

The present invention relates to Ti/Si mixed oxides modified by organosilicon groups, to a process for preparing them and to their use as a catalyst.

5 The use of $\text{SiO}_2/\text{TiO}_2$ mixed oxides in heterogeneous catalysis is known, particularly for epoxidizing alkenes. Likewise known is the preparation of mixed oxides modified by organic groups for the purpose of enhancing their activity and their selectivity.

Mixed oxides are generally prepared by hydrolysing
10 alkoxides. For example, US 5,935,895 describes the preparation of an "Si,Ti mixed oxide" aerogel by a process including a step of hydrolysing a silicon alkoxide and a titanium alkoxide-chelate complex in dispersion in an alcohol at acid pH, a step of condensing Si hydroxide and Ti
15 hydroxide which are formed, to give a sol, a step of ageing the sol by stirring under an inert atmosphere, and a step of drying the sol aged and gelled by washing with liquid CO_2 in order to remove the alcohol under water, followed by removal of CO_2 under supercritical conditions to give a mesoporous
20 solid.

Yi Deng, et al., [Journal of Catalysis 199, (2001) 115-122] describes the preparation of Ti-Si mixed oxides bearing methyl groups by a process involving mixing methyl-triethoxysilane, tetraethoxysilane and titanium propoxide
25 with stirring for 15 minutes, subsequently diluting the mixture with ethanol, then acidifying the medium by adding HCl. Subsequently, depending on the way in which gelling and drying are carried out, a microporous mixed oxide or a mesoporous mixed oxide is obtained. The time needed to
30 synthesize the mesoporous oxide is approximately 4 months.

C. A. Muller et al., ["Topics in Catalysis 11/12 (2000) 369-378" or "Journal of Catalysis 184(1999) 280-293] describe the preparation of a Ti-Si mixed oxide modified by organic (methyl or phenyl) groups, by a process involving the steps
35 of the process of US-5,935,895 and an additional step of pre-hydrolysing the methyl- or phenyltriethoxysilane precursor, and also the use of the mixed oxide as a catalyst for epoxidizing olefins.

H. Kochkar et al. [Journal of Catalysis 171(1997) 420-430] describe the preparation of Ti-Si mixed oxide modified by organic (methyl or phenyl) groups, by a process similar to that of US-5,935,895, but using a non-chelated titanium alkoxide precursor. The use of the modified mixed oxide as a catalyst for epoxidizing olefins is also described.

It appears, therefore, that the processes for preparing mixed oxides modified by organic groups involve a multiplicity of steps, which are expensive (especially the drying step) and use alkoxide-type precursors which are not always commercially available or which are difficult to prepare.

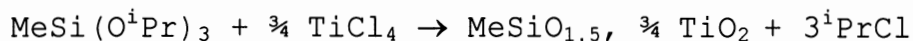
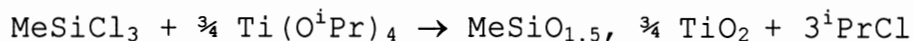
Consideration has also been given to preparing SiO₂/TiO₂ mixed oxides by non-hydrolytic processes.

For example, V. Lafond, et al, [Journal of Molecular Catalysis A: Chemical 182-183 (2002) 81-88] describe the preparation of oxides by non-hydrolytic condensation of chlorides with alkoxides or ethers, illustrated by the following example:



The mixed oxides thus obtained do not, however, carry organic groups.

Moreover, L. Crouzet, et al., [Chem. Mater. 2003, 1530-1534] describe the following reactions, carried out at 100°C:



The reactants used do not include SiO₂ precursors. Analysis by IR spectroscopy on the products obtained shows the absence of Si-O-Ti vibration. Elemental analysis by microprobe (EDX) shows the existence of Si-rich domains and Ti-rich domains, the said domains being greater than a micron in size, which signifies that the solids obtained are heterogeneous.

The objective of the present invention is to provide Si-Ti mixed oxides modified by organosilicon groups, by a non-hydrolytic process.

The compound according to the present invention is a mixed oxide of Ti and Si having a mesoporous structure and carrying organic groups, which can be represented by the formula $(\text{TiO}_2)(\text{SiO}_2)_x(\text{R}_u\text{SiO}_{2-(u/2)})_y$ in which $2 < x < 100$, $0 < u < 4$,

$x+y>3$, $0.1<y<100$, and R is an organic group selected from alkyl groups and aryl groups, or else R is a divalent arylene or alkylene group connecting two Si atoms. It is characterized in that

- 5 - it carries on its surface halogen atoms X and alkoxide groups OR', attached respectively by an M-X and M-OR' bond, M representing Si or Ti, and R' representing an organic group selected from alkyls and aryls;
- it has a pore volume V_p of between 0.2 and 3 cm³/g, and
- 10 a specific surface area S_{BET} of between 100 and 1500 m²/g;
- it is homogeneous on the micron scale and contains Si-O-Ti bonds.

