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New silver- and vanadium-containing multimetal oxides for oxidation of aromatic hydrocarbons

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ABSTRACT

Carboxylic acids and carboxylic anhydrides such as benzoic acid, maleic anhydride, phthalic anhydride or pyromellitic anhydride are produced industrially by catalytic gas-phase oxidation of aromatic hydrocarbons such as benzene, o-xylene, naphthalene, toluene or durene in fixed-bed multitube reactors. Although the processes for the oxidation of o-xylene and/or naphthalene to phthalic anhydride have been studied very intensively for decades, there still is a need for improved catalysts with a selectivity to phthalic anhydride which is higher than 82 mol%. We have found a novel multimetal oxide catalyst of the formula $Ag_{a-b}M_bV_2O_x$ which allow significantly higher phthalic anhydride yield, since the new silver vanadium oxide catalysts can oxidize o-xylene significantly more selectively to form phthalic anhydride or intermediates than by using catalysts of the vanadium oxide/anatase type. By combining the new silver vanadates with conventional V_2O_5/TiO_2 catalysts, a PA yield of more than 84 mol% could be reached.

1. Introduction

The side chain oxidation of alkyl aromatics is one of the most important processes in the production of industrial intermediates. The oxyfunctionalized aromatics are then further reacted to higher value products. The most important of these products on an industrial scale with regards to world production are terephthalic acid, phthalic anhydride and benzoic acid. Products manufactured on a smaller scale include the higher priced aldehydes such as benzaldehyde and terephthalaldehyde [1]. Phthalic anhydride and pyromellitic anhydride are used in the production of plasticizers, alkyd- and polyester-resins, phthalocyanin dyes and a variety of fine chemicals. Benzoic acid finds use as an intermediate in the dye and perfume industries and as a raw material for the production of phenol. Benzaldehyde is used as an aroma compound (bitter almond) and as a starting material in a variety of aromatic and flavoring product syntheses.

Phthalic anhydride (PA) has been commercially produced continuously since 1872 when BASF developed the naphthalene oxidation process. The break-through that led to commercial production of PA was the development of the gas-phase oxidation of naphthalene or o-xylene over a vanadium oxide catalyst [2]. Starting in 1960, naphthalene was replaced by o-xylene as single feed source. Today, 87% of the world PA capacity is produced by o-xylene oxidation and it is possible to achieve initial yields of 112–115 g PA/100 g o-xylene on an industrial scale. This is equivalent to a molar yield of 80–82%. Review articles concerning the state of the art and the reaction mechanism can be found in [3,4].

The commercially utilized PA-catalyst is a shell catalyst with the active mass being coated on hollow cylinders that exhibit diameters ranging from 6 to 10 mm. The layer is about 150–200 μm thick and accounts for about 5–14 wt.%. The carrier material is composed of non-porous steatite or SiC exhibiting a low pressure loss geometry and is inert under PA production conditions. The active mass consists predominantly of TiO_2-particles with a diameter of 50 nm that are coated with vanadium oxide. The vanadium content within the active mass ranges from 4 to 10 wt.%. A complete coverage of a 1 m^2 TiO_2 surface (monolayer) is achieved with 0.12 wt.% V_2O_5 without the formation of V_2O_5-crystallites. The BET surface of the TiO_2 carrier ranges from 6 to 25 m^2/g so that the surface of the TiO_2-particles is fully covered by multiple V_2O_5 monolayers. The use of TiO_2 in its anatase modification is essential for high selectivities. Alkaline, phosphorous and Sb components, as well as some transition metal complexes, are used in small amounts as reaction promoters.

