

Oxidation reactions in the synthesis of fine and intermediate chemicals using environmentally benign oxidants and the right reactor system*

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Abstract: This review outlines several approaches for designing new and environmentally friendly heterogeneously catalyzed oxidation processes for the synthesis of fine and intermediate chemicals. Environmentally benign oxidants such as molecular oxygen, hydrogen peroxide or nitrous oxide can be activated on suitable heterogeneous catalysts showing high activity and selectivity toward the desired oxygenated products. Several examples illustrate that features known from the synthesis of bulk chemicals can successfully be applied for manufacturing intermediate and specialty chemicals applying conventional industrial reactor systems. Direct oxidation of isoprenol, β -picoline, and benzene are chosen as examples for continuous gas-phase processes, oxidation of pinene and propylene as examples for semi-continuous or batchwise processes in the liquid phase.

INTRODUCTION

Environmental concerns and regulations have increased in the public, political, and economical world over the last 15 years because quality of life is strongly connected to a clean environment. Also, in recent years increasingly stringent environmental constraints have led to a great interest in the application of new catalytic oxidation methods for synthesizing fine and intermediate chemicals. Although the manufacture of bulk and fine/intermediate chemicals have some common features, there are some typical differences which have important drawbacks on the environmental assessment of these processes (Fig. 1).

In the bulk chemical industry for manufacturing (e.g., ethylene oxide, formaldehyde, phthalic anhydride) environmentally unacceptable processes have already been replaced by cleaner catalytic procedures a long time ago, whereas fine and intermediate chemicals are still widely produced via traditional stoichiometric oxidations. Still up to date, organic chemists employ stoichiometric oxidants such as dichromate/sulfuric acid, chromium oxides, permanganates, periodates, osmium oxide, or hazardous chlorine causing high salt freights and heavy metal-containing dump unable to be recycled, as well as relatively expensive hydroperoxides, alkylperoxides, and peroxy-carbonic acids. In the case of bulk chemicals heterogeneously catalyzed processes have been developed employing cheap and abundantly available molecular oxygen.

Due to their thermal instability fine chemicals often must be produced in the liquid phase at moderate temperatures. They are generally complex and multifunctional, and chemo-, regio- and stereoselectivity play an important role in their synthesis. The reactor systems of choice are batch or semi batchwise operated multipurpose units. Bulk chemicals, mostly consisting of relatively small, thermostable molecules, can be produced in continuously operated fixed-bed or fluidized-bed reactors in the gas phase allowing much higher space time yields, thus minimizing investment costs.

*Pure Appl. Chem. Vol. 72, No. 7, 2000. A special topic issue on green chemistry.

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The case of fine chemicals is especially critical due to the relatively small scale of the production (<1000–10 000 t/a), the complex synthetic routes, and the short development time to meet market demands leading to tremendously higher E-factors (25–>100) compared to those for manufacturing bulk chemicals (<1–5) [1]. Still, this effect is tolerable from an economic point of view because of the high value added, but it is getting more and more difficult to carry out industrial scale oxidations in such a manner. There is currently a general trend to develop clean and eco-efficient catalytic oxidation processes which minimize the generation of unwanted and harmful by-products.

Differences in oxidation reactions of bulk and fine/intermediate chemicals

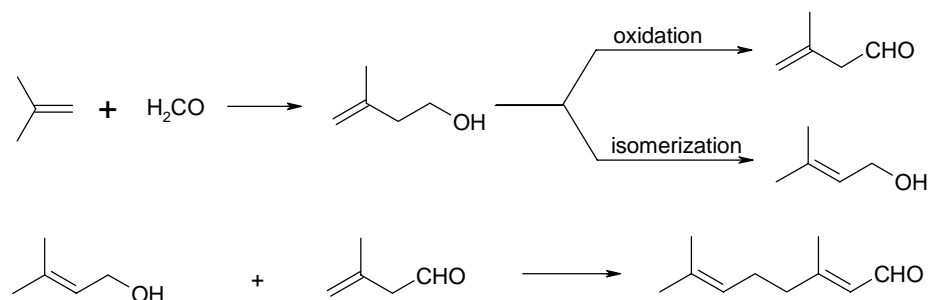
Sustainable and green processes	versus	Traditional stoichiometric oxidants
Molecular oxygen	versus	Inorganic/organic peroxides
Small molecules	versus	Bulkier molecules
Temperature stable	versus	Temperature sensitive
Higher temperature	versus	Lower temperature
Fixed-bed reactor	versus	Slurry reactor
Gas phase	versus	Liquid phase
One purpose unit	versus	Multipurpose unit
Continuous production	versus	Batchwise production
Good E-factor	versus	Bad E-factor

Fig. 1 Differences in the production of bulk and fine/intermediate chemicals.

Because of their versatility, their ease of separation, the lack of corrosion problems, the long life time and regenerability, solid catalysts for heterogeneously catalyzed direct oxidations can contribute to solutions of the above-mentioned problems. These catalysts offer a wide variety of different sites for the activation of clean oxidants such as molecular oxygen, hydrogen peroxide, and nitrous oxide, in some cases an available off-gas. In the case of intermediate chemicals the realistic target is extensive use of molecular oxygen in gas-phase reactions, allowing cost- and eco-efficient manufacturing as known for the production of bulk chemicals. For fine chemicals and specialties this will rather be the exception due to the reasons outlined above, but in this case the replacement of stoichiometric oxidants by “mister clean” H_2O_2 , in liquid-phase oxidations is a cheap and realistic alternative. The heterogeneous catalysts applied thereby can be oxometal or peroxometal species, supported noble metals, heteropolyacids, noble metal pyrochlore oxides, metal containing layered double hydroxides, immobilized complexes (ship-in-the-bottle concept) and, last but not least, metal-substituted molecular sieves (for an extensive review see, e.g., [2]). In the following we present some examples which illustrate that catalyst development closely joined with reaction engineering aspects leads to sustainable production methods of high-value-added chemicals.

