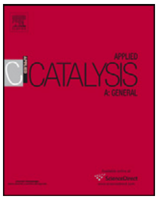
Applied Catalysis A: General 398 (2011) 37–43

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Reaction scheme of o-xylene oxidation on vanadia catalyst

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ARTICLE INFO

Article history:
Received 24 January 2011
Received in revised form 3 March 2011
Accepted 3 March 2011
Available online 10 March 2011

In honor of Helmut Knözingers 75th birthday.

Keywords:
Phthalic anhydride
Vanadia
Partial oxidation
Mechanism
Kinetics

ABSTRACT

The oxidation of o-xylene (OX) to phthalic anhydride (PA) is one of the important industrial processes based on selective oxidation reactions. However, the fundamental understanding of the by-product formation is still an open task. By using a sample port pilot plant, a detailed investigation was conducted for the first time of the by-product formation at different operation conditions. Several hitherto unknown intermediates could unambiguously be identified. The combination of process conditions and by-product formation enables the discussion of a new improved reaction scheme for the catalytic oxidation of o-xylene.

The reaction path from OX to PA is commonly described by a rake mechanism consisting of a number of parallel and serial reactions. Tolualdehyde and phthalide are seen as the main intermediates. The most important by-products are maleic anhydride (MA), CO and CO_2. The reaction paths towards these by-products are widely unknown.

Several gas phase components, such as toluquinone and 2,3-dimethyl-p-benzoquinone not reported yet in the current literature, were observed for the first time in this study. Most of these previously unknown components are reaction intermediates, which later do not form the desired reaction product, PA.

1. Introduction

With an annual production of 4.5 million tons in 2005, phthalic anhydride is a significant commodity in chemical industry with applications in the manufacture of phthalate plasticizers, phthalocyanine dyes, polyester resins and numerous fine chemicals [1]. Historically, the feedstock for phthalic anhydride production was naphthalene, which has gradually been replaced by o-xylene throughout the past 50 years.

In the industrial process, the oxidation of o-xylene is conducted in fixed bed tubular reactors with up to 30,000 tubes. Reaction temperatures range from 300 to 450 °C with o-xylene feed concentrations between 0.5 vol% and 1.8 vol% in air. The reaction is conducted at nearly atmospheric pressure and the cooling temperature, typically adjusted by a molten saltbath, ranges from 340 °C to 390 °C [2,3].

Catalysts most widely applied for the reaction of both naphthalene and o-xylene consist of vanadium and titanium oxides. Historically, vanadium oxide catalysts were applied as bulk catalysts [4,5] and loaded to industrial reactors as extrudates. This resulted in poor selectivities and limited catalyst lifetimes. In the last decades the development went more and more towards the application of egg-shell catalysts with an inactive ceramic carrier, which the active mass is fixed to [6]. In addition, the industrial catalytic systems were gradually modified by adjusting the catalytic behavior dependent on the axial position in the reactor tube. Nowadays, the industrial catalyst consists of up to four catalyst layers with optimized activities and selectivities. Modern catalytic systems for this reaction, such as the Süd-Chemie PHTHALIMAX^{TM} benchmark, allow molar selectivities of up to 83%. Considering the quantities produced on an industrial scale, even an increase of 1% in selectivity has a substantial economic effect.

In the course of this reaction 12 bonds need to be broken and 12 new bonds are formed [7]. Consequently, the reaction does not comprise only a single step, but passes through a number of intermediates. In addition, by-products such as maleic anhydride (MA), CO and CO_2 account for the loss in selectivity. However, in spite of the industrial importance of this process and numerous studies [8–16] in this respect, the reaction scheme still lacks a number of linking elements. Especially the formation of non-selective oxidation products is yet not well understood. In this communication any oxidation product, which cannot be converted to PA in a subsequent reaction path is considered non-selective.

The by-product formation is not only crucial in terms of selectivity, i.e. PA yield, but also in terms of plant product quality. Although the largest fraction of annual PA production is utilized for

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doi:10.1016/j.apcata.2011.03.006