The PA process is carried out almost exclusively in fixed-bed multitube reactors cooled by a molten salt, e.g., developed by Deggendorfer Werft und Eisenbau GmbH (DWE) [5]. The heat formed by the strongly exothermic reaction (1109 kJ/mol) is dissipated via the salt-bath and further utilized for steam production. Each reactor contains between 3000 and 25,000 tubes. The reactor tubes have a diameter of about 21–25 mm and are up to 4 m

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long. The PA production occurs in the explosible region, where each reaction tube is dosed with 2.4–4.2 Nm^3/h air and the xylene concentrations of up to 2.5 vol.%. Although the processes for the oxidation of o-xylene and/or naphthalene to phthalic anhydride have been studied very intensively for decades, there still is a need for improved catalysts with a selectivity to phthalic anhydride which is higher than 82 mol% [6,7].

Mixed oxides of silver and vanadium having an atomic ratio of $Ag/V < 1$ are known as silver vanadium oxide bronzes [8]. Generally, such semiconducting or metallically conductive oxidic solids preferably crystallize in layer or tunnel structures in which part of the vanadium is present as V^{4+} embedded in the $[V_2O_5]_\infty$ host lattice. Usually, these compounds are prepared by joint melting of the starting materials silver or silver nitrate and V_2O_5 at about 750 °C, giving a multiphase mixture which, owing to the preparation method, has a low BET surface area. When such silver vanadium oxide bronzes are used as oxidation catalysts for the selective oxidation of o-xylene or naphthalene and toluene [9], in all cases the activity, selectivity and desired product yield are unsatisfactory. In the case of o-xylene, PA selectivities of ca. 55% at ca. 75 mol% o-xylene conversion were obtained. For toluene oxidation, even at only 30% conversion, the combined benzaldehyde and benzoic selectivity is 62 mol% only.

It was an objective of the present work to provide novel silver- and vanadium-containing catalysts and also processes for producing such catalysts [10]. We have found a novel multimetal oxide catalyst of the formula $Ag_{a-b}M_bV_2O_x$, wherein M is a metal selected from the group consisting of Li, Na, K, Rb, Cs, Tl, Mg, Ca, Sr, Ba, Cu, Zn, Cd, Pb, Cr, Au, Al, Ce, Fe, Co, Ni and/or Mo, $a = 0.3–1.9$, $b = 0–0.5$, $c = 0–20$ and x is a number determined by the valence and amount of elements different from oxygen. The novel catalysts were evaluated both for o-xylene and for toluene oxidation.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of silver vanadate precursor powder

Synthesis of $Ce_{0.02}Ag_{0.71}V_2O_x$: 102 g V_2O_5 (0.56 mol) were added whilst stirring to 7 L of deionised water at 60 °C. The suspension was admixed with an aqueous solution of 4.94 g of $CeNO_3 \cdot 6H_2O$ (0.011 mol, Aldrich, 99% purity). An aqueous solution of 68 g of $AgNO_3$ (0.398 mol) in 1 L of water was added to the resulting orange suspension while continuing to stir. The temperature of the suspension obtained was subsequently increased to 90 °C over a period of 2 h and the mixture was stirred for 24 h temperature. The dark brown suspension obtained was then cooled and spray dried (inlet temperature (air) = 350 °C, outlet temperature (air) = 110 °C).

2.1.2. Coating of the silver vanadate catalysts

The multimetal oxides were used as precursors for preparing coated catalysts on either steatite (magnesium silicate) spheres or on steatite rings. For the coating of silver vanadates on steatite spheres, 300 g of the spheres having a diameter from 3.5 to 4 mm were coated with 40 g of the powder and 4.4 g of oxalic acid with addition of 35.3 g of a mixture of 60 wt.% water and 40 wt.% glycerol at 20 °C in a coating drum over a period of 20 min were subsequently dried. The weight of the catalytically active composition applied in this way, determined on a sample of the precatalyst obtained, was 10 wt.% after heat treatment at 400 °C for 1 h, based on the total weight of the finished catalyst. For the coating of silver vanadates on steatite rings, 350 g of steatite rings having an external diameter of 7 mm, a length of 3 mm and a wall thickness of 1.5 mm were coated with 84.4 g of the powder and 9.4 g of oxalic acid with addition of 66.7 g of a mixture of 60 wt.% water and 40 wt.% glycerol at 20 °C in a coating drum over a period of 20 min were subsequently dried. The weight of the catalytically active composition applied in this way, determined on a sample of the precatalyst obtained, was 18 wt.% after heat treatment at 450 °C for 1 h, based on the total weight of the finished catalyst. The formation procedure was accomplished by a two-step procedure, starting with a reduction of the carbon content in nitrogen atmosphere at ca. 150 °C in the first step and a adjustment of the vanadium oxidation stage at 450–500 °C in an oxygen-containing atmosphere.