ACTIVATION OF THE OXIDANT BY NOBLE METALS: BASF CITRAL PROCESS

Gas-phase oxidation of ethylene to ethylene oxide (EO) over supported silver catalysts is one of the most prominent examples for the use of noble metals in oxidation catalysis and one of the important industrial scale processes (8–10·10⁶ t/a). Ethylene is converted to EO either with air (Scientific Design, UCC) or with mixtures of oxygen and methane (Shell process) in tube bundle reactors at temperatures of 200–300 °C with addition of inhibitors, such as 1,2-dichloroethane or vinyl chloride. The yields per pass are approximately 50%. The catalyst is a silver loaded (7–20 %) aluminium oxide with a very low specific area (<2 m²/g) promoted by alkali salts [3]. Thereby the oxygen is activated by silver, other oxidation processes using noble metals such as Pt, Pd, Au, Ir, Ru are known, too [2]. In the following we will describe that a “similar” process technology can also be applied for regioselective oxidation of much larger and more temperature-sensitive reactive molecules, such as isoprenol [2,4].



Scheme 1 BASF process for the production of citral.

Citral is a very valuable intermediate for the production of α - and β -ionone which have importance as fragrances possessing violet smell and are used in perfumes and household cleaners or as building units for carotenoids and vitamin A. It can be isolated from fruits. However, this method makes no sense because the demand is several thousand tons per year. The conventional industrial route uses β -pinene as starting material and chlorine as oxidant. In a five-step procedure β -pinene is converted to citral in low yields and chlorinated side products are formed, too. Those drawbacks can be overcome by the new environmentally benign BASF-citral-process.

The BASF route (Scheme 1) starts from cheaply available isobutene and formaldehyde. In this condensation reaction 3-methyl-butene-ol (isoprenol) is formed. A part of that is isomerized by shifting the double bond, the other part is oxidized to the corresponding aldehyde. Afterwards, a Cope-rearrangement of those compounds takes place to form citral with more than 95% overall yield. The regioselective oxidation of isoprenol to isoprenal is a remarkable environmentally benign process step. Patent literature reports that alcohols can readily be converted to the corresponding aldehydes over supported and massive metallic copper, silver and gold catalysts and alloys thereof ([4] and references therein). The best results have been obtained with coated inert shapes, for example, silica spheres where metallic silver (>10 wt %) has been applied by flame spraying. In a continuous-flow fixed-bed reactor at 300–600 °C and an extremely short residence time of about 0,001 sec, undiluted isoprenol is oxidized in the presence of pure oxygen surprisingly almost without deep oxidation. The trick thereby is the use of a short fixed-bed reactor temperature controlled by a salt melt in order to run the reaction more or less isothermal and with an ultra short residence time [2]. These facts and an efficient quench allow the production of several thousand tons/a of citral with extremely high selectivity, even though oxygen is used as oxidant at high temperatures in a gas-phase reaction.

Another approach to carry out oxidation reactions of sensitive compounds such as isoprenol to isoprenal could be the use of honeycomb-structured carrier doped or impregnated with noble metals. In such cases, also, very short residence times can be achieved due to the almost complete lack of pressure drop. But such a new technology has to be developed in such a way as to overcome the difficulties which may occur in the catalyst preparation, in the adjustment of isothermy etc.

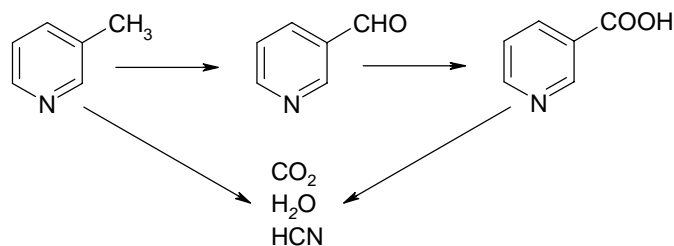
In conclusion, this example demonstrates clearly how even a sensitive chemical such as isoprenol can be oxidized in very high yields, and how catalyst development, process conditions, and reactor design have to meet each other. “Just” by changing the construction of a conventional multitubular reaction system and the modification of a silver catalyst the oxidation of an intermediate chemical can be carried out similar to the production of a bulk chemical in an environmentally benign and sustainable way.

ENHANCEMENT OF ACTIVITY OF THE OXIDANT BY BRØNSTED ACID SITES: DIRECT OXIDATION OF β -PICOLINE

Nicotinic acid is an important intermediate for pharmaceuticals and serves as a provitamin in food additives for animal feeding. It is produced via the Lonza-process or the Degussa-process. The Lonza-process is the oxidation of 2-methyl-5-ethylpyridine by using nitric acid [5]. This process suffers from the separation of nicotinic acid, a high amount of harmful salts due to the neutralization of nitric acid and NO_x -formation, as well as the loss of valuable framework carbon in form of CO_2 . A two-step reaction is the Degussa process: hydrolysis of b-cyanopyridine [6] produced by the ammonoxidation of b-picoline [7]. The disadvantages are the high investment costs (two reactors, distillation) and the still improvable yield.

Selective vapor-phase oxidation of β -picoline catalyzed by vanadium titanium oxide catalysts has been described in the past [8–13]. Thereby the temperature and the molar oxygen/water/ β -picoline-ratio were varied over a wide range from 250 °C to 450 °C and between 40/80/1 and 41/470/1, and air is used as the oxygen source. All authors describe a binary vanadia/carrier system as the essential basis for their catalysts using TiO_2 -carriers with a BET-surface area of 10–50 m^2/g impregnated with amounts of 1–10 wt % V_2O_5 [14–17]. The BET-surface of the final catalyst was kept below 50 m^2/g . Further sources examining the vapor-phase oxidation of organic compounds confirm that anatase has a positive effect on the vanadia layer although it is not active in this reaction itself (see, e.g., [12]).

The side-products of this reaction are pyridine-3-carbaldehyde as reaction intermediate and CO_2 , CO, and HCN as thermodynamically stable products [12–14]. According to our experiments [14] deep oxidation mainly takes place via oxidation of the substrate and the desired product, whereas pyridine-3-carbaldehyde proved to be remarkably stable. Blank tests in the empty tube with β -picoline/ H_2O and nicotinic acid/ H_2O mixtures showed conversions of up to 40% with 100% selectivity to CO_x and HCN, especially in the presence of high excesses of water. Pyridine-3-carbaldehyde was stable in the empty tube and converted to the corresponding acid in the presence of the catalyst. From these observations we developed the simplified reaction scheme (Scheme 2).



