

Selective electrocatalytic oxidation of hydrocarbons

The invention relates to an electrochemical process for the selective preparation of partially oxidized organic compounds.

The direct selective oxidation of organic compounds has hitherto been possible only in a few cases, since the partially oxidized products are usually more reactive than the starting materials used, which leads to complete oxidation to form carbon dioxide. In particular, the problem of the direct oxidation of alkanes has up to now not been able to be solved satisfactorily.

Only maleic anhydride can be produced by direct oxidation using n-butane as starting material; here, the stabilization of the oxidation product by ring formation plays a decisive role.

Many attempts to carry out the partial direct oxidation of nonreactive organic compounds concentrate on the development of new heterogeneous catalysts, but the yield of the partially oxidized product is frequently not industrially relevant.

In comparison, less attention has been paid to electrochemical partial oxidation. In this area, the main focus of development work was, in contrast, the utilization of total oxidation of suitable compounds for the generation of electric energy in fuel cells.

An example of the electrochemical oxidation of organic compounds is described in US 4 329 208, namely the

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oxidation of ethene to give ethylene oxide. This oxidation is carried out at an anode consisting of silver or a silver alloy by means of a solid electrolyte system comprising zirconium oxides.

Another process for the electrochemical oxidation of organic compounds is disclosed in US 4 661 422. Here, hydrocarbons are oxidized at a metal/metal oxide anode in a salt melt as electrolyte. The salt melt comprises carbonate, nitrate or sulfate salts while the cathode is made up of mixed oxides of metals of groups I B, II B, III A, V B, VI B, VII B and VIII of the Periodic Table.

In Catalysis today **1995**, 25, 371, Takehira et al. studied the partial oxidation of propene in a construction similar to a fuel cell. As electrolyte, they used Y-stabilized ZrO_2 . The anode material employed was Au coated with an Mo-Bi mixed oxide as catalyst and the cathode material was Ag. The reaction temperature was 475°C.

The yield of the oxidation product desired in each case is generally so low that none of these processes has industrial relevance. Here, too, the problem of the total oxidation of the organic substrate to carbon dioxide has not yet been solved. In addition, the electrolyte acts as an "oxygen pump", i.e. the oxygen required for the oxidation is reduced at the cathode and then migrates in ionic form through the electrolyte to the anode. The anode space contains only the substrate to be oxidized and possibly an inert gas. The feeding of oxygen into the anode space does not lead to an increase in the yield of the desired oxidation product.

Another disadvantage is that the reaction temperature is determined by the oxygen conductivity of the electrolyte. The electrolytes used have a sufficient conductivity only at temperatures which are significantly above the optimum temperatures for such oxidation reactions,

which must partly explain the low selectivity of the processes examined.

Particularly processes which use salt melts as electrolyte are forced to have such high reaction temperatures (up to 750°C) that decomposition of the product is virtually unavoidable. Processes of this type are unsuitable for preparing thermally unstable compounds (e.g. Michael systems).

The discovery of the NEMCA effect (Non Faradaic Electrochemical Modification of Catalytic Activity) opened up the opportunity of developing more economical electrochemical processes. In "Studies in Surface Science and Catalysis", R. K. Grasselli, S. T. Oyama, A. M. Gaffney, J. E. Lyons (Editors), 110, 77 (1997) and Science (1994), 264, 1563, Vayenas et al. described an electrochemical process based on a conductive, porous metal (oxide) film on a solid electrolyte such as Y-stabilized ZrO₂. Gastight separation of the anode and cathode spaces is no longer necessary here and the oxidizing agent can also be fed into the anode space. However, it was found that the main product of the oxidation, carbon dioxide, still results from the total oxidation of the substrate and the selectivity to a desired partially oxidized product is very low even at low conversions.

It is therefore an object of the present invention to develop an electrochemical process for the partial oxidation of organic compounds.

It has surprisingly been found that organic compounds can be electrochemically oxidized very selectively if the anode material comprises mixed oxides of the type $\text{Mo}_a\text{Bi}_b\text{X}^1_c\text{X}^2_d\text{X}^3_e\text{X}^4_f\text{X}^5_g\text{O}_h$.

The present invention accordingly provides a process for the electrochemical oxidation of organic compounds,

wherein the anode material used is a mixed oxide of the formula $\text{Mo}_a\text{Bi}_b\text{X}^1_c\text{X}^2_d\text{X}^3_e\text{X}^4_f\text{X}^5_g\text{O}_h$ (I) where

X^1 = V, Nb, Cr, W, Ta, Ga, Ce and/or La,

X^2 = Li, La, K, Rb, Cs, Cu, Ag, Au, Pd and/or Pt,

X^3 = Fe, Co, Ni and/or Zn,

X^4 = Sn, Pb, Sb and/or Te,

X^5 = Ti, Zr, Si and/or Al, where

a = 0-3,

b = 0-3,

c = 0-12.5,

d = 0-5,

e = 0-1.5,

f = 0-1 and

g = 0-25

with the proviso that $a+d \geq 0.15$

The number h of the oxygen atoms is determined by the valence and number of elements different from oxygen in the formula (I).