2.1.3. Preparation of the V/Ti catalysts

The V_2O_5/TiO_2 two-layer reference catalyst (catalysts A and B) was prepared by conventional techniques. 1400 g of steatite rings having an external diameter of 8 mm, a length of 6 mm and a wall thickness of 1.6 mm were heated to 160 °C in a coating drum and, together with 13.8 g of an organic binder comprising a copolymer of acrylic acid–maleic acid (weight ratio 75/25), sprayed with a suspension comprising 466 g of anatase having a BET surface area of 21 m^2/g, 67.2 g of vanadyl oxalate, 14.4 g of antimony trioxide, 3.15 g of ammonium hydrogenphosphate, 2.87 g of cesium sulphate, 721 g of water and 149 g of formamide. The catalytically active composition applied in this way comprised, on average, 0.16 wt.% of phosphorous (calculated as P), 7.5 wt.% of vanadium (calculated as V_2O_5), 3.2 wt.% of antimony (calculated as Sb_2O_3), 0.40 wt.% of cesium (calculated as Cs) and 88.74 wt.% of titanium dioxide (catalyst A).

The coated catalyst obtained in this way was heated to 160 °C in a coating drum and, together with 14 g of an organic binder comprising a copolymer of acrylic acid–maleic acid (weight ratio 75/25), sprayed with a suspension comprising 502 g of anatase having a BET surface area of 21 m^2/g, 35.8 g of vanadyl oxalate, 2.87 g of ammonium hydrogenphosphate, 2.87 g of cesium sulphate, 720 g of water and 198 g of formamide. The catalytically active composition applied in this way comprised, on average, 4 wt.% of vanadium (calculated as V_2O_5), 0.4 wt.% of cesium (calculated as Cs) and 88.8 wt.% of titanium dioxide. The weight of the layers applied was 9.3 wt.% of the total weight of the finished catalyst (catalyst B).

2.2. Characterization

The BET surface areas were determined by measuring 5 points between $p/p_0 = 0.06–0.20$ after activating the samples at 200 °C at a pressure below 0.1 mbar. X-ray powder diffraction patterns were recorded by means of a D 5000 diffractometer from Siemens using Cu Kα radiation (40 kV, 30 mA). The diffractometer was equipped with an automatic primary and secondary diaphragm system and a secondary monochromator and scintillation detector.

Transmission electron microscopy images were obtained on a electron microscope Tecnai F-20 (FEI, Eindhoven/The Netherlands) operated at an accelerating voltage of 200 kV. The samples were prepared by embedding the powder into a resin and ultramicrotoming into slices.

The oxidation state of the vanadium was determined by potentiometric titration. For the determination, in each case from 200 to 300 mg of the sample are added under an argon atmosphere of 15 mL of 50% strength sulphuric acid and 85% strength phosphoric acid and are dissolved with heating. The solution is then transferred to a titration vessel which is equipped with two Pt electrodes. The titrations are conducted in each case at 80 °C. First, a titration is carried out with 0.1 M potassium permanganate solution. If two steps are obtained in the potentiometric curve, the vanadium was present in an average oxidation state from +3 to less than +4. If only one step is obtained, the vanadium was present in an oxidation step from +4 to less than +5.