Nomenclature

AAc	acetic acid ($C_2H_4O_2$)
BA	benzaldehyde ($C_7H_6O_1$)
BAc	benzoic acid ($C_7H_6O_2$)
BQ	benzoquinone ($C_6H_4O_2$)
BZ	benzene (C_6H_6)
CA	citraconic anhydride ($C_5H_4O_3$)
DMBQ	2,3-dimethyl-p-benzoquinone ($C_8H_8O_2$)
DMMA	2,3-dimethyl maleic anhydride ($C_6H_6O_3$)
HQ	hydroquinone ($C_6H_6O_2$)
MA	maleic anhydride ($C_4H_2O_3$)
oX	o-xylene (C_8H_{10})
PA	phthalic anhydride ($C_8H_4O_3$)
PAld	phthalaldehyde ($C_8H_6O_2$)
PH	phthalide ($C_8H_6O_2$)
PL	phenol (C_6H_6O)
TA	tolualdehyde (C_8H_8O)
TAc	toluic acid ($C_8H_8O_2$)
TOL	toluene (C_7H_8)
TQ	toluquinone ($C_7H_6O_2$)

the production of PVC, a number of other applications especially also in pharmaceutical industry, require higher product purities. The knowledge of by-product formation paths can also help in this respect, since any impurity that is not formed, later does not need to be removed from the final product.

The majority of studies engaged with identifying the o-xylene reaction scheme have been conducted with small lab-scale apparatuses, which are limited in the concentrations of intermediates and by-products produced. The pilot-scale sample port reactor developed and applied in this research in combination with an industrial catalyst offers promising opportunities in this respect. Both theoretical and experimental approaches have been made in order to better understand oxidation paths of o-xylene.

It is commonly accepted that tolualdehyde (TA) and phthalide (PH) are the main intermediates in the selective o-xylene (oX) oxidation to phthalic anhydride (PA).

Bernardini et al. [8,17,18] succeeded in directly oxidizing all intermediates and by-products previously identified in the o-xylene oxidation in presence of a vanadium oxide catalyst. Selective oxidation products include PA, PH, toluic acid (TAc), TA and methylbenzylalcohol. Also non-selective oxidation to CO, CO_2 and MA is observed. On the same vanadia catalyst, TAc oxidation yields MA, citraconic anhydride (CA) and benzoic acid (BAc), which are commonly known impurities in crude PA (reaction paths 12–14 in Fig. 1).

Blanchard and Vanhove [19] have studied the reaction mechanism by radioactive tracing of methyl groups of o-xylene. Apart from intermediates and by-products mentioned above, dimethylmaleic anhydride was identified. Due to lacking radioactivity of MA, they concluded that MA formation, no matter from which source occurs by oxidative attack of the aromatic ring. A theoretical MA formation path via quinones (benzoquinone (BQ), toluquinone (TQ) and 2,3-dimethyl-p-benzoquinone (DMBQ)) is postulated in analogy to benzene [20–22] and toluene oxidation [22,23] paths observed on vanadia catalyst.

Recently, Ballarini et al. [12] reported benzoic acid, phthalic acid (PAc) and phthalaldehyde (PAld) as intermediates or by-products in o-xylene oxidation. The involvement of PAld and PAc in the reaction scheme was investigated by feeding PAld dissolved in toluene comparing the product spectrum to that of toluene oxidation. A secondary reaction path towards PA, paths 9–11 in Fig. 1, can be thereby derived.

While the focus of Bond [7] lay on the investigation of the reaction mechanism on the catalyst surface, the reaction scheme suggested consists of a rake mechanism with the main intermediates detectible in the gas phase (paths 1 and 5–8 in Fig. 1) along with surface species thereof.

Saleh and Wachs [11] have conducted a study of the reaction network based on conversion selectivity profiles obtained by controlling different reaction temperatures. According to their experimental results, MA is formed mainly by oxidation of PA (path 15 in Fig. 1). Possible intermediates in this path are not indicated.

The phthalic anhydride formation path in o-xylene oxidation is quite well described and experimentally backed. In contrast, the formation paths of by-products such as benzoic acid, maleic anhydride, CO and CO_2 and especially their sources are widely unknown.

This communication is aimed towards giving more insight in the oxidation paths of o-xylene and its intermediates, especially considering by-product formation.

2. Experimental

2.1. Reactor

The reaction was carried out in a continuous, pilot scale, single tube fixed bed sample port reactor, supplied by MAN/DWE. With a length of 4 m and an inner tube diameter of 25 mm, reactor dimensions are equivalent to industrial conditions. The cooling temperature is adjusted by means of a molten salt bath, which is stirred to ensure isothermicity and mixing. Flow rates of air are measured by mass flow controllers with thermal measurement principle (Brooks), while the organic feed stream is controlled by a Coriolis-type mass flow controller (Brooks). Flow measurement of the liquid stream is therefore independent of its composition. The organic reaction feed is vaporized by a preheated hot air flow in a separate self-constructed evaporator. Mixing of the feed gas stream is ensured by an inert bed prior to the catalyst bed. In analogy to the industrial process, the reaction product, crude PA is collected in switch condensers, which are operated in parallel with typical cycle times of 48 h. Cooling agent is water during operation at 50 °C, while the condensers can be heated with steam at 160 °C in order to melt and recover the product.