Scheme 2 Simplified reaction network for the gas-phase oxidation of β -picoline.

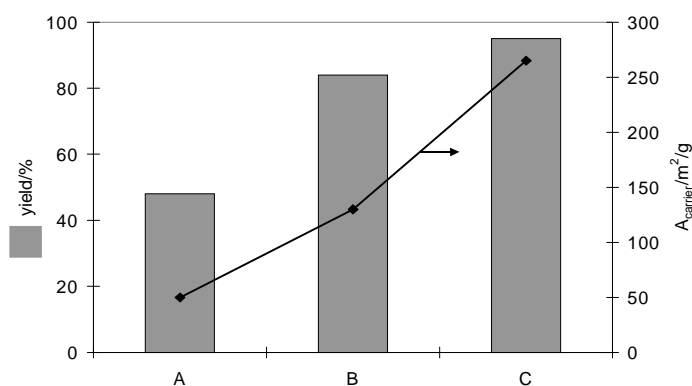
The precise control of residence time will be crucial for this reaction in order to avoid the consecutive oxidation of nicotinic acid. The selectivity towards nicotinic acid could be tremendously improved by appropriate process design, thereby avoiding the parallel reaction. It is very important that the procedure is carried out by separate feeding of β -picoline and water, as well as the mixing of both components just at the catalyst bed and a rapid quenching of the product stream after leaving the catalyst bed [18].

Concerning the catalyst development we used a series of TiO_2 -carriers of the anatase modification with different BET-surfaces, impregnating them with adequate amounts of vanadia (Table 2).

The catalytic performance of those catalysts depicted in Fig. 2 clearly shows that the increase of original TiO_2 -carrier surface enhances activity and selectivity of the catalyst at identical reaction condi-

Table 1 V/Ti-oxide catalysts with various BET-surface of the carriers.

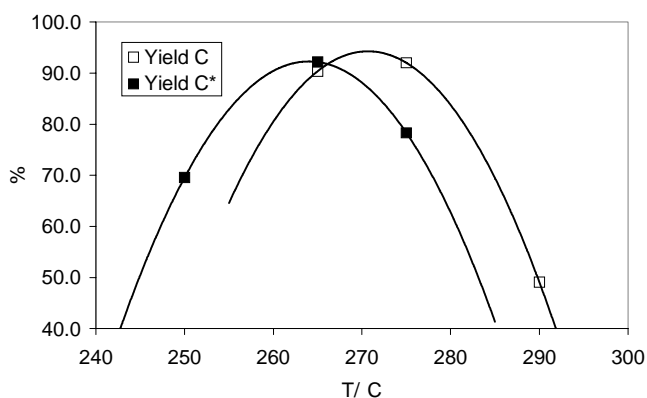
Catalyst	TiO ₂ carrier	BET-surface carrier [m ² /g]	V ₂ O ₅ -content [wt %]	BET-surface catalyst [m ² /g]
A	TiO ₂ -P25	50	2,3	25
B	Anatase B	130	17	65
C	Anatase C	265	19	40

**Fig. 2** Relation between variation of BET-surface of the carrier and the yield of nicotinic acid.

Reaction conditions: $T = 265 - 275$ °C, $WHSV = 0,04$ g/(g_{Kat} h), $O_2/H_2O/\beta\text{-Pic} = 35/55-70/1$ (molar).

tions. First, due to the higher surface area of the carrier material, a higher amount of vanadia could be impregnated upon them. Nevertheless it has to be considered, that other parameters of these catalysts were changed, too. Furthermore, the V₂O₅ and therewith the active sites can be much better dispersed on the larger surface of the catalyst carrier. This higher dispersion should be maintained, even though the BET surface of the final catalysts is drastically reduced (Table 1).

Regarding the differing chemical composition of the TiO₂ materials the way they were produced has to be considered. The TiO₂-P25 material has been produced by burning TiCl₄, yielding an anatase material with a slight amount of rutile formation. In contrast, the TiO₂ materials Anatase B and Anatase C were synthesized by the sulfate process, yielding a higher surface area and Brønsted acid sites due to sulfate residue which was the subject of further investigations. TiO₂ materials with a BET surface of around 270 m²/g and sulfate contents of 0.5 wt % (Anatase C) and 1.5 wt % (Anatase C*) have been impregnated with 20 wt % V₂O₅. The BET surface of the catalysts was in both cases around 40 m²/g (Fig. 3) clearly demonstrates that the total sulfate content has not such a strong influence on conversion

**Fig. 3** Temperature dependence of Catalyst C (0.5 wt % SO₄) and C* (1.5 wt % SO₄), $WHSV = 0,04 - 0,05$ g/(g_{Kat} h), $O_2/H_2O/\beta\text{-Pic} = 35/55/1$ (molar).

and selectivity as the actual surface area of the TiO_2 -carrier does. It can be observed that the reaction temperature where the maximum yield is obtained, is shifted with a higher sulfate content from 275 °C to approximately 255 °C (i.e., the higher the sulfate content the better the activity).

In conclusion our experiments present a clear statement: It is necessary that β -picoline and water have to be added separately to the catalyst bed in order to avoid the parallel reaction to the deep oxidation products. That can be managed by appropriate reactor design. The main parameter which improves the performance is the original surface area of the TiO_2 -carrier. This might happen in combination with the sulfate content. Thereby, the Brønsted acid centers promote the activation of oxygen resulting in lowering the optimum of the reaction temperature. Therefore, it is possible to improve the yield of nicotinic acid to values up to 98% [18].

ACTIVATION OF THE OXIDANT BY LEWIS ACID SITES: DIRECT HYDROXYLATION OF BENZENE

There are several processes for the production of hydroxy-aromatics. For production of phenol the cumene-process is mainly used nowadays. The disadvantage of this three-step process is the low conversion at every step in order to keep the selectivity high. At the last step, the decomposition of cumene-hydroperoxide, equal molecular amounts of phenol and acetone are produced. The economical efficiency of this process is strongly dependent on the market price of the inevitable by-product acetone. Therefore, efforts to develop a new route to phenol free of acetone are of interest.