In the first mentioned case (two steps), the solution contains no V^{5+}, i.e., all of the vanadium was detected titrimetrically. The amount of V^{3+} and V^{4+} is calculated from the consumption of 0.1 M permanganate solution and the position of the two steps. The weighted average then gives the average oxidation state. In the second mentioned case (one step), the amount of V^{4+} can be calculated from the consumption of 0.1 M potassium permanganate solution. By then reducing all of the V^{5+} in the resulting solution with a 0.1 M ammonium iron(II) sulphate solution and further oxidation with 0.1 M potassium permanganate solution, the total amount of vanadium can be calculated. The difference between the total amount of vanadium and the amount of V^{4+} gives the amount of V^{5+} originally present. The weighted average then gives the average oxidation state.

The equipment for the in situ XRD measurements is described in detail in [11] and consists of three parts: (1) the dosing unit for the gaseous and liquid reactants, (2) the XRD diffractometer equipped with the in situ reaction chamber, and (3) the online GC analytical part. Dosing of toluene and air was done as described in Section 3.1. The gaseous feed consisting of toluene and air and was preheated to 473 K and introduced directly into the in situ chamber. The in situ XRD chamber was a commercially available Paar high-temperature chamber which was modified with a special sample holder having a 5 mL catalyst bed volume and a modified heating system. The thermocouple was embedded in the catalyst bed. The temperature was controlled within ±2 K. The catalyst was granulated into particles from 0.2 to 0.4 mm in size.

2.3. Catalyst testing

2.3.1. Single-layer tests

For the single-layer tests, the catalysts (120–140 g coated spheres) were placed into an iron tube reactor having a length of 80 cm and an internal diameter of 15 mm. The preheated o-xylene/air mixture (360 L (S.T.P.)/h air) with o-xylene loadings of 40–50 g/m^3 (S.T.P.) were passed through the reactor. In the case of toluene oxidation, the preheated toluene/air/steam mixture (360 L (S.T.P.)/h air and 30–40 L (S.T.P.)/h steam) with toluene loadings of 40–50 g/m^3 (S.T.P.) were passed through the reactor. The reactor outlet gas composition was determined by gas chromatography or by an infrared gas analyzer.

2.3.2. Multi-layer tests

The combination of the silver vanadate catalyst with conventional V/Ti catalysts was done in the following way: 80 cm of the coated silver vanadate rings at the reactor inlet, 140 cm of catalyst B as middle layer and 80 cm of catalyst A at the reactor outlet were introduced into a 385 cm long iron tube having an internal diameter of 25 mm. To regulate the temperature, the iron tube was surrounded by a salt melt. 4.0 standard m^3/h of air with a loading of 80 g of 98.5% wt.% o-xylene per standard m^3 of air were passed through the tube from the top downward.

3. Results and discussion

3.1. Kinetic aspects and approach

It is well established that the synthesis of PA proceeds via the intermediates toluic aldehyde, toluic acid and phthalide, as schematically shown in Fig. 1. Studies into the reaction mechanism and kinetics can be found in [12–18]. PA selectivity is lost by the total oxidation of o-xylene to CO and CO_2, which predominantly occurs in the first step of the reaction scheme. By using the intermediates as reactor feed it was found by the authors that conversion into PA can be achieved with very high selectivities (>93%). From these experiments it is clear that the total PA selectivity can be increased by increasing the conversion of o-xylene to any of the above-mentioned intermediates. Experiments to this respect are ongoing and are based on a two-stage process with upstream liquid phase oxidation [19].

Besides the continuous improvement of conventional catalyst systems, the challenge lies in the development of new catalysts that allow the highly selective conversion of xylene to the reaction intermediates. Ideally, this catalyst would be placed as the first layer in a reactor with conventional V/Ti catalyst layers and exhibit working temperatures around 350–380 °C. In a preferred embodiment of the process for partial oxidation, o-xylene is first reacted over a bed of the catalyst, which is a carrier coated with the silver vanadium oxide, to convert it mainly into phthalic anhydride and other oxidation intermediates such as o-toluic aldehyde, o-toluic acid and phthalide. For toluene oxidation, the challenge is similar, i.e., activating the methyl group in a selective way. The novel catalysts were, therefore, evaluated both for o-xylene and for toluene oxidation.