Reaction temperatures are measured by means of a multiposition thermocouple positioned in a 3 mm thermo-well in the center of the reactor tube (Fig. 2).

The 14 sample ports (including reactor inlet and outlet) are connected to an analysis station where both the organic compounds and the remaining gas phase compositions are analyzed online. The transfer lines to the analysis station are heated by a heat exchanger using oil as heating medium at a temperature of 250 °C. A potential homogeneous reaction in the sampling lines at this temperature was investigated through several tests without catalyst filling and is regularly checked by closely analyzing the gas composition at the reactor inlet. O-xylene conversions in these tests are inferior to 1% with CO and CO_2 as only products. The carbon balance was regularly closed with deviation of 1–2%.

Analysis of organic compounds is conducted by a standard gas chromatograph (Agilent 6820N) using a capillary column (Zebron ZB-5, 60 m). After the sample loop for the gas chromatograph, the sample stream is passed through a series of condensers to clean it from heavy components. Concentrations of total oxidation products (CO and CO_2) as well as oxygen in the remaining gas phase are analyzed in an infrared analyzer (Emerson NGA2000) with a paramagnetic channel for oxygen.

2.2. Identification of intermediates

In order to identify unknown intermediates, samples of the organic composition of the gas stream were taken at different

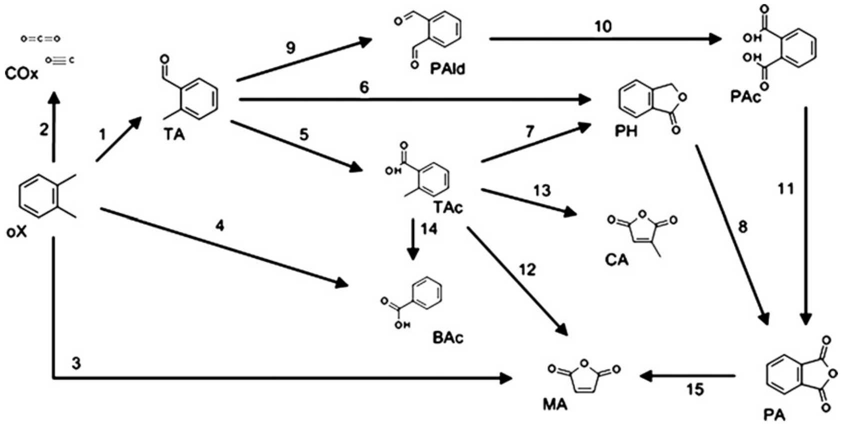

Fig. 1. Reaction scheme of o-xylene oxidation with experimentally confirmed reaction paths as reported in the literature, compare to sources [7–12].

sample ports by means of a cooling finger suspended in a cold trap with a mixture of isopropanol and dry ice. The gas sample is passed through cooled acetone or pentanone, in which the organic compounds within the gas stream are dissolved. Samples are analyzed offline by a standard GC (5890II, Hewlett Packard) equipped with a mass spectrometer (5971A, Hewlett Packard). Mass spectral identification was carried out applying corresponding data supplied in the NIST database [24].

2.3. Catalyst

The catalyst applied in this investigation is the industrial PHTHALIMAX^{TM} S4 catalyst supplied by Süd-Chemie [6,25–27], which can be considered the most selective of catalysts currently available on the market. It consists of V_2O_5 supported on TiO_2 as an eggshell catalyst on an inert carrier. Four different catalyst layers were filled in the reactor. The total length of the catalyst bed applied in this investigation was 350 cm. The catalyst bed is not diluted with inert material.

Calcination and formation of the catalyst were conducted according to the procedures described in the literature [28,29].

2.4. Dosage experiments

In order to determine oxidation paths of each of the intermediates, a series of dosage experiments was conducted. In each of