The homogeneity on the micron scale signifies that the mixed oxide does not include domains which are greater than a
 15 micron in size and some of which are very Ti-rich and Si-poor while the others are very Si-rich and Ti-poor (which would indicate phase separation). This characteristic is determined by microprobe analysis (EDX). Qualitative proof of the existence of Si-O-Ti bonds is supplied, for example, by the
 20 presence of a vibration band at approximately 950 cm⁻¹ in the IR spectrum.

The homogeneous nature of the mixed oxides of the invention is favoured by the selection of a high Si/Ti = $x+y/1$ ratio. Very particular preference is given to mixed
 25 oxides in which $x+y > 8$.

X is a halogen selected from Cl, Br, I and F. Chlorine is particularly preferred.

R represents preferably a linear or branched alkyl or alkylene, particular preference being given to alkyl groups
 30 having 1 to 18 carbon atoms.

R may also be a fused or non-fused polycyclic or monocyclic aromatic radical. The phenyl group is particularly preferred.

The substituents R of alkyl type or of aryl type may
 35 carry functional groups selected for example from halides, esters and amines.

R' is preferably a linear or branched alkyl having preferably 1 to 4 carbon atoms. R' may also be an aryl

radical, for example a phenyl group.

The groups R' carried by the mixed oxide of the present invention may be identical or different.

Similarly, $(R_uSiO_{2-(u/2)})_y$ may represent a single type of

units or a number of types of units $(R^i_uSiO_{2-(u^i/2)})_{y^i}$ in which

- the different radicals R^i represent independently of one another an alkyl group or an aryl group, or a divalent arylene or alkylene group connecting two Si atoms;

- the indices u^i , which are identical or different, are such that $0 < u^i < 4$;

- the indices y^i , which are identical or different, are such that the sum of the indices y^i satisfies the conditions set out for y in the present text.

The process for preparing the mixed oxides of the present invention consists in reacting at least one halide selected from TiX_4 , SiX_4 and R_tSiX_{4-t} with at least one oxygen donor selected from dialkyl ethers $R'-OR'$, titanium tetraalkoxides $Ti(R'O)_4$, silicon tetraalkoxides $Si(R'O)_4$, organoalkoxysilanes $R_sSi(OR')_{4-s}$ and alcohols $R'OH$ in accordance with the following overall reaction scheme:



in which a, b, c, d, e, f and g represent the number of moles of the respective reactants, with the following conditions: $a+b>0$, $c+d>0$, $e+f>0$, $0 < t < 4$, $0 < s < 4$.

The duration of the reaction is from a number of hours to a number of days, in accordance with the implementation conditions. A duration of 1 to 6 days is generally appropriate.

When the oxygen donor is other than an ether or an alcohol, the number n_x of halogen atoms and the number $n_{R'}$ of groups R' provided by the precursors are preferably such that $0.9 \leq n_x/n_{R'} \leq 1.1$, in other words $0.9 \leq 4a + 4c + f(4-t) / 4b + 4d + e(4-s) + 2g \leq 1.1$.

When an ether $R'OR'$ is the only oxygen donor, the number n_x of halogen atoms and the number $n_{R'}$ of groups R' provided by the ether are preferably such that $0.9 \leq n_x/n_{R'}$, in other words $0.9 \leq 4a + 4c + f(4-t) / 2g$.

When the alcohol $R'OH$ is the only oxygen donor, the

number n_x of halogen atoms and the number $n_{R'}$ of groups R' provided by the alcohol are preferably such that $1.8 \leq n_x/n_{R'}$, in other words $1.8 \leq 4a + 4c + f(4-t) / 2g$.

In the overall reaction scheme above, the organosilane halide R_tSiX_{4-t} may be a single compound or a mixture of organosilane halides $R^i_tSiX_{4-t^i}$ in which the radicals R^i are selected independently of one another from the radicals defined above for R , and the indices t^i , which are identical or different, are such that $0 < t^i < 4$. Similarly, the organo-alkoxysilane $R_sSi(OR')_{4-s}$ may be a single compound or a mixture of compounds $R^j_sSi(OR')_{4-s^j}$ in which the radicals R^j are selected independently of one another from the radicals defined above for R , and the indices s^i , which are identical or different, are such that $0 < s^i < 4$.