Oxidizing a mixture of cyclohexanone/cyclohexanol with nitric acid to adipic acid yields equimolar amounts dinitrogen oxide, which could serve as a cheap feedstock for direct hydroxylation of benzene. Phenol in turn can easily be converted to a mixture of cyclohexanone/cyclohexanol which again serves as feedstock for oxidation to adipic acid. This process, first proposed by Solutia, formerly Monsanto [19], is a fine example for eco-efficiency and sustainability. Solutia announced a commercial plant to go on stream by the end of 1999 or the beginning of 2000 [20]. But it seems this project has been postponed.

Since 1983 there has been a lot of research concerning the hydroxylation of benzene with N_2O to phenol [21–29]. G. I. Panov et al. [25–28] found a correlation of the amount of iron in the ZSM-5 zeolite and the conversion of benzene with N_2O to phenol. They suggested that only the coordinatively unsaturated iron atoms in extra-framework iron hydroxide complexes, formed at the thermal treatment step after the synthesis of the zeolite, are catalytically active. The idea of our work was to create coordinatively unsaturated extra-framework aluminium (EFA) by mild steaming of H-[Al] ZSM-5 zeolites avoiding collapse of the zeolite structure. The Lewis acid sites created thereby should activate the N_2O and catalyze the hydroxylation of benzene [30,31].

The steaming of the H-[Al] MFI-zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$ occurs at 550 °C and a water partial pressure of 300 mbar. The period of steaming varied in order to find a dependency of steaming duration and catalytic properties. FTIR spectra of pyridine-loaded samples of H-[Al] ZSM-5 after various steaming times demonstrate the increase of the intensity of the band at 1455 cm^{-1} , which represents pyridine adsorbed at Lewis acid sites [30]. From such measurements we derived a quantitative estimation about the ratio of the band intensities representing pyridine adsorbed at Lewis acid sites and pyridine adsorbed at Brønsted acid sites, respectively (Fig. 4).

This ratio increases due to steaming and dealumination. After 3–7 h of steaming the further increase of this ratio is insignificant. For a longer steaming time the Lewis to Brønsted ratio is rather constant with only a slight decrease after 7 h of steaming. This slight decrease of the ratio is probably caused by agglomeration of the extra-framework aluminium (EFA) to clusters exposing fewer Lewis acid sites than numerous smaller EFA species. Such an agglomeration was already observed as an effect of steaming [32,33]. These FTIR investigations were supported by MAS NMR measurements [30,31].

Such H-[Al]ZSM-5 zeolite catalysts were used for the conversion of benzene (25 mol %) and N_2O (75 mol %) to phenol at 350 °C and $WHSV = 1\text{ h}^{-1}$ (Fig. 5). In the case of steamed samples the

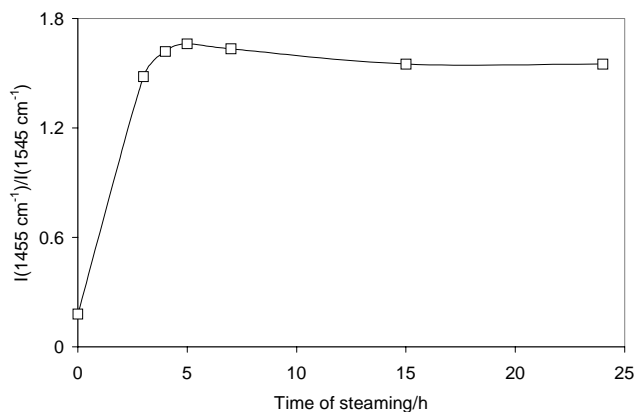


Fig. 4 The ratio of the band intensities representing pyridine adsorbed at Lewis acid sites and pyridine adsorbed at Brønsted acid sites as a function of steaming time (steamed 550 °C, 30% H₂O).

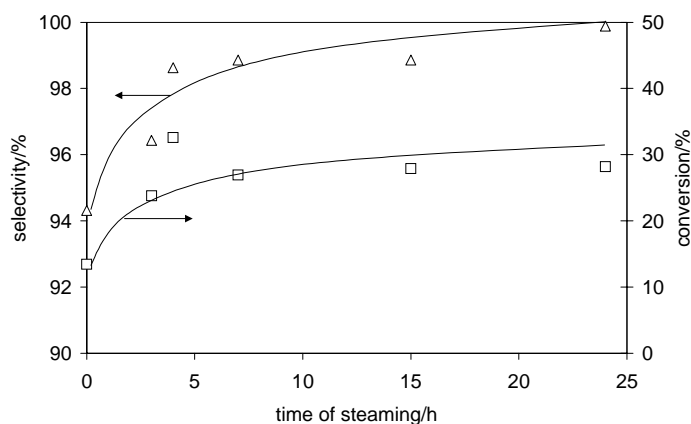


Fig. 5 Conversion (□) and selectivity (Δ) to phenol obtained with hydrothermally treated samples. Feed composition: 25 mol % C₆H₆, 75 mol % N₂O, 350 °C, $WHSV = 1 \frac{\text{g}_{\text{benzene}}}{\text{g}_{\text{cat}} \cdot \text{h}}$.

conversion increased from 15% to nearly 30% and the selectivities from 94% to 98% (Fig. 5) in the same manner as the ratio of band intensities representing Lewis and Brønsted acid sites (Fig. 4). The increase of conversion as a function of steaming time can be explained with an increase of Lewis acid sites created by EFA. There is a direct correlation between the amount of EFA created (Fig. 4) and the conversion observed (Fig. 5). With respect to the mechanism, we believe the N₂O adsorbs with the electron-rich nitrogen on the Lewis acid site weakening the N₂O bond and at a certain stage cleaving this bond. Also, in the case of Fe-zeolites [25–28] and of Ga zeolites [29] the Lewis acid site can be responsible for the activation of N₂O.