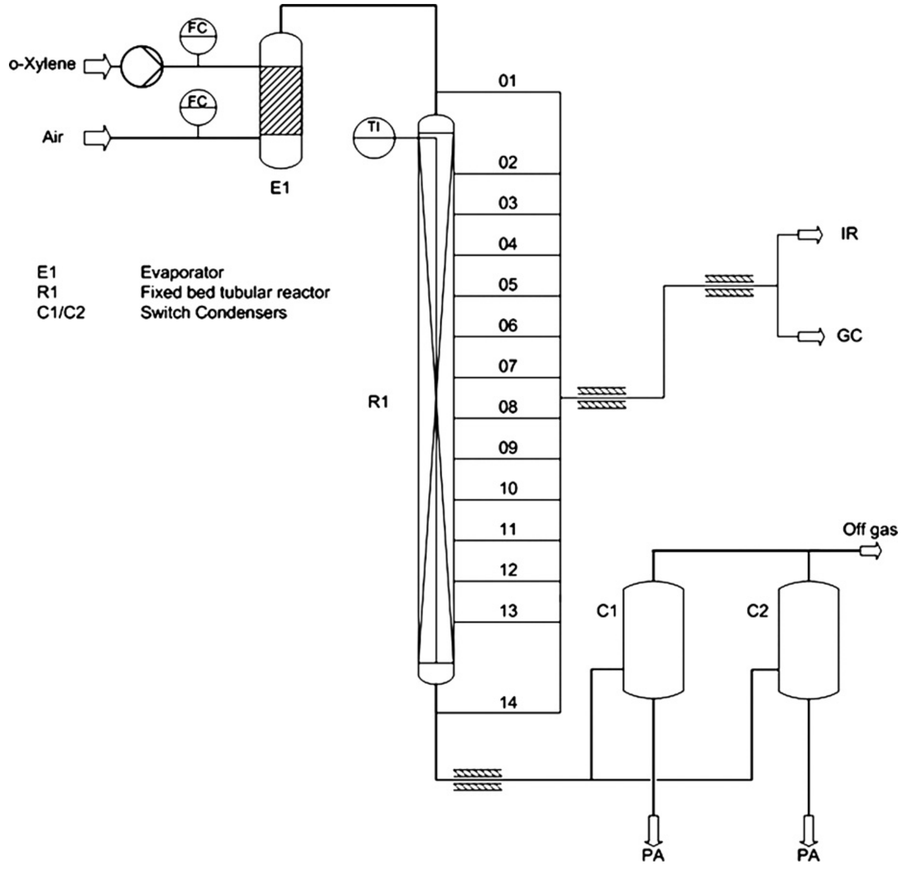

Fig. 2. Simplified flowsheet of the fixed bed sample port reactor set-up.

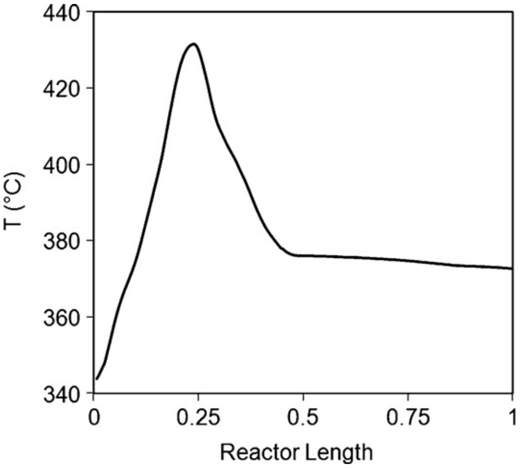

Fig. 3. Typical temperature profile recorded during the equilibration phase.

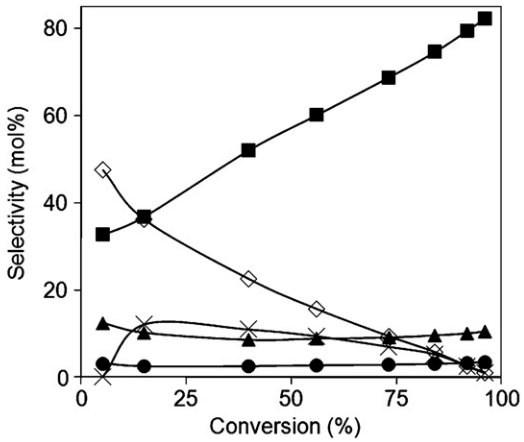

Fig. 4. Conversion selectivity plot of o-xylene oxidation where TA (◇) has a profile of a primary intermediate, PH (×) that of a secondary intermediate and PA (■) the profile of a final product; CO (●) and CO_2 (▲) are produced mainly in parallel reactions to the selective oxidation.

these experiments a given intermediate was dissolved in o-xylene and the organic solution was fed to the reactor. The distinction of o-xylene and intermediate selectivities was conducted by comparing the concentration profiles of the respective dosage experiment with those of a reference experiment conducted with only o-xylene feed at the same total organic inlet concentration just prior to the dosage experiment.