For the purposes of the present invention, the term "mixed oxides" includes multimetal oxide compositions as metal oxides existing side by side. In each case, phase precipitations are possible, depending on the stoichiometry and thermal treatment of the mixed oxides.

Mixed oxides of the abovementioned type are known from another industrial field and are used, for example, as heterogeneous catalysts for gas-phase reactions. The preparation and use of these compounds is described, for example, in EP 0 417 723.

Mixed oxides of this type are used as heterogeneous catalysts in chemical reactions which do not involve electric current; their use as anode material in electrochemical processes is unknown.

The anode can consist completely or partly of the mixed oxides of the formula I. In general, an existing elec-

trode, e.g. of platinum, can also be provided with a surface comprising these mixed oxides.

It has been found useful in practice first to apply a film of the mixed oxides to the electrolyte by means of screen printing and to bond it on by means of a heating step. An example of this technique may be found in JP 09 239 956.

The electrocatalytic layer advantageously has a rough surface having a BET surface area of from 5 to 20 m²/g.

The organic compound to be oxidized is, if desired in admixture with oxygen and/or an inert gas such as nitrogen, conveyed past such an anode. The starting materials can be fed in in gaseous or liquid form, but gaseous feed has been found to be useful at the reaction temperatures according to the invention.

Many organic compounds such as aromatics, aliphatics, olefins or alicycles can be oxidized by means of the process of the invention. The present invention is particularly suitable for the oxidation of ethane, propane, ethene, ethyne, propene, benzene, butane, butadiene, butene, cyclohexane, octane, octene, cyclododecane or cyclododecene.

The electrolyte used in the process of the invention can be a solid which conducts oxygen ions, in particular a metal oxide.

In a particular embodiment of the present invention, a perovskite of the formula



where

$\text{X}^6 = \text{Ca}, \text{Sr}, \text{Ba}$

$\text{X}^7 = \text{Ga}, \text{Al},$

$$i = 0.3-0.9$$

$$k = 0.1-0.7,$$

with the proviso that $i+k = 0.9-1.0$,

$$l = 0.3-0.9,$$

$$m = 0.1-0.7,$$

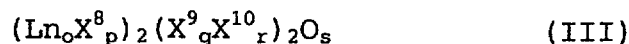
with the proviso that $l+m = 1-1.1$,

is used as the solid which conducts oxygen ions.

The number n of oxygen atoms is determined by the valence and the number of elements different from oxygen in the formula (II).

Other metal oxides which are suitable as the solid which conducts oxygen ions are, for example, ZrO_2 stabilized by CaO , Sc_2O_3 , Y_2O_3 or Yb_2O_3 and also CeO_2 stabilized by La_2O_3 , Y_2O_3 , Yb_2O_3 or Gd_2O_3 .

In a further embodiment of the present invention, pyrochlore compounds of the formula



where

$Ln = La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb$ or Lu

$X^8 = Mg, Ca$ or Sr ,

$X^9 = Ti$ or Zr ,

$X^{10} = Fe, Al, Sc, Ga$ or Y ,

$o = 0.4-1$

$p = 0-0.6$

$q = 0.4-1$

$r = 0-0.6$

can be used as the solid which conducts oxygen ions.

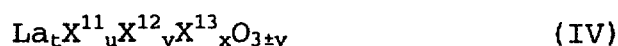
The number s of oxygen atoms is determined by the valence and number of elements different from oxygen in the formula (III).

These compounds can be prepared, for example, by means of drip pyrolysis [P. Gordes et al., Den. J. Mater. Sci. (1995), 30 (4), 1053-8] or decomposition methods [e.g. N. Dhas et al., India J. Mater. Chem. (1993), 3 (12), 1289-1294, or D. Fumo et al., Port. Mater. Res. Bull. (1997), 32 (10), 1459-1470].

The cathode used in the process of the invention can be a metal, preferably silver or platinum.

One or more metal oxides or a mixed metal oxide can also be used as cathode.

Furthermore, perovskites of the formula



where

X^{11} = Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er,
Tm, Yb or Lu,

X^{12} = Ca, Sr, Ba,

X^{13} = Mn, Fe,

X^{14} = Cr, Co, Ni, Al,

t = 0.5-1,

u = 0-0.5,

v = 0.1-0.4

with the proviso that $t+u+v \leq 1$,

w = 0.6-1.1,

x = 0-0.7

with the proviso that $w+x \geq 1$,

can be used as cathode.

