FID detectors.

Various test runs were conducted according to a pre-designed experimental plan to study the influence of the partial pressure of the reactants (DCT, NH_3, O_2 and water). The tests revealed that with increasing reaction temperature, the conversion of DCT and yield of DCBN continuously increased and, however, total oxidation product proportion too. Interestingly, a significant raise in nitrogen formation occurred, which is undoubtedly caused by accelerated ammonia oxidation. Furthermore, the results showed that with increasing proportion of DCT in the feed, the DCBN concentration in the product rises. However, in parallel to this observation a slight increase in nitrogen formation due to ammonia combustion and an increased total oxidation is also observed [14]. The increase in the amount of ammonia in the feed leads to decreasing conversion of DCT due to competitive adsorption between the two reactant molecules for the same sites. Therefore, a dropping amount of DCT adsorption sites is possible especially at higher partial pressures of NH_3. This situation in turn causes a decline in DCBN formation. On the other hand, nitrogen formation is significantly increased due to progressive increase in ammonia combustion. Furthermore, oxygen concentration was also varied with the aim to study its influence on the rate of formation of CO, CO_2, DCBN and nitrogen. The oxygen partial pressure was related to the inert gas concentration in the feed. The concentration of the oxygen portion was set between 6.8 and 13.5 mol%. Two results of these kinetic experiments are given in Fig. 4. The composition of the product with increasing oxygen concentration significantly changes with changing experimental conditions. DCT conversion increases whereas oxygen conversion decreases; DCBN yield is more or less constant. Under the chosen conditions increase in oxygen concentration leads to both increased total oxidation and ammonia combustion only.

The dependence of the reaction temperature on the product selectivity and reaction yield is one of the most important issues in every design work. In the case of exothermal oxidation of aromatics, the temperature influence is much more crucial for process safety. Keeping this aspect in mind, the influence of the temperature on the reactant conversion and product selectivity is investigated and presented in Fig. 5. Moreover, the degree of ammonia combustion to nitrogen is plotted. It is obvious that higher reaction temperature improves the conversion of oxygen and thereby increased selectivity of undesired total oxidation products. In addition, the temperature increase also leads to raised ammonia oxidation. As expected, the higher selectivity of DCBN is obtained in the lower temperature range between 633 and 643 K. This observation is in a good agreement with long-term pilot plant runs, where a process optimum was found under comparable reaction conditions and temperature (643 K).

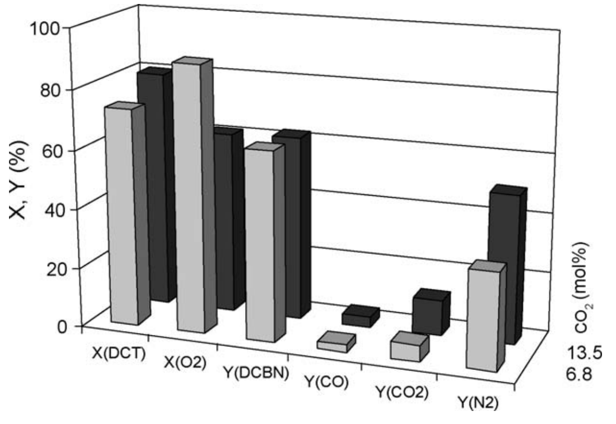

Fig. 4. Dependence of conversion of DCT and O_2 and yield of DCBN, CO, CO_2 and N_2 on the oxygen concentration (CO_2 (mol%)) in the feed; $T = 630$ K; feed mol composition DCT: 2.4%; ammonia: 10%; water: 20%; inert: $(67.6 - x)$%; oxygen: x%.

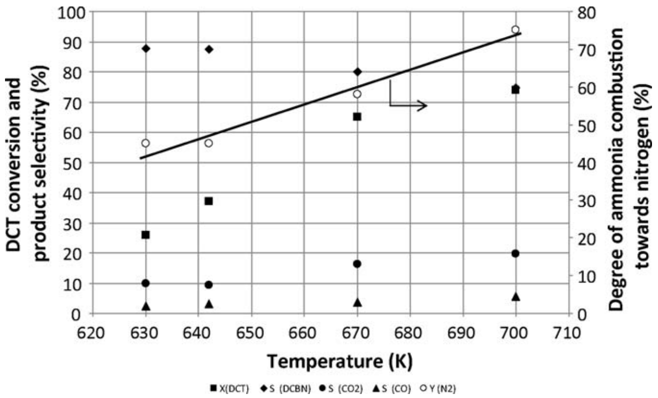

Fig. 5. Influence of reaction temperature on DCT conversion and product selectivity; feed mol composition DCT: 2.4%; ammonia: 10%; water: 20%; inert (Ne): 54.6%; oxygen: 13% (full line: degree of ammonia combustion towards nitrogen).