Total concentration of the organics within the feed gas ranged from 0.5 to 1.5 mole%, with an air flowrate of constant 4 N m^3/h while the cooling temperature was controlled to values between 340 °C and 390 °C. The pilot reactor was conducted at non-isothermal conditions which resulted hotspots of up to 465 °C.

Inlet concentrations of intermediates were up to 10 mole% in o-xylene for those components which have good solubility in o-xylene and the respective solubility limit for those with lower solubility. Higher intermediate concentrations proved to significantly change the temperature profiles, interfering with the comparability of reference and dosage experiments. Intermediate concentrations between 2% and 10% allowed quantification by means of product selectivities with respect to the intermediate under scrutiny. Generally, the concentrations of the additionally dosed components in the feed gas stream were kept within the range of their maximum intermediate concentrations during the industrial o-xylene oxidation process.

3. Results and discussion

3.1. Intermediates

After complete activation the catalyst, a typical hotspot profile as shown in Fig. 3 can be observed during steady-state operation of the pilot reactor. Depending on the actual operation conditions, hotspots form of up to 465 °C.

A typical conversion selectivity plot of the main components recorded in o-xylene oxidation is depicted in Fig. 4. The PA selectivity rises with conversion to reach a value above 80% at 95% conversion. TA has a high selectivity at low conversions which then decreases to zero at nearly full conversion. The shape of the PH selectivity profile, showing a distinct maximum, can be attributed to the fact that it is a secondary intermediate [30]. Both CO and CO_2 selectivities remain nearly constant throughout the course of the reaction. However, they slightly rise to reach a lumped value of about 15 mole% at high conversions.

Selectivities of components with lower concentrations are shown in Fig. 5. The most important component in this respect is MA. Its selectivity rises with o-xylene conversion to reach a value of 2.3% at nearly full conversion, leading to the conclusion that it is a final product, which is produced in a consecutive reaction. According to its selectivity profile with a maximum at about 20% conversion, TAc is also a secondary intermediate.

BAc selectivity shows a very interesting selectivity profile. It reaches a maximum at lower conversions to subsequently decrease. However, at conversions above 60%, BAc selectivity begins again to rise. This leads to the conclusion, that BAc is produced via multiple reaction paths.

The selectivity profile of CA shows a broad maximum where it remains nearly constant at conversions between 20% and 80%. However, at high conversions, the CA selectivity decreases to reach a value close to zero at full conversion.

Beyond the literature known by-products and intermediates, acetic acid (AAc), toluene (TOL), TQ and 2,3-dimethyl-p-benzoquinone (DMBQ) were identified as intermediates of o-xylene oxidation, which have previously never been reported of in the literature on this reaction.

DMBQ has a high selectivity at very low conversions, which first sharply and then only slightly decreases to reach zero at full conversion. This component is therefore a primary intermediate to non-selective o-xylene oxidation.

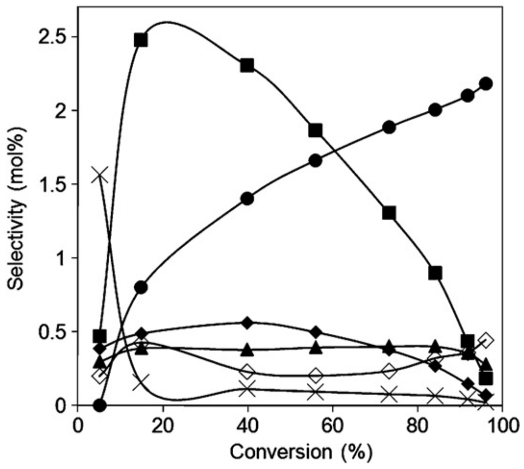

Fig. 5. Conversion selectivity plot of the components with low concentrations; dimethyl-p-benzoquinone (×) yields the run of a primary intermediate, TAc (■), TQ (◆) and CA (▲) that of secondary intermediates and MA (●) the run of a final product; the run of the BAc profile (◇) shows two maximums.

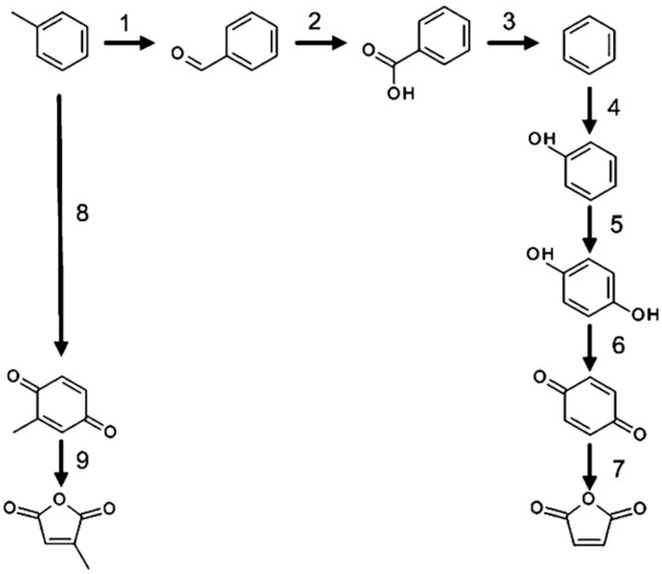

Fig. 6. Reaction scheme of toluene oxidation as reported by Andersson [23].