When mixtures of organosilane halides and/or mixtures of organoalkoxysilanes are used, the proportions are selected such that the sum of the various expressions $f^i(4-t^i)$ and the sum of the various expressions $e^j(4-s^j)$ satisfy the conditions set out for $f(4-t)$ and for $e(4-s)$.

When the oxygen donor is other than an alcohol, the reaction is carried out at a temperature greater than 80°C , preferably between 90°C and 200°C . When an alcohol is used as oxygen donor, the reaction can be carried out at a lower temperature.

The reaction may be carried out in any solvent in which the compounds formed are soluble, for example dichloromethane. When certain precursors used are liquid, they may act as solvent, optionally under heat, for the other precursors and for the intermediates obtained. Thus the alcohols or the ethers which can be used as oxygen donor are liquid and may be used as a solvent. Moreover, the chlorides and certain alkoxides which can be used in the process of the invention are liquids in which the compounds obtained are soluble under heating. For example, $Si(O^iPr)_4$ at $Ti(O^iPr)_4$ are liquid, whereas $Ti(OEt)_4$ is solid.

In one particular embodiment a Lewis acid is added as catalyst, for example $FeCl_3$ or $ZrCl_4$. In this case the reaction is more rapid and may be carried out at a lower

temperature.

The mixed oxide obtained may be separated from the reaction mixture by filtration, washing and drying.

The mixed oxides of the present invention may be used advantageously as a catalyst for epoxidizing olefins. The tests carried out on the epoxidation of cyclohexene by cumyl hydroperoxide have shown that the catalysts are selective and active. The fact that the mixed oxides of the invention are particularly active as a catalyst confirms their homogeneity. TiO_2 , indeed, is a poor catalyst. It is thought that the active sites are Ti atoms bonded to Si atoms by way of Si-O-Ti bonds.

The present invention is illustrated in more detail by the examples which follow, but which are not intended to impose any limitation on the present invention.

Example 1

This example was carried out with:

- diisopropyl ether $^i\text{Pr}_2\text{O}$ as oxygen donor
- TiCl_4 as Ti precursor
- SiCl_4 as Si precursor
- MeSiCl_3 and Me_3SiCl as precursors of the organic group and of Si.

The reactants were mixed as follows: the precursors were introduced into a reactor containing dichloromethane under an inert atmosphere, after which the mixture was left in the closed reactor at 110°C for 4 days. Subsequently the solid formed was separated by filtration and washed 3 times with dichloromethane. Finally the solid was dried at 120°C under vacuum for 12 h.

A number of samples were prepared with different proportions of precursors, which are indicated in Table 1 below. For each sample the first line gives the amounts in g, the second line the amounts in mmol.

Table 1

Sample	$i\text{Pr}_2\text{O}$	TiCl_4	SiCl_4	MeSiCl_3	Me_3SiCl	CH_2Cl_2	Composition
VL452	13.4	1.4	4.7	6.2	0	18.2	$\text{TiO}_2.4\text{SiO}_2.6\text{MeSiO}_{1.5}$
	130.8	7.2	27.7	41.1	0		
VL453	14.9	1.4	8.6	3.2	0	19.6	$\text{TiO}_2.7\text{SiO}_2.2\text{MeSiO}_{1.5}$
	146.2	7.2	50.7	21.5	0		
VL454	13.4	1.3	9.4	0	1.5	18.2	$\text{TiO}_2.8\text{SiO}_2.2\text{Me}_3\text{SiO}_{0.5}$
	130.8	6.9	55.3	0	13.7		
VL456	12.4	1.3	6.8	2.1	1.5	17.2	$\text{TiO}_2.6\text{SiO}_2.2\text{MeSiO}_{1.5}.2\text{Me}_3\text{SiO}_{0.5}$
	121.1	7.0	39.9	13.9	14.1		

Example 2

This example was carried out with:

- $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Si}(\text{O}^i\text{Pr})_4$ as oxygen donors and as precursors of Si and of Ti
- 5 - SiCl_4 as precursor of Si
- Me_3SiCl as precursors of the organic group and of Si.