3.2. Preparation and characterization of silver vanadates

The basis for the new high performance catalyst for o-xylene oxidation to intermediate oxidation products like toluic aldehyde, toluic acid or phthalide, is a new preparation route resulting in silver vanadate precursors with BET surface areas of ca. 60 m^2/g. The new preparation route is rather simple and straight forward and described in detail in Section 2. The X-ray powder pattern of the prepared silver vanadium oxides shows a new diffraction pat-

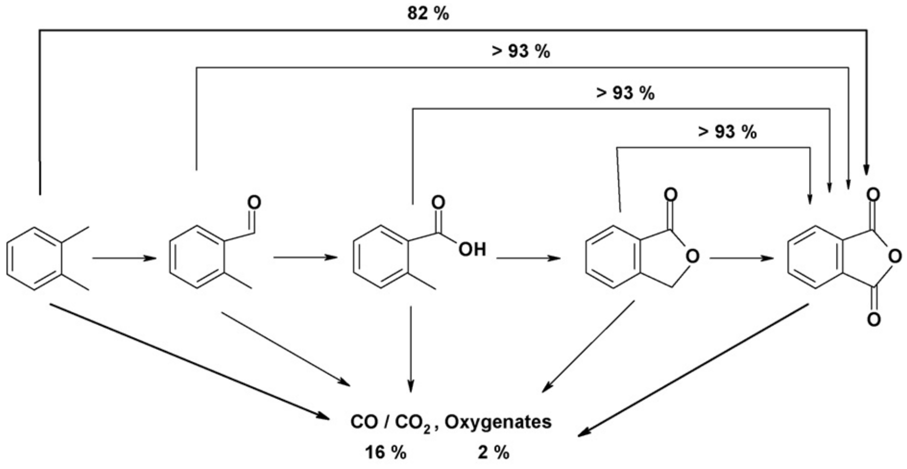

Fig. 1. Reaction scheme of the PA synthesis (selectivity data measured by the authors).

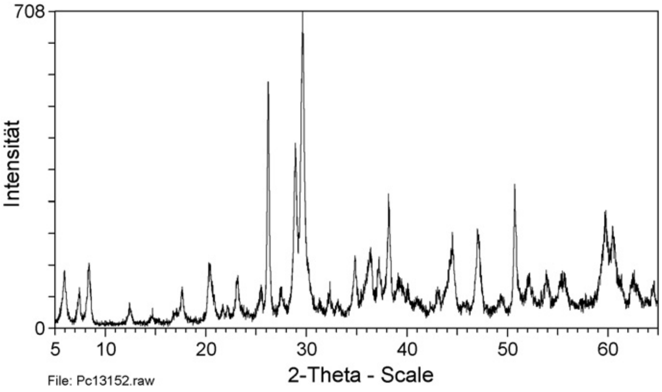

Fig. 2. X-ray powder diffraction pattern of the silver vanadate catalyst precursor.

tern which does not correspond to known silver vanadium oxide bronzes [20] (see Fig. 2). This means that the low-temperature synthesis leads to a new crystal structure. Potentiometric titration showed that the oxidation state of the vanadium in the powder obtained is predominantly +5 while a very small amount of the vanadium (less than 5 at.%) is in the oxidation state of +4. The new material crystallized in a fibrous morphology with fibre diameters of up to ca. 1 μm with typical ratios of fibre diameter to fibre length of below 0.6. The TEM image in Fig. 3 shows double layers of vanadium oxide octahedra with intermediate silver layers.

3.3. *Catalytic testing of the silver vanadates in o-xylene oxidation (single-layer tests)*

This new silver vanadate was tested as catalyst precursor (Fig. 3). At the first day on stream, such a material almost completely burns the o-xylene feed to CO and CO_2. The test was not stopped but continued for a week. During that week, a formation process occurred during which the silver vanadate reached a stable state and the total oxidation tendency continuously decreased. This behaviour is completely different compared to a conventional V/Ti catalyst, which reaches the final selectivity already after 2 days.