The TQ selectivity shows the typical run shape of a secondary intermediate. The maximum in selectivity is reached at an o-xylene conversion of 40%. At higher conversions it is completely consumed.

Small traces of toluene can also be detected as an impurity in the o-xylene feed. However, the concentrations of toluene rise significantly along the reactor length and decrease again to zero at high o-xylene conversions. Taking into account the repeatedly high concentrations of toluene oxidation products such as toluquinone, benzoic acid or citraconic anhydride, it is safe to conclude that toluene is an intermediate of o-xylene oxidation.

The general comportment of the product and intermediate selectivities has been reproduced in over 100 measurements at different operating conditions.

In order to identify oxidation paths of the different reaction intermediates, a series of dosage experiments was conducted. The catalyst applied for this investigation, was completely activated according to the above method and has gone through several weeks of steady state operation at the design inlet concentration of 1.5% o-xylene in air.

3.2. Toluene dosage experiments

Toluene seems to be a key intermediate in identifying formation paths of the by-products from overoxidation like BAc and MA. Although the selectivities to toluene are very small, a number of further intermediates, such as TQ, CA or BAc which themselves have significant selectivities are reported of in the literature as products or intermediates of toluene oxidation on vanadia catalyst [22,23,31].

Fig. 6 shows a toluene oxidation scheme based on experimental data as reported by Andersson [23]. Toluene accordingly decomposes via two possible paths, either by a direct oxidative attack of the aromatic ring (path 8 in Fig. 6) or by an attack of the methyl group (path 1) and subsequent oxidation of the aromatic ring. The former path yields CA as product with TQ as an intermediate, while the latter leads to MA through a series of different intermediates.

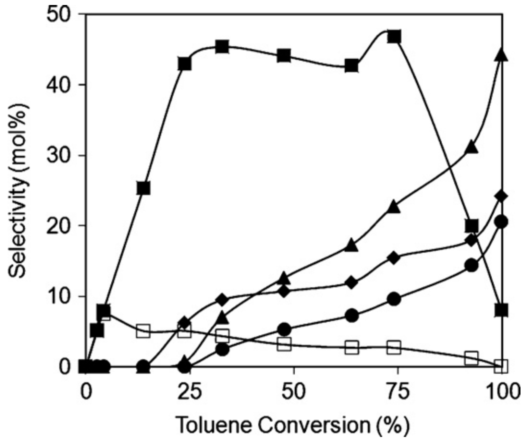

Fig. 7. Selectivities of toluene oxidation (I); BAc (■) and BQ (□) are intermediates while CO_2 (▲), CO (●) and MA (◆) are final products in toluene oxidation; about 25% of toluene is converted to MA, while 65% is totally oxidized to CO and CO_2.

The oxidation of toluene added to the feed over the applied catalyst yields results which are in good accordance with the presented literature data. The main final selectivities (Fig. 7) of toluene are MA, CO and CO_2. Components with high intermediate selectivities in toluene oxidation are especially BAc, but also BQ. AAc can be determined as final product (Fig. 8), while TA and CA show minor intermediate selectivities. Additional components detected in traces by GC/MS analysis are benzaldehyde (BA), benzene (Bz) and phenol (PL).

In order to further refine and confirm the reaction scheme, the main intermediates of toluene oxidation, BAc, TQ, BQ and CA were separately added to the reactor feed.

3.3. Supplementary dosage experiments

The main products of BAc oxidation on said catalytic system are MA and CO_2 while BQ shows selectivities of an intermediate component. Additional products identified in traces comprise hydroquinone, phenol and benzene.

Products of BQ oxidation are MA, CO and CO_2. Intermediates could not be established. GC/MS analysis of reaction products also did not yield any unexpected components specific to BQ oxidation.

TQ oxidation products comprise CO, CO_2, MA and CA, with CA showing the concentration profile of an intermediate. In addition, AAc showed increasing selectivities at nearly complete TQ conversion. Selectivities towards BQ could not be observed. Also GC/MS analysis of the gas sample did not yield any unexpected components.