Despite the excellent activity and selectivity of these catalyst systems, all the research groups observed a rapid decline in activity due to coking, which is a serious obstacle for commercializing this process. Concerning the reaction engineering aspects, Solutia Inc. [19] claims to have improved the lifetime of a MFI catalyst enabling the performance of this reaction in an adiabatic fixed-bed reactor operated with periodical regeneration by burning of coke deposits, but thereby the use of a high excess of benzene and expensive recyclization is needed. Another reactor concept could be a circulating fluidized-bed unit including continuous regeneration of the spent catalyst analogous to the FCC process. This concept enables excellent temperature control in the reactor, as well as in the regenerator and can be run in a steady-state mode, thus facilitating the downstream process control (e.g., distillation columns). Rooks et al. [34] propose a circulating process with riser downer concept analogous to the maleic anhydride process of DuPont [35,36] where in the riser reactor the catalyst is loaded with surface oxygen, which then reacts with benzene in the downer reactor. The advantage of this concept is the high level of safety by avoiding hot spots and explosive gas mixtures.

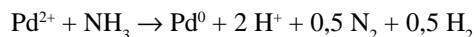
In conclusion, it could be demonstrated that N_2O can be activated by Lewis acid sites. The right reactor system for the commercial process is still under discussion, but Solutia plans to run it in an adiabatic fixed bed [37–39].

ACTIVATION OF THE OXIDANT BY H_2 OVER A BIFUNCTIONAL CATALYST: EPOXIDATION OF PROPYLENE BY H_2 AND O_2

The direct oxidation of propylene to propylene oxide (PO) is one of the most challenging subjects in catalysis in order to avoid the disadvantages of the currently employed chlorohydrine process, ARCO- and SHELL-processes such as the formation of $CaCl_2$ contaminated with toxic chlorinated compounds and formation of the inevitable coupling products styrene and MTBE, respectively. The invention of Titanium Silicate-1 (TS-1) by Taramasso et al. opened a new route for the synthesis of propylene oxide according to the Enichem technology using hydrogen peroxide as oxidant [40,41]. Because of the relatively high and steadily changing cost of hydrogen peroxide this process has not been commercialized up to date. In order to overcome this economic obstacle the use of hydrogen peroxide generated *in situ* is currently under research. Different approaches are employed for the *in situ* formation of hydrogen peroxide. The first approach makes use of the conventional anthraquinone (AQ) process for the production of hydrogen peroxide by feeding propylene and oxygen to the oxidation stage of anthrahydroquinone (AHQ). Contacting AHQ with oxygen leads to the formation of hydrogen peroxide, which is then consumed in the oxidation of propylene to PO catalyzed by TS-1 [42]. The second concept [43,44] is based on the oxidation of propylene by a H_2 - O_2 gas mixture over a precious metal containing titanium silicalite in the liquid phase, i.e., the combination of the DuPont-process for the production of H_2O_2 [45] with the Enichem-process [41]. In a third approach Haruta et al. [46] use a highly dispersed Au/TiO_2 catalyst in a gas-phase reaction. However, the reported propylene conversions are below 2% whereas the selectivity is very high (>95%).

Since the generation of hydrogen peroxide seems to be the rate determining step, we investigated opportunities to increase the PO-yield by varying the precious metal species on a TS-1 catalyst, using a mixture of palladium and platinum for the *in situ* formation of hydrogen peroxide studying the reduction procedure, the addition of alkali salts and the influence of the reaction procedure in batch and semi-continuous manner respectively [47]. An ESCA study was carried out and the fraction of “Pd(II)” species was used to assess the oxidation state of the Pd clusters as a function of reduction methods and platinum loading.

Samples of a TS-1 impregnated with 1 wt % Pd and 0.1 wt % Pt were reduced under atmospheres of H_2 , 5% H_2 in N_2 and N_2 at temperature ranging from 50 °C to 350 °C and applied for the epoxidation of propylene (Fig. 6). Two trends, one related to the gaseous medium used and one related to the temperature, can be observed. PO yield and PO selectivity as well as the fraction of Pd(II) species are favored by reduction under a pure nitrogen atmosphere, i.e., these catalysts are autoreduced as the thermal decomposition of the precious metal amine complexes used for impregnation creates locally a reducing atmosphere. Such a reduction behavior has been already found by W. Sachtler et al. [48]:



These autoreduced samples exhibited a peak in the PO-yield of 5.1% at a reduction temperature of 150 °C. Adding hydrogen to the reduction medium causes a strong decrease of the PO-yield and PO-selectivity. Catalysts reduced with pure hydrogen gave the lowest yield and selectivity. More propane is formed because a high concentration of Pd^0 is formed under hydrogen reduction [49,50]. PO formation is favored by “mild” reduction conditions, i. e., no calcination step prior to reduction, reduction temperatures around 150 °C and a very low hydrogen concentration or no hydrogen at all (autoreduction).

The fraction of the “Pd(II)”-species, that was found to be the highest for the autoreduced catalyst (56%), decreased drastically to 28% for the catalyst reduced with 5 vol % H_2/N_2 or H_2 . The calcined and reduced sample contained the least amount of “Pd(II)”-species (18%).

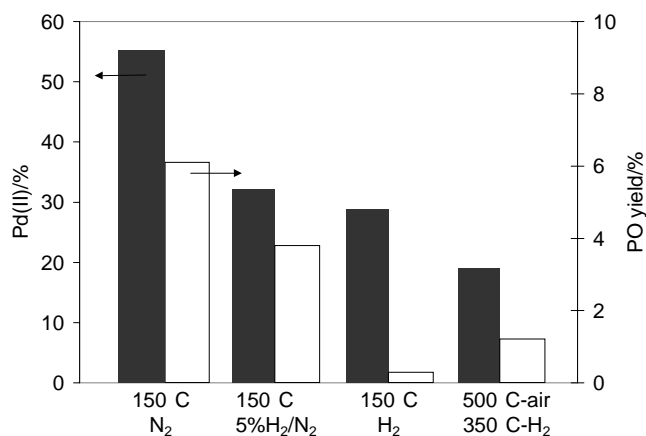


Fig. 6 Pd(II) content and PO yield as a function of the reduction method, 1 wt % Pd + 0.1 wt % Pt on TS-1, reaction conditions: 0.2 g catalyst, 43 °C, 15 g MeOH, 5 g H₂O, H₂/O₂/N₂/C₃H₆ = 15:15:15:1 (molar).