The silver vanadate catalyst shows an extremely low CO_x selectivity. The PA selectivity is ca. 55%. Besides, 10% phthalide, 2% o-toluic acid and 24% o-toluic aldehyde are formed. The total C_8 oxygenate selectivity is ca. 91%. At these reaction conditions (silver vanadate on spheres, 325 °C) the o-xylene conversion is 30% and can only be increased with concomitantly decreasing the C_8 oxygenate selectivity significantly (e.g., 88.6 mol% C_8 oxygenate selectivity at 55% o-xylene conversion). For comparison, silver vanadate catalysts described in [9], show C_8 oxygenate selectivities of ca. 78 mol% at similar o-xylene conversion of ca. 30%.

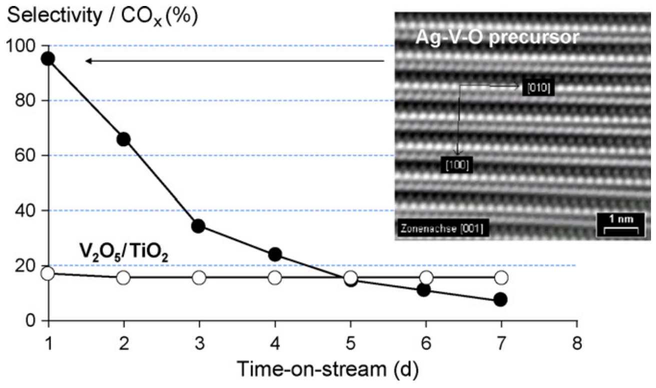

Fig. 3. Silver vanadium oxide catalyst with crystalline structure.

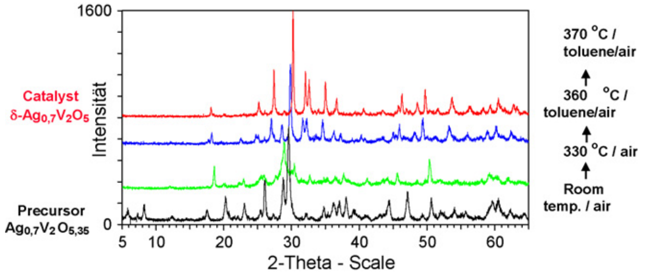

Fig. 4. In situ XRD study of the silver vanadate catalyst.

3.4. *In situ XRD investigations*

In order to study the transformation process of the catalyst precursor to the final catalyst in more detail, in situ XRD investigations were done. A precursor sample was, therefore, heated in air from room temperature to 330 °C. The gas atmosphere was, then, changed from air to a toluene/air mixture and the temperature was raised stepwise to 370 °C. During the heating of the sample, X-ray powder diffractions patterns were measured. Fig. 4 shows selected XRD patterns of that study. The XRD at room temperature corresponds to the XRD of the catalyst precursor already shown in Fig. 2. After heating in air to 330 °C, significant changes in the XRD pattern can already be seen (Fig. 4). The phase transformation was completed after heating the sample in a toluene/air mixture to 370 °C. The diffraction pattern of the catalyst precursor is not visibly any more in that XRD, while the pattern of the δ-$Ag_{0.7}V_2O_5$ phase has formed. The measurements under reaction conditions have shown that under reducing conditions V^{4+}-containing δ-$Ag_{0.7}V_2O_5$ is formed. The crystal structure of this phase is known [20]. The δ-$Ag_{0.7}V_2O_5$ is organized in a layer structure with double layers of VO_6 octahedra and single Ag layers. Statistically, the Ag positions are about 70% occupied.