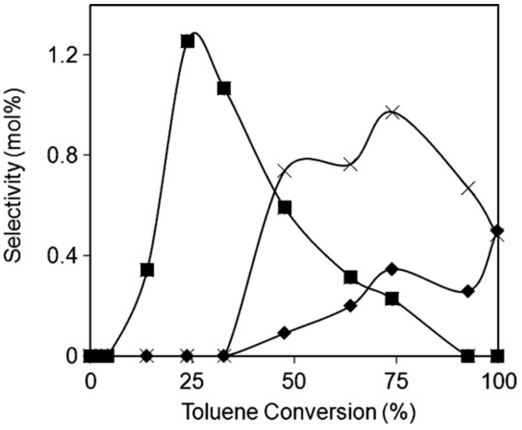

Fig. 8. Selectivities of toluene oxidation (II); toluquinone (■) and citraconic anhydride (×) have intermediate selectivities while acetic acid (◆) is a final product.

Table 1
Summary of the results of all dosage experiments. I stands for intermediate, P for product and T for traces of the respective component found in the oxidation of the intermediate.

	Tac	PAld	PAc	PH	PA	DMBQ	IDMMA	AAc	TOL	BA	BAc	BZ	PL	HQ	BQ	MA	TQ	CA	CO	CO_2
o-Xylene	I	I	I	I	P	I	I	I	I	–	I	–	–	–	I	P	I	I	P	P
Tolualdehyde	I	I	I	I	P	–	–	–	I	–	–	T	–	–	–	P	–	–	P	P
Toluic acid	–	–	–	I	P	–	–	I	I	T	–	T	–	–	–	–	–	–	P	P
Toluene	–	–	–	–	–	–	–	I	–	T	I	T	T	T	I	P	I	I	P	P
Benzoic acid	–	–	–	–	–	–	–	–	–	–	–	T	T	T	I	P	–	–	P	P
Toluquinone	–	–	–	–	–	–	–	I	–	–	–	–	–	–	–	P	–	I	P	P
Benzoquinone	–	–	–	–	–	–	–	–	–		–	–	–	T	–	P	–	–	P	P
Citraconic anhydride	–	–	–	–	–	–	–	I		–		–	–	–	–	–	–	–	P	P

CA appears to be comparably stable and is oxidized only in minor amounts. Oxidation products of CA are CO, CO_2 and AAc. On the applied catalyst, MA is not formed from CA oxidation.

In a next step, it was attempted to identify the source of toluene production. Bernardini et al. [8] reported on MA selectivities in TAc oxidation. Also, it seems likely that the acid group of TAc is abstracted to give toluene. However, a dosage experiment of TAc unambiguously revealed that main products are PA and PH. While selectivities to other components such as CO_x or MA could not clearly be identified, measured toluene concentrations in the dosage experiment are significantly higher than in the reference experiment.

TA is another possible source of toluene, which in dosage experiments yields PA with a final selectivity of around 90%. However, at full tolualdehyde conversion, MA exhibits a selectivity of about 1.6%. Combined CO and CO_2 selectivities range around the same value. Intermediates with high maximum selectivities are toluic acid and phthalide, which account for the selective path to PA. Toluene can be detected with a smaller selectivity of an intermediate. The oxidation products of toluene, BQ, TQ and BAc, too show significant intermediate selectivities while traces of benzene, phenol and benzaldehyde can be identified by GC/MS analysis of intermediate gas samples.

Consequently, it can be concluded that both TAc and TA can be sources of toluene. Its main source however appears to be TA. The results of all dosage experiments are summarized in Table 1.

3.4. Reaction scheme

This spectrum of by-products and intermediates can be divided into two different reaction schemes. The first describes the oxidation of o-xylene with a selective reaction path to PA together with the non-selective paths to MA via DMBQ and to CO and CO_2. The selective oxidation of TA occurs via TAc and PH or PAld and PAc as intermediates. TA is converted to PA with relatively high selectivity. However, both TA and TAc have non-selective paths to toluene (Fig. 9).

The second reaction scheme consists of the toluene oxidation paths. A large number of intermediates lead to the formation of CO_x, MA and CA.

At certain operating conditions, the PA selectivity profile shows a clear maximum, while the BAc selectivity reveals a second maximum, and the selectivities to MA, CO and CO_2 increase. PA oxidation on vanadia catalyst has been investigated by Volfson [32], who concludes that MA and CO_2 are its oxidation products. However PA oxidation on metal oxide catalysts is reported to yield benzoic acid as well [33]. In consequence, a possible PA oxidation path is most likely the decarboxylation to BAc, which then further decomposes to MA and CO_x.