The preparation was carried out in the same way as in Example 1. Two samples were prepared with different proportions of precursors, which are indicated in Table 2. In the case of VL365 the mixture was left at 110°C for 6 days. In the case of VL366 the mixture was left at 150°C for 6 days. The solids were washed and dried as in the preceding example.

Table 2

Sample	$\text{Ti}(\text{O}^i\text{Pr})_4$	SiCl_4	$\text{Si}(\text{O}^i\text{Pr})_4$	MeSiCl_3	Me_3SiCl	CH_2Cl_2	Composition
VL365	1.1	4.6	7.6	0	3.2	15.9	$\text{TiO}_2.15\text{SiO}_2.7.5\text{Me}_3\text{SiO}_{0.5}$
	3.8	26.9	28.9	0	29.2		
VL366	0.39	4.4	8.3	0	3.2	15.9	$\text{TiO}_2.47\text{SiO}_2.23.5\text{Me}_3\text{SiO}_{0.5}$
	1.37	25.9	31.2	0	29.2		

Example 3

- 15 The samples prepared in Examples 1 and 2 were characterized by elemental analysis, by ^{29}Si NMR, by nitrogen adsorption/desorption, by electronic probe microanalysis, by

X-ray scattering and by IR spectroscopy. The composition of the materials, particularly the Si/Ti ratio, is confirmed by elemental analysis. The presence of organic groups R (methyl) is shown by elemental analysis, ^{29}Si NMR and IR spectroscopy.

5 The amorphous nature of the materials is shown by XR scattering. Electronic probe microanalysis shows the high homogeneity of the materials, which is confirmed by IR spectroscopy, which indicates the presence of Si-O-Ti bonds. The presence of MCl and of MO^iPr is demonstrated by elemental
10 analysis, ^{13}C NMR and IR spectroscopy.

The samples obtained exhibit type IV isotherms typical of mesoporous solids, very high specific surface areas S_{BET} , and average pore diameters D_p (calculated on the basis of the total pore volume V_p by the formula $D_p = 4V_p/S_{\text{BET}}$) of greater
15 than 2 nm, showing the majority presence of mesopores. The results are given in Table 3 below.

Table 3

	S_{BET} (m^2/g)	D_p (nm)
VL452	1060	4.8
VL453	1020	4.1
VL454	930	3.4
VL456	700	2.9
VL365	470	2.7
VL366	480	2.9

Example 4

The mixed oxides of ref. VL452, VL454 and VL365 prepared in accordance with Examples 1 and 2 were used for epoxidizing
20 cyclohexene by cumyl hydroperoxide at 65°C in toluene. The tests were carried out under the following conditions: 50 mg of the test material were introduced into a round-bottomed flask under an inert atmosphere, followed by the addition of 5 ml of dry toluene, 150 mg of nonane (internal standard) and
25 2.1 g (25 mmol) of cyclohexene. After heating to 65°C , 1 g (5 mmol) of cumyl hydroperoxide (at 80%) was injected. The reaction was halted after 155 minutes and the products were

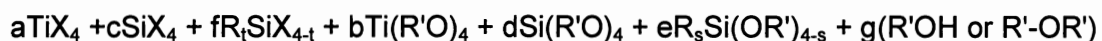
analysed by gas chromatography. In all cases the yield was greater than 80% of the theoretical yield, and the selectivity for cyclohexene oxide was greater than 95%. These results show that the catalysts are selective and active.

Claims

1. Mixed oxide of Ti and Si having a mesoporous structure and carrying organic groups, represented by the formula $(\text{TiO}_2)(\text{SiO}_2)_x(\text{R}_u\text{SiO}_{2-(u/2)})_y$ in which $2 < x < 100$, $0 < u < 4$, $x+y > 3$, $0.1 < y < 100$, and R is an organic group selected from alkyl groups and aryl groups, or else R is a divalent arylene or alkylene group connecting two Si atoms, the said oxide being characterized in that
 - it carries on its surface halogen atoms X and alkoxide groups OR', attached respectively by an M-X and M-OR' bond, M representing Si or Ti, and R' representing an organic group selected from alkyls and aryls;
 - it has a pore volume V_p of between 0.2 and 3 cm^3/g , and a specific surface area S_{BET} of between 100 and 1500 m^2/g ;
 - it is homogeneous on the micron scale and contains Si-O-Ti bonds.
2. Mixed oxide according to Claim 1, characterized in that $x+y > 8$.
3. Mixed oxide according to Claim 1, characterized in that X is chlorine.
4. Mixed oxide according to Claim 1, characterized in that R represents a linear or branched alkyl or alkylene.
5. Mixed oxide according to Claim 1, characterized in that R is an alkyl group having 1 to 18 atoms.
6. Mixed oxide according to Claim 1, characterized in that R is a fused or non-fused polycyclic or monocyclic aromatic radical.
7. Mixed oxide according to Claim 1, characterized in that the organic group R carries functional groups selected from halides, esters and amines.
8. Mixed oxide according to Claim 1, characterized in that R' is an alkyl radical having 1 to 4 carbon atoms.
9. Mixed oxide according to Claim 1, characterized in that the groups R' are identical or different.
10. Mixed oxide according to Claim 1, characterized in that $(\text{R}_u\text{SiO}_{2-(u/2)})_y$ represents a number of types of units $(\text{R}_{u^i}^i\text{SiO}_{2-(u^i/2)})_{y^i}$ in which