Though we were able to improve the PO-yield by varying the reduction methods we could not suppress the propane formation sufficiently. The platinum loading of 0.1 wt % offered an explanation for the low PO selectivities as platinum is known for its hydrogenation activity. In order to verify this assumption we conducted a series of experiments over TS-1 catalysts with 1 wt % palladium and varying platinum loadings: 0 wt %, 0.01 wt %, 0.02 wt %, 0.1 wt %. The impregnated catalysts were autoreduced under nitrogen atmosphere at 150 °C. We found [49] that by adding as little as 0.01 or 0.02 wt % Pt to the 1 wt % Pd/TS-1 catalyst the yield increased to 10.3 or 11.7%, respectively. The increase in yield was accompanied by an increase in the selectivity, i.e., 41.0% and 46.0%, respectively. However a platinum loading of 0.1 wt% leads to a decrease in yield and selectivity (Fig. 7).

The addition of little amounts of Pt has a strong impact on the oxidation state of Pd and is accompanied by an improvement of the catalytic performance (Fig. 7), which is consistent to the results of the optimization of the reduction method. This observation is also in accordance with the results of Grosser et al. [45] who found enhanced activity for H₂O₂ formation by adding low amounts of Pt to palladium catalysts. Higher loadings of Pt, however, lead to a saturation effect concerning the oxidation state of the Pd species, but cause decreasing PO yields because of the Pt-catalyzed hydrogenation of propylene.

The formation of H₂O₂ from H₂ and O₂ is favored by the addition of promoters like HCl, H₂SO₄ and NaBr or NaCl [51]. This effect can be observed in the direct synthesis of PO as well [47], no matter

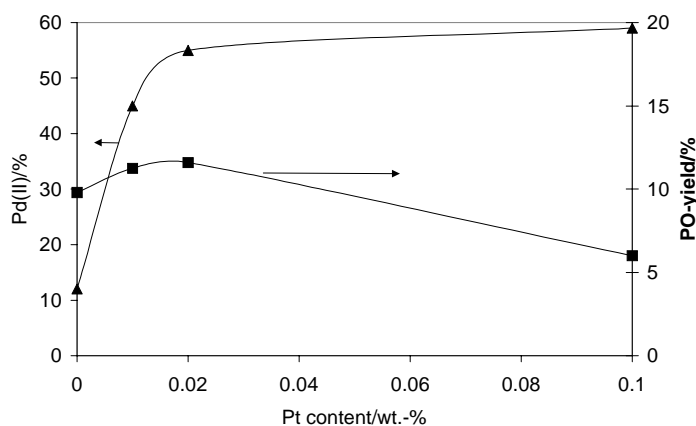


Fig. 7 Fraction of Pd(II) and yield of PO as a function of the Pt loading, Pd loading always 1 wt %, reduction 150 °C under N₂, Reaction conditions: 0.2 g catalyst, 43 °C, 15 g MeOH, 5 g H₂O, H₂/O₂/N₂/C₃H₆ = 15:15:15:1 (molar).

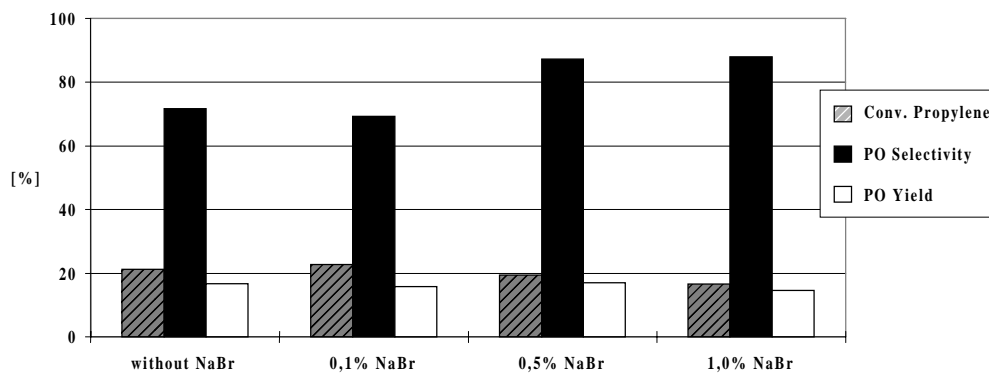


Fig. 8 Influence of impregnation the catalysts with salt; Conditions: 0,2 g Cat., 15 g MeOH, 5 g H₂O, 43 °C, 120 min; Feed: 1,3 l/h H₂, 1,3 l/h O₂, 1,4 l/h N₂, 0,1 l/h Propene; 7 bar.; Catalyst: 1 wt% Pd + 0.1 wt % Pt/TS-1, reduced at 150 °C.

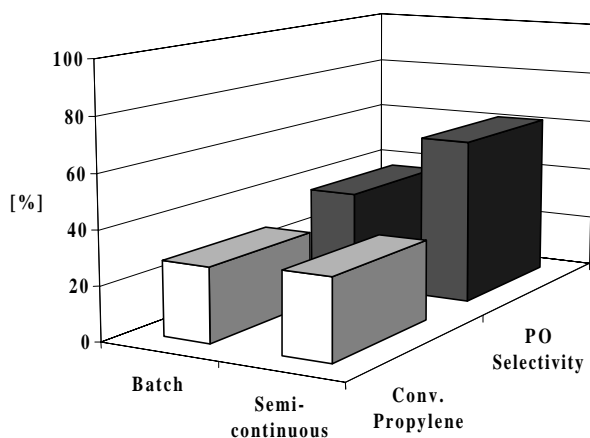


Fig. 9 Comparison batch and semi-continuous modus; Conditions: 0,2 g Cat., 15 g MeOH, 5 g H₂O, 43 °C, 120 min; Batch: 10 g propene, 7 bar H₂, 10 bar O₂, 15 bar N₂; Semi-continuous: 1,3 l/h H₂, 1,3 l/h O₂, 1,4 l/h N₂, 0,1 l/h propene, 7 bar; Catalyst: 1% Pd + 0,01% Pt/TS-1, reduced at 150 °C under N₂.

if the salt was dissolved in the reaction mixture or the catalyst was impregnated prior to the reaction. Among the different salts, especially alkali halogenides (e.g., NaBr) showed positive results. It was found that both the conversion of propylene and selectivity of PO show a maximum with respect to the salt concentration in the solution. In the case that the Pd/Pt/TS-1 catalyst was impregnated with NaBr, the selectivity could be dramatically increased up to 85% whereby the conversion could be almost maintained at a constant level of between 15–20% (Fig. 8). However, these investigations have been carried out in a semi-continuous procedure as explained in the following.