The provisos regarding the sums of t , u and v (≤ 1) and also w and x (≥ 1) represent particular embodiments of the present invention. In other embodiments, $t+u+v$ can be from 0.85 to 1. Furthermore, $w + x$ can be from 1 to 1.1.

The number of oxygen atoms ($3\pm y$) is defined by the valence and number of elements different from oxygen.

German Patent 197 02 619 C1 describes the preparation of nonstoichiometric perovskites of the formula $L_wM_xMn_yCo_zO_3$ as cathode material for high-temperature fuel cells. However, fuel cells have been developed for a different industrial process, namely the production of electric energy from total oxidation of a substrate.

The electrochemical oxidation of organic compounds by the process of the invention is carried out at elevated temperatures, preferably from 200 to 750°C, particularly preferably from 250 to 550°C.

The application of superatmospheric pressures is likewise possible; pressures of from 1 to 100 bar, preferably from 1 to 10 bar, can be applied.

In the process of the invention, oxygen is converted into an ionic form at the cathode and conducted through the electrolyte to the anode and at the anode it is activated so that a reaction with the organic compound conveyed past occurs. The oxygen can also be fed in through a porous solid electrolyte which is not impermeable to gas. The gas stream in the anode space can further comprise an inert gas in addition to the organic compound to be oxidized and oxygen.

An example of an apparatus for carrying out the process of the invention is shown in Fig. 1.

The cathode B and the Anode C are applied to the electrolyte A which conducts oxygen ions. Here, care has to be taken to ensure that an electrical connection is achieved between the materials e.g. by heat treatment. The two electrodes are supplied with electric power by means of the voltage source D. The gas streams are passed to or from the electrodes via an external gas duct G and an internal gas duct F, the cell being sealed from the surroundings by means of seals E of the external gas ducts G.

Starting material and oxygen are conveyed as gas stream a) to the anode C and the resulting product gas c) is removed either by the pressure of the gas stream a) or by means of an appropriate reduced pressure. Gas stream b) on the cathode side can consist of air, oxygen or another oxygen-containing gas mixture and is, depleted in oxygen, removed via the gas streams d).

The three-dimensional arrangement of anode, cathode and electrolyte is not restricted to flat plates or continuous layers. It is also possible to use tube reactors for the process of the invention. Here, anode and cathode materials are either applied to a tube made of the electrolyte or a support tube made of an inert material (for example Al_2O_3) is provided with appropriate layers. The necessary power leads are adapted appropriately.

Furthermore, anode or cathode layer can be configured as a woven fabric or a structured surface layer with regular depressions or elevations.

The following examples illustrate the invention without restricting its scope.

Examples:

1. Catalytic oxidation of propene (Comparative example)

A porous catalytic film having a BET surface area of $16 \text{ m}^2/\text{g}$ is applied by screen printing and subsequent heat treatment to an electrolyte film of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_2$. Pt is vapor deposited as counterelectrode. The reaction temperature is 400°C . A mixture of 5% of propene, 5% of oxygen and 90% of nitrogen is passed at 2 l/h over the anode. Air is passed over the cathode at the same rate.

Results:

Anode material (catalytic film)	Acrolein formation [mmol/h*g]
MoO ₃	0.05
Mo ₃ Bi _{1.25} FeCo ₂ Ca _{0.025} K _{0.025} O _x	0.25
Mo ₃ Bi _{0.25} Ni _{2.07} Fe _{0.49} Si _{2.5} K _{0.0125} Na _{0.0375} O _x	0.45

2. Electrocatalytic oxidation of propene under Faradaic conditions

A porous catalytic film having a BET surface area of 16 m²/g is applied by screen printing and subsequent heat treatment to an electrolyte film of La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O₂. Pt is vapor deposited as counterelectrode. The reaction temperature is 400°C. A mixture of 5% of propene and 95% of nitrogen is passed at 2 l/h over the anode. Air is passed over the cathode at the same rate. The applied voltage for controlling the oxygen ion flux is 1 V.

Results:

Anode material (catalytic film)	Acrolein formation [mmol/h*g]
MoO ₃	0.75
Mo ₃ Bi _{1.25} FeCo ₂ Ca _{0.025} K _{0.025} O _x	0.45
Mo ₃ Bi _{0.25} Ni _{2.07} Fe _{0.49} Si _{2.5} K _{0.0125} Na _{0.0375} O _x	0.85

3. Electrocatalytic oxidation of propene using oxygen in the starting material stream

A porous catalytic film having a BET surface area of 16 m²/g is applied by screen printing and

subsequent heat treatment to an electrolyte film of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_2$. Pt is vapor deposited as counterelectrode. The reaction temperature is 400°C . A mixture of 5% of propene, 5% of oxygen and 90% of nitrogen is passed at 2 l/h over the anode. Air is passed over the cathode at the same rate. The applied voltage for controlling the oxygen ion flux is 0-3 V. Under these conditions, the electrochemical reactor operates under Faradaic conditions.