The results from kinetic observations were consequently used in the scale-up strategy. The best results obtained in the pilot plant showed a DCT conversion close to 100% and a DCBN selectivity of ca. 83–84%. Total oxidation leads to the formation of CO and CO_2 and the sum selectivity of these two unwanted products amounts to ca. 15%. The oxygen conversion reached ca. 93% [14]. Table 2 summarizes some reaction characteristics.

4. Comparison of catalytic run results and process simulation

After successful completion of lab-scale tests, an extended effort has been further focussed on the development of kinetics and process description of the presented ammoxidation system. The best pilot plant runs were fitted by process model, based on overall kinetics description. The kinetic study performed in lab-scale showed strong non-isothermicity. The non-ideal behaviour of the reaction system was confirmed in the pilot plant runs. Therefore, it was necessary for evaluation of kinetic data to apply a non-isothermal reactor model. For this purpose, a steady-state pseudo-homogeneous fixed bed tubular reactor model with negligible axial and radial diffusion was used. The details of kinetics model can be found elsewhere [14,24,25].

The results of process simulation and experimental results obtained at 653 K and at a residence time of 4600 $kg_{cat}\,s/m^3$ (STP) are compared in Fig. 6. A very good agreement between measured and simulated results could be observed. It is also evident that the yield of main product DCBN around 80% is achieved at almost total conversion of both oxygen and DCT. It is worth mentioning that

Table 2
Reaction characteristics.

Parameter	Dimension	Value
Reaction heat of ammoxidation of DCT	kJ/mol	−517
Adiabatic temperature increase[a]	K	85–350
Overall heat transfer coefficient	$J/(s\,K\,m^2)$	70–120

[a] Due to reaction conditions at chosen catalyst dilution.

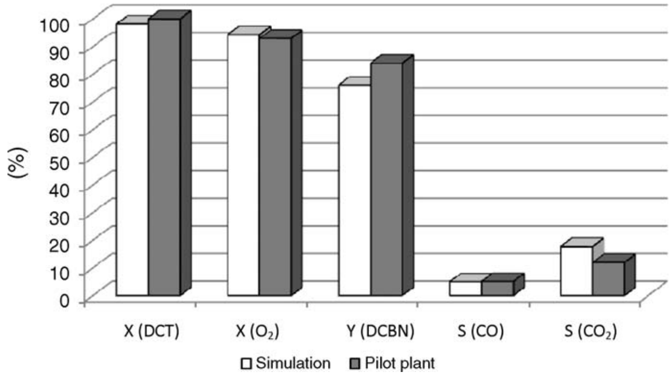

Fig. 6. Comparison of pilot plant experiment and process simulation; Optimized feed composition DCT: 2.85%; ammonia: 12%; water: 42.1%; inert: 29.85%; oxygen: 13.2% (catalyst: VPPpp).

these results have been reproduced in another long term pilot plant run, which gave quite comparable results. Finally, the catalyst developed and the process set up was successfully applied in the industrial scale.

5. Conclusions

Various VPO based catalyst compositions were explored and optimum composition and suitable promoters could be identified. The VPOs prepared through organic route are found to exhibit superior performance compared to the ones prepared by aqueous route. The efforts to enhance the conversion of DCT and the yield of DCBN were successful. P:V ratio is a crucial factor on improving the performance. Nature of promoter has a clear influence on the catalytic properties of VPO solids. Among different promoters applied, Cr is observed to exhibit better performance giving the yield of DCBN close to 80%. The objective of pilot plant set up, product separation, and the scale-up studies from first trials to pilot plant runs were also quite successful. Oxygen concentration in the feed and temperature of reaction showed significant influence on the product distribution. Finally, a good agreement between simulated and experimental results is obtained.

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