Because of the simplicity of the experimental setup most of the catalyst development and optimization was done in a batch system. Running the reaction in such a manner the selectivity towards PO never exceeded 50%, because of the high initial pressure of propylene and H₂, leading preferably to the formation of propane. Carrying out the reaction in a semi-continuous setup (i.e., liquid phase and catalyst in a steady phase and continuous gas supply), however, allows isobar conditions over the whole reaction time and thus lower reactant pressures compared to the batch system and provides more effective dispersion of the reactants in the liquid phase thus minimizing mass transfer limitations. While

obtaining comparable conversions of about 20%, the selectivity could be improved from 40% to 60% (Fig. 9) (i.e., an improvement of yield of 50% relative).

In conclusion, we can constitute that the physical characteristics and the catalytic performance of Pd-Pt-TS-1 catalysts strongly depend on the reduction method and the platinum loading. The formation of PO was found to be favored by a high fraction of the "Pd(II)-species" whereas fully reduced Pd and large clusters favored propane production. The fraction of "Pd(II)" was increased by autoreduction by the tetraamine ligand of the noble metal in the absence of hydrogen in the reduction medium. Reduction temperatures above 150 °C or calcination lead to cluster agglomeration on the external TS-1 surface and thus to decreasing PO yields and PO selectivities. Adding minor amounts of platinum also drastically increased the fraction of "Pd(II) -species" in comparison to the Pd⁰ species. Since platinum also catalyzes the hydrogenation of propylene to propane there is an optimum Pt loading to achieve maximum PO-yields and selectivities in the range of 0.01–0.02 wt % Pt. Addition of low amounts of alkali halogenides led to an improvement of PO yield because of the promoting and stabilizing effect for the formation of hydrogen peroxide. By the application of a more suitable reactor system such as a semi-continuous procedure the yield could be tremendously improved, too. The next step must be to develop continuous reactor systems for direct synthesis of PO.

ACTIVATION OF THE OXIDANT BY IMMOBILIZED HOMOGENEOUS COMPLEXES: STEREOSELECTIVE EPOXIDATION OF OLEFINS

Due to the steadily increasing demand for optically pure compounds in the pharmaceutical and agrochemical field the use of chiral catalysts has become a powerful tool in synthetic organic chemistry [52]. Numerous attempts have been made at the immobilization of homogeneous chiral catalysts [53–60]. In this regard, the "ship-in-a-bottle" approach dating back to 1977 offers several advantages over homogeneous or conventional heterogeneous catalytic systems where the metal complex is attached to a solid surface by covalent or ionic bond [61,62]. The "ship-in-a-bottle" catalyst's main feature is the host-guest interaction which is neither covalent nor ionic. The guest is retained in the zeolite matrix by restrictive pore openings and will, in principle, keep all properties of the homogeneous complex. The superiority of these catalysts to homogeneous systems is based on their easy separation from the reaction mixture and, thus, their recyclability and environmental compatibility [63]. Furthermore, it is likely that the zeolitic host bestows size and shape selectivity to the catalyst as well as a stabilizing effect on the organometallic complex since multimolecular deactivation pathways such as formation of μ -oxo- or peroxy-bridged species will be rendered impossible due to the site isolation of the single complexes [59,64]. However, even a large-pore zeolite such as zeolite Y, whose structure consists of almost spherical 13 Å supercages interconnected tetrahedrally through smaller apertures of 7.4 Å in diameter, is limited regarding the size of guest molecules by the space available in these cavities, whereas the use of mesoporous molecular sieves, such as USY zeolites and MCM-41 suffers from leaching as an effect of the pores being open to the external surface.

The (salen)manganese-catalyzed oxidation of olefins is currently being investigated by various groups, Jacobsen and co-workers being only one of them [56,58,65,66]. Immobilization of the Jacobsen catalyst is an attractive target. However, its outstanding activity, selectivity and chiral induction are accompanied by several disadvantages, such as quick deactivation, difficult separation and salt formation due to the use of sodium hypochlorite as oxidant. Immobilization of the Jacobsen catalyst has been attempted [56], however, its entrapment in zeolitic space has presented a problem so far, with the average faujasite supercage being a cavity too small for such a spacious complex. Thus only complexes of the less bulky bis(salicylidene)-1,2-cyclohexanediamine have been successfully occluded in faujasites [58,60].

However, we have been able to synthesize various metal salen-2 and -5 complexes in the mesopores of a zeolitic host which are surrounded by micropores to prevent leaching [67]. Such catalysts were tested for the stereoselective epoxidation of α -pinene (Scheme 3).

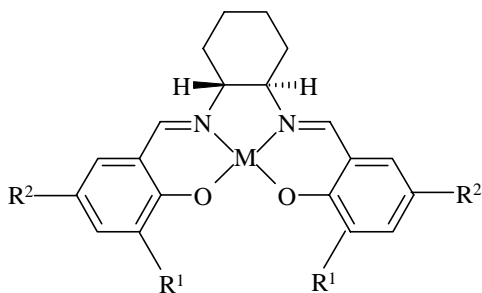
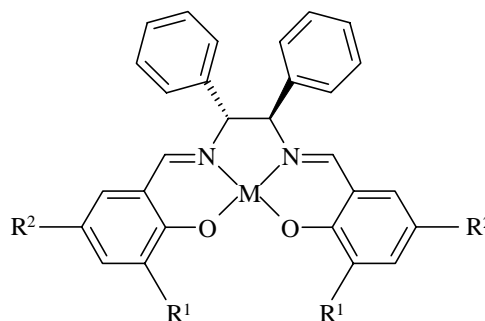
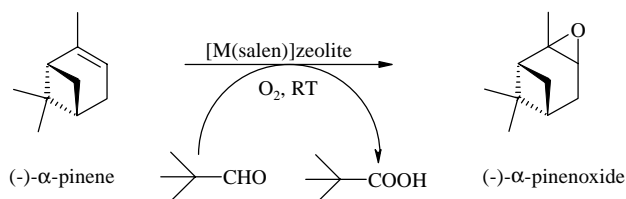
salen-2: $R^1 = t\text{-Bu}$, $R^2 = t\text{-Bu}$ **Fig. 10** Salen complexes based on (R,R)-cyclohexanediamin.salen-5: $R^1 = t\text{-Bu}$, $R^2 = t\text{-Bu}$ **Fig. 11** Salen complexes based on (R,R)-diphenylethylendiamin.**Scheme 3** Oxidation of (-)- α -pinene.