Results:

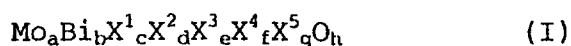
Anode material (catalytic film)	Acrolein formation [mmol/h*g]
MoO_3	2.5
$\text{Mo}_3\text{Bi}_{1.25}\text{FeCo}_2\text{Ca}_{0.025}\text{K}_{0.025}\text{O}_x$	1.1
$\text{Mo}_3\text{Bi}_{0.25}\text{Ni}_{2.07}\text{Fe}_{0.49}\text{Si}_{2.5}\text{K}_{0.0125}\text{Na}_{0.0375}\text{O}_x$	3.2



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Claims:

1. A process for the electrochemical oxidation of organic compounds, wherein the anode material used is a mixed oxide of the formula



where

X^1 = V, Nb, Cr, W, Ta, Ga, Ce and/or La,

X^2 = Li, La, K, Rb, Cs, Cu, Ag, Au, Pd and/or Pt,

X^3 = Fe, Co, Ni and/or Zn,

X^4 = Sn, Pb, Sb and/or Te,

X^5 = Ti, Zr, Si and/or Al, where

a = 0-3,

b = 0-3,

c = 0-12.5,

d = 0-5,

e = 0-1.5,

f = 0-1 and

g = 0-25

with the proviso that $a+d \geq 0.15$.

2. The process as claimed in claim 1, wherein the electrolyte used is a solid which conducts oxygen ions.
3. The process as claimed in claim 2, wherein the solid which conducts oxygen ions comprises a metal oxide.
4. The process as claimed in claim 3, wherein the solid which conducts oxygen ions is a perovskite of the formula



where

X^6 = Ca, Sr, Ba

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$x^7 = \text{Ga, Al,}$

$i = 0.3-0.9$

$k = 0.1-0.7,$

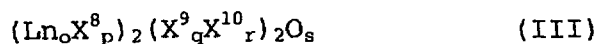
with the proviso that $i+k = 0.9-1.0,$

$l = 0.3-0.9,$

$m = 0.1-0.7,$

with the proviso that $l+m = 1-1.1.$

5. The process as claimed in claim 2, wherein the solid which conducts oxygen ions is ZrO_2 stabilized by CaO , Sc_2O_3 , Y_2O_3 or Yb_2O_3 or else CeO_2 stabilized by La_2O_3 , Y_2O_3 , Yb_2O_3 or Gd_2O_3 .
6. The process as claimed in claim 2, wherein the solid which conducts oxygen ions is a pyrochlore compound of the formula



where

$\text{Ln} = \text{La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu}$

$\text{X}^8 = \text{Mg, Ca or Sr,}$

$\text{X}^9 = \text{Ti or Zr,}$

$\text{X}^{10} = \text{Fe, Al, Sc, Ga or Y,}$

$o = 0.4-1$

$p = 0-0.6$

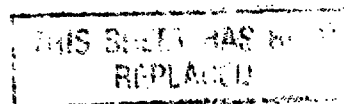
$q = 0.4-1$

$r = 0-0.6.$

7. The process as claimed in any of claims 1 to 6, wherein the cathode used is a metal.
8. The process as claimed in claim 7, wherein the cathode used is silver or platinum.
9. The process as claimed in any of claims 1 to 6, wherein the cathode used comprises one or more metal oxides or a mixed metal oxide.

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10. The process as claimed in claim 9, wherein the cathode used is a perovskite of the formula



where

- X^{11} = Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu,
 X^{12} = Ca, Sr, Ba,
 X^{13} = Mn, Fe,
 X^{14} = Cr, Co, Ni, Al,
 t = 0.5-1,
 u = 0-0.5,
 v = 0.1-0.4

with the proviso that $t+u+v \leq 1$,

w = 0.6-1.1,

x = 0-0.7

with the proviso that $w+x \geq 1$.

11. The process as claimed in any of claims 1 to 10, wherein the electrochemical oxidation is carried out at temperatures of from 200 to 750°C.
12. The process as claimed in claim 11, wherein the electrochemical oxidation is carried out at temperatures of from 250 to 500°C.
13. The process as claimed in any of claims 1 to 12, wherein the electrochemical oxidation is carried out at pressures of from 1 to 100 bar.
14. The process as claimed in claim 13, wherein the electrochemical oxidation is carried out at pressures of from 1 to 10 bar.

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