In general, two main mechanisms can be observed. The first is the nucleophilic oxidative attack of the methyl group, the other the electrophilic attack of the aromatic ring. Once the side chain is oxidized, the attack of the aromatic ring is prevented, unless one side chain is completely consumed. In a similar way, once the aromatic

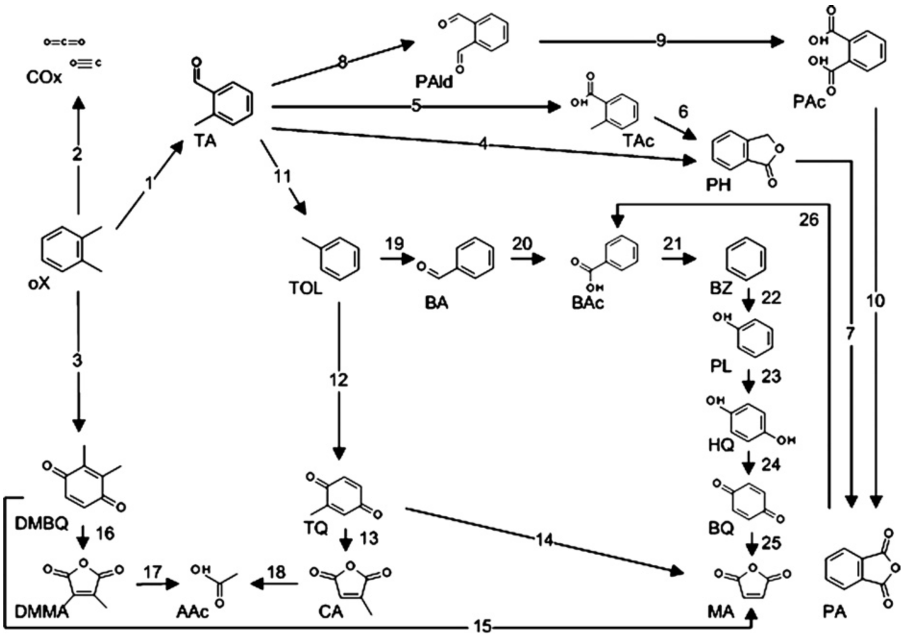

Fig. 9. Experimentally confirmed reaction scheme of o-xylene oxidation.

structure of the ring is cracked, the oxidation of the side chains becomes less likely.

In analogy to the formation of MA from TQ, it is assumed that DMBQ is an intermediate to MA formation directly from o-xylene. In addition in analogy to CA, dimethyl-maleic anhydride (DMMA), which only occurs in minor concentrations, is a rather stable product which may be oxidized to AAc but not to MA.

Some of the components observed in higher quantities in dosage experiments, are only detected in traces in the o-xylene oxidation process. Consequently, several consecutive reactions, e.g. the oxidation route of benzene in Fig. 9, appear to have high intrinsic reaction rates and desorption of the surface intermediates is not favored.

4. Conclusions

The reaction scheme of o-xylene oxidation on industrial vanadia–titania catalyst was refined especially considering the reaction paths leading to undesired by-products such as maleic anhydride and benzoic acid. Maleic anhydride formation occurs via three different reaction paths. The main path to maleic anhydride is the direct oxidation of o-xylene with DMBQ as an intermediate. A second formation path leads via a larger number of identified intermediates, where toluene, which is produced by oxidation of tolualdehyde and toluic acid, intermediates in selective o-xylene oxidation to phthalic anhydride, appears to be a key component. Toluene reacts to maleic anhydride via different reaction paths. Finally, also phthalic anhydride can be oxidized to maleic anhydride, where benzoic acid appears to be an intermediate.

Rather than being a final product, benzoic acid apparently serves as an intermediate for different paths leading to maleic anhydride. The main sources of benzoic acid are toluene and phthalic anhydride.

There are multiple sources for CO_x. However, the intermediates leading to maleic anhydride are more likely to be completely oxidized than the selective intermediates leading to phthalic anhydride. Also, in the course of the oxidation of any intermediate to maleic anhydride, substantial amounts CO and CO_2 are formed.

The quantitative results presented in this communication enable an improved understanding of the oxidation paths of o-xylene on vanadia–titania catalyst and will be used to derive a detailed kinetic understanding of the reaction network.

Acknowledgement

The authors would like to thank Mr. Bernd Mischke of “Chromatographie und Service” for conducting the GC/MS measurements.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.03.006.

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