Figure 12 shows that the (salen-2) complexes of Fe and V and the Co(salen-5) complex retained their catalytic properties upon entrapment in the host materials. In contrast to the Mn(salen-2) complex which loses only some of its epoxide selectivity upon immobilization, the corresponding Co and Cr complexes show an additional decrease in stereoselectivity as well. Strikingly, the immobilized Co(salen-5) complex achieved with 100% conversion, 96% selectivity and 91% de even better results in the

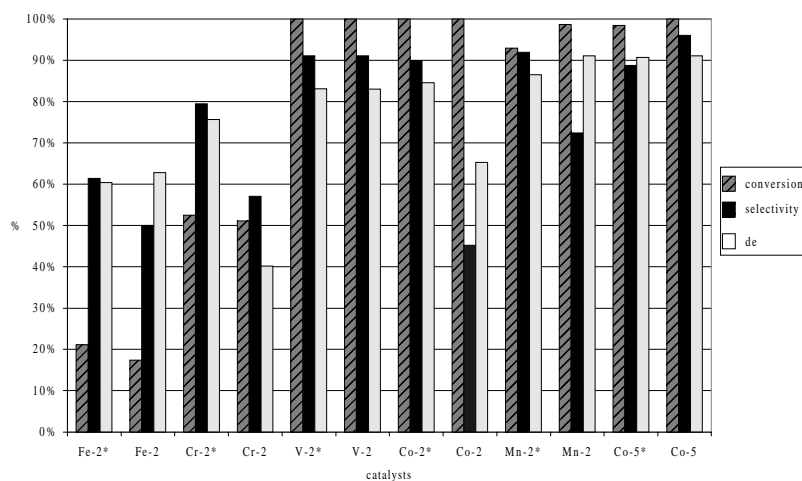


Fig. 12 Epoxidation of (-)- α -pinene in the presence of various homogeneous and immobilized transition metal (salen) complexes, * = homogeneous complex. Reaction Conditions: 10ml C_6H_5F , 4.6 mmol pivalic aldehyde, 1.85 mmol (-)- α -pinene, 25 mg Catalyst, 30 bar O_2 , RT.

epoxidation of (-)- α -pinene than its homogeneous counterpart. However, it is worth notifying that among the (salen-2) complexes neither the homogeneous nor the occluded Jacobsen complex catalyzed the epoxidation of (-)- α -pinene best.

We can conclude that a comparison of the respective catalytic results of these new heterogeneous catalysts and their homogeneous counterparts showed that the entrapment of the organometallic complex was achieved without considerable loss of activity and selectivity. The immobilized catalysts are reusable and do not leach. The oxidation system applies only O₂ at RT instead of sodium hypochlorite at 0 °C. The use of pivalic aldehyde for oxygen transformation via the corresponding peracid results in the formation of pivalic acid which has to be separated from the reaction mixture that is at the present state a disadvantage. The best results so far—100% conversion, 96% selectivity and 91% de—were achieved with the immobilized Cobalt(salen-5) complex in the epoxidation of (-)- α -pinene.

SUMMARY

Catalyst and process development has to be seen as a unit. The above-described examples demonstrate the potential of sustainable and green processes for replacing traditional technology in intermediate and fine chemistry which are no longer acceptable from an ecological and economical point of view. It has been pointed out that heterogeneous catalysts offer a variety of different sites for activation of non-stoichiometric (O₂, N₂O) oxidants. Thus, the strategies, needs, and targets for future catalyst and process development include:

- Optimization of atomic efficiency and E-factor [1]; 100% yield or selectivity is the challenging target.
- New oxidation processes using environmentally benign oxidants (e.g., O₂, H₂O₂, H₂/O₂, and N₂O) thus avoiding inorganic and organic peroxides as well as chlorine.
- Catalyst and process development have to be seen as a joint challenge to be faced and solved in an integrated way, for example, extensive use of Mars–van Krevelen principle via riser downer concept (maleic anhydride production of DuPont), development of catalytic membrane, monolithic, and wall reactors.
- Reproducibility of oxidation catalyst preparation, especially true for oxide catalysts synthesized by precipitation methods.
- Development of redox catalysts with acid and basic properties, i.e., oxidation reactions in the presence of materials with acid or basic or acid/base sites.
- Activation of oxygen by hydrogen, i.e., *in situ* H₂O₂.
- Development of multifunctional catalysis, for example, combining several individual reaction steps in one step, development of direct synthetic routes saving energy and starting material, e.g., oxidation of aromatic compounds (“One-Pot” reactions).
- Extensive use of by-products in other syntheses (e.g., use of the exhaust gas N₂O).
- Use of regenerable and biodegradable resources, such as sugar and starch.
- Direct C–H activation (i.e., using natural gas and alkanes); for example, CH₃OH from CH₄, CH₃COOH from C₂H₆, CH₂=CHCN, and CH₂=CHCHO from C₃H₈.
- Development of true chiral heterogeneous catalysts; for example, immobilization of chiral homogeneous catalysts is not a real solution.
- Development of heterogeneous catalysts for treatment of polluted water, wet air oxidation.

In oxidation catalysis for the synthesis of fine and intermediate chemicals using heterogeneous catalysts there is still much more to be investigated than in acid base catalysis.

ACKNOWLEDGMENTS

The authors express their sincere thanks to Aventis Research and Technology (former HOECHST AG), DEGUSSA AG, the state North-Rhine Westfalia, and Sonderforschungsbereich 380 of the Deutsche Forschungsgemeinschaft for generous financial support.

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