- the different radicals R^i represent independently of one another an alkyl group or an aryl group, or a divalent arylene or alkylene group connecting two Si atoms;
- the indices u^i , which are identical or different, are such that $0 < u^i < 4$;
- the indices y^i , which are identical or different, are such that the sum of the indices y^i satisfies the conditions set out for y .

11. Process for preparing a mixed oxide according to Claim 1, characterized in that it consists in reacting at least one halide selected from TiX_4 , SiX_4 and R_tSiX_{4-t} with at least one oxygen donor selected from dialkyl ethers $R'-OR'$, titanium tetraalkoxides $Ti(R'O)_4$, silicon tetraalkoxides $Si(R'O)_4$, organoalkoxysilanes $R_sSi(OR')_{4-s}$ and alcohols $R'OH$ in accordance with the following overall reaction scheme:



in which a , b , c , d , e , f and g represent the number of moles of the respective reactants, with the following conditions: $a+b>0$, $c+d>0$, $e+f>0$, $0 < t < 4$, $0 < s < 4$.

12. Process according to Claim 11, characterized in that the oxygen donor is other than an ether or an alcohol, and in that the number n_X of halogen atoms and the number $n_{R'}$ of groups R' provided by the precursors are such that $0.9 \leq n_X/n_{R'} \leq 1.1$, in other words $0.9 \leq 4a + 4c + f(4-t) / 4b + 4d + e(4-s) + 2g \leq 1.1$.

13. Process according to Claim 11, characterized in that the only donor is an ether $R'OR'$, and in that the number n_X of halogen atoms and the number $n_{R'}$ of groups R' provided by the ether are such that $0.9 \leq n_X/n_{R'}$, in other words $0.9 \leq 4a + 4c + f(4-t) / 2g$.

14. Process according to Claim 11, characterized in that the alcohol $R'OH$ is the only oxygen donor, and in that the number n_X of halogen atoms and the number $n_{R'}$ of groups R' provided by the alcohol are such that $1.8 \leq n_X/n_{R'}$, in other words $1.8 \leq 4a + 4c + f(4-t) / 2g$.

15. Process according to Claim 11, wherein the oxygen donor is other than an alcohol, characterized in that the reaction is carried out at a temperature greater than 80°C .

16. Process according to Claim 11, characterized in that the organosilane halide R_tSiX_{4-t} is a mixture of organosilane halides $R_t^iSiX_{4-t^i}$ in which the radicals R^i are selected independently of one another from the radicals defined for R, and the indices t^i , which are identical or different, are such that $0 < t^i < 4$, and in that the proportions f^i of the various organosilane halides are selected such that the sum of the various expressions $f^i(4-t^i)$ satisfies the conditions set out for $f(4-t)$.

17. Process according to Claim 11, characterized in that the organoalkoxysilane $R_sSi(OR')_{4-s}$ is a mixture of compounds $R_s^jSi(OR')_{4-s^j}$ in which the radicals R^j are selected independently of one another from the radicals defined for R, and the indices s^j , which are identical or different, are such that $0 < s^j < 4$, and in that the proportions e^j of the various organoalkoxysilanes are selected such that the sum of the various expressions $e^j(4-s^j)$ satisfies the conditions set out for $e(4-s)$.

18. Process according to Claim 11, characterized in that a catalyst selected from Lewis acids is added to the reactants.

19. Process according to Claim 11, characterized in that the mixed oxide obtained is separated from the reaction mixture by filtration, washing and drying.

20. Process for epoxidizing an olefin with a hydroperoxide, characterized in that a mixed oxide according to Claim 1 is used as catalyst.