3.5. *Combination of the new silver vanadates with V/Ti catalysts for o-xylene oxidation (multi-layer tests)*

As already shown in Fig. 1, the intermediates can be converted into PA with very high selectivities (>93%). Based on that knowledge, we have combined properties of the new silver vanadate catalyst with conventional V/Ti catalysts (see Fig. 5). State of the art catalysts for oxidation of o-xylene to phthalic anhydride consist of two to four different V/Ti catalysts in one reactor. A typical setup is the combination of one so-called selective catalyst layer at the reactor inlet (high selectivity at partial conversion, e.g., catalyst B) and one active catalyst layer at the reactor outlet (higher catalyst activity in order to ensure high o-xylene conversion and conversion of intermediate oxidation products to PA, e.g., catalyst A). For an further increase in PA yield, such a conventional 2-layer setup was complemented by an additional catalyst layer, which can be

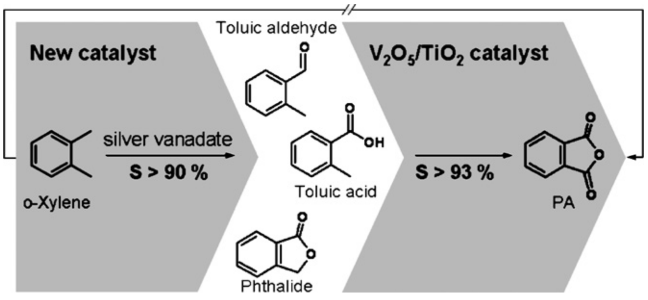

Fig. 5. Combination of two different catalyst systems.

operated at comparably low conversion, but high selectivity, the new silver vanadate catalyst. In order to do so, it was necessary to optimize various parameters: length of the silver vanadate catalyst layer, number and length of the V/Ti catalyst layers, variation of the chemical composition of the V/Ti catalyst layers, operation point (reaction temperature) and start-up conditions. One successful way to adapt all these parameters is the following: 80 cm of the coated silver vanadate rings at the reactor inlet, 140 cm of catalyst B as middle layer and 80 cm of catalyst A at the reactor outlet. In order to start-up such a catalyst with a load of 30 g/Nm^3 it was necessary to use a formation procedure to adjust the carbon content and the vanadium oxidation state of the silver vanadate catalyst (vanadium oxidation state = 4.68, dark green colour). Upon doing so, the extremely low CO_x selectivities of the silver vanadate catalyst can be used from the first day on stream.

Upon optimizing all these parameters, the new catalyst configuration showed PA yields up to 84.2 mol% at o-xylene loadings of 80 g/Nm^3 and 4 Nm^3/h air flow. Compared to conventional V/Ti catalyst technology, this a significant increase of PA yield. From an ecological perspective, the higher PA yield correlated with a decreased CO_2 emission of ca. 50 kg of carbon dioxide per ton of produced PA.

3.6. Upscaling and technical application

As a next step, the lab scale catalyst preparation was scaled up to production scale. The most difficult production step is the silver vanadate crystallization. After a stirring time of several hours, the silver vanadate formation starts and is typically completed after ca. 12 h. Upon formation of the silver vanadate, the viscosity of the suspension increases first and then decreases again afterwards with longer stirring times. The morphology of the particles at the end of the crystallization step is fibrous. In order to ensure the handling of the suspension during the viscosity changes, the content of solid material in the suspension was limited.

A combination of silver vanadate catalyst with V/Ti catalysts is used on commercial scale in the mean time. BASF SE has filed a series of patents on silver vanadate catalysts for o-xylene oxidation to PA, both concerning the synthesis of the silver vanadates and their application in o-xylene oxidation in the oxidation of aromatic hydrocarbons, especially for combination with conventional V_2O_5/TiO_2 catalysts [10,21–25].

3.7. Oxidation of toluene to benzoic acid and benzaldehyde

The processes of DOW, Snia Viscosa and Amoco for the oxidation of toluene are known [1]. The processes of DOW and Snia Viscosa involve liquid phase air oxidation over cobalt catalysts with partial conversion. The Amoco process, on the other hand, applies a liquid phase air oxidation process over cobalt catalysts in the presence of bromine as co-catalyst with full conversion. It is possible to produce benzoic acid with a selectivity of ca. 90 mol%.

Benzaldehyde is produced as a byproduct during the oxidation of toluene with an approximate yield of 7–8% with respect to benzoic acid. It is possible to vary the ratio of benzaldehdye produced during the manufacture of benzoic acid. Benzaldehyde can alternatively be produced via the hydrolysis of benzylidene chloride. It is also possible to produce benzoic acid and benzaldehyde via heterogeneously catalyzed gas-phase oxidation. The selectivities achieved in such processes are, however, significantly lower. Recently, research into the V_2O_5–TiO_2 PA catalyst system has been a particular focus of scientific literature.

A firm conclusion from experimental data is that the presence of vanadium as active component is essential. Benzoic acid can be formed over V_2O_5–TiO_2 catalyst systems with short dwell times and high steam vapor content with lower selectivities than liquid phase oxidation. It is possible to increase the selectivity via doping, for example with Sb-oxides, whereby benzaldehyde is formed only at low temperatures in low conversions. Renken et al. have published comprehensive studies into the reaction kinetics and the nature of the active sites [21]. The formation of benzaldehyde in high selectivities is possible by isolation of the active vanadium oxide centers, for example via integration into microporous silica [18]. The conversions achieved by such processes are, however, far from industrial application.

There are further examples of V-containing systems that are able to produce benzaldehyde with selectivities of 30–80% with low conversions. Of particular interest are the Ag-containing vanadium oxide systems that show different redox properties to the vanadium oxide catalysts and that are able to form either benzaldehyde alone or benzaldehyde and benzoic acid in higher conversions with high product selectivities. When such silver vanadium oxide bronzes are used as oxidation catalysts for the selective oxidation of toluene [9], in all cases the activity of the catalyst is comparably low due to the low BET surface area of the catalyst precursor of ca. 0.5 m^2/g. 30% toluene conversion was achieved at 400 °C with a combined benzaldehyde and benzoic selectivity of 62%. By our new preparation route, catalyst precursors with significantly higher BET surface areas of up to 60 m^2/g can be synthesized resulting in a significantly higher catalyst activity. 30% toluene conversion could be reached at 340 °C already with a combined benzaldehyde and benzoic selectivity of 76%.

During catalyst development, both activity and selectivity of the silver vanadate catalysts were increased further. Upon doping the silver vanadate catalyst, 44% toluene conversion could be reached at 340 °C instead of 360 °C without doping. Besides, benzaldehyde and benzoic acid selectivity could be improved from 71.3 to 78.8 mol%. One disadvantage is that, at higher conversions, benzoic acid is produced as a byproduct alongside the more valuable benzaldehyde (at 40% toluene conversion, the benzaldehyde to benzoic acid ratio is ca 1:1). The limited influence affected on the ratio of products by varying parameters such as conversion, dwell time and the steam partial pressure means that the industrial application of such a process is improbable at the moment.

4. Conclusions

A new silver- and vanadium-containing multimetal oxide for the oxidation of aromatic hydrocarbons was identified and its catalytic performance for the phthalic anhydride synthesis from o-xylene and the toluene oxidation to benzoic acid and benzaldehyde was demonstrated. The preparation route of the new catalytic material is simple and was scaled up to production scale. The formation procedure of the catalyst was analyzed. Besides, the material was chemically modified. Upon combination of the new silver vanadate catalyst with conventional V_2O_5/TiO_2 catalysts we were able to develop a new catalyst generation for o-xylene oxidation to phthalic anhydride, which is already applied commercially. Silver vanadate catalysts can also be applied for toluene oxidation to benzoic acid and benzaldehyde. Currently, the industrial application of such a gas-phase toluene oxidation process is improbable. In conclusion, the new silver vanadate catalysts are a new development platform for a mature field of activity in heterogeneous oxidation catalysis.

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