PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C01B 37/00, B01J 29/04

A1

(11) International Publication Number: **WO 98/35910**

(43) International Publication Date: 20 August 1998 (20.08.98)

(21) International Application Number: PCT/EP98/00765

(22) International Filing Date: 11 February 1998 (11.02.98)

(30) Priority Data:
9703093.6 14 February 1997 (14.02.97) GB

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(81) Designated States: CA, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METAL MOLECULAR SIEVE CATALYSTS

(57) Abstract

The present invention relates to metal and in particular titanium isomorphous substituted molecular sieve catalysts and to their manufacture. A particularly important feature of the process of their manufacture is that templating agents which are relatively impure in relation to alkali metal cations may be used.

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Metal Molecular Sieve Catalysts

The present invention relates to metal containing molecular sieve catalysts, in particular titanium molecular sieve catalysts and in particular to a method of manufacture of such catalysts.

Titanium containing molecular sieve catalysts are well known. Examples of such catalysts are the titanium containing silicalite catalysts based on a crystalline synthetic material comprising silicon and titanium oxides and which are characterised by an infra red absorption band at around 950 cm^{-1} to 960 cm^{-1} and typically are of the general formula:

$$xTiO_2(1-x)SiO_2$$

where x is from 0.0001 to 0.10, preferably 0.1 to 4. These catalysts known as TS-1 and TS-2 are typically prepared in the absence of aluminium from a mixture containing a source of silicon oxide, a source of titanium oxide, a nitrogenated organic base and water. Various specific processes for the preparation of titanium silicalite catalysts are described in for example Belgian Patent 886812, EP 0190609 A, US 3329481, US4410501,US 4666692 , US4701428 , EP 0311983, EP 0376453, M.G. Clerici et. al., Journal of Catalysis, 129, 159-167, (1991), M.A. Ugina, et. al., Applied Catalysis A: General, 124, 391-408, (1995), A.J.H.P. van der Pol, et. al., Applied Catalysis A, 92, 93, (1992), J. A. Martens, et. al., Applied Catalysis, A, 99, 71, (1993), A. Thangaraj, et. al., Zeolites, 12, 943, (1992), M. Padovan, Stud. Surf. Sci. Cat., 63, 431, (1991), D. P. Serrano, et. al., Microporous Materials, 4, 273-282, (1995), GB 2071071, EP 0226258), J. Catal. 130 (1991) pages 1-8. More recently aluminium containing titanium silicalites have been reported as well, for example in EP 0293950 and in Zeolites 12 (1992) 135-137. In this case, the catalysts exhibit both oxidizing and acidic catalytic activities. In EP 0230949 the treatment of TS-1 catalyst with neutralizing agents (e.g. alkaline compounds is reported). The examples given in the patent show that TS-1 catalyst treated with alkaline compounds give better yields of epoxides and lower amounts of by-products when they are used as catalysts for the epoxidation of olefins by H_2O_2. It is suggested that the applied treatments have a neutralizing effect on the catalyst's acidity, and thus prevent the catalyst to initiate undesirable side reactions.

Recently, the synthesis of a titanium containing zeolite isomorphous to zeolite Beta has also been reported (J. Chem. Soc. Chem. Comm. 1992 (8) 589-590). In the described synthesis method low concentrations of aluminium (Si/Al = 192) are used for the preparation of the synthesis mixture. Like TS-1 and TS-2, the titanium containing zeolite Beta is characterised by an IR absorption at ± 960 cm^{-1}. Further methods of sytnthesis have been described for example in WO94/02245. J. Chem. Soc. Chem. Commun., 8, 589-590, 1992 (low concentrations of aluminium are present in the synthesis mixture), WO95/03249. WO95/03250. A. Corma, et. al., J. Chem. Soc. Chem. Commun., page 1635, (1995), M. A. Camblor, et. al., Applied Catalysis A: General, 133, L185-L189, (1995). US5474754. M. A. Camblor et al, Zeolites, 202 to 210, (1991)

Typical synthesis mixtures yielding Ti-Beta zeolite after hydrothermal treatment have an initial molar composition within the following ranges:

SiO_2(1); TiO_2 (0.0001 to 0.10 preferaby 0.04); Al_2O_3 (0.005 to 0.100)
H_2O (10 to 100); and TEAOH (0.1 to 1)

Advantageously the Ti plus Si:Al molar ratio is within the range of from 10 to 200:1. Hydrogen peroxide is advantageously present in the synthesis mixture, although it may decompose before or during hydrothermal treatment, preferably in a proportion of 10 to 200 moles H_2O_2 per mole of TEOT when that is used as the source of titanium.

A further example of a titanium containing zeolite is Ti MCM-41. Various methods for the manufactute of this catalyst are described in for example in A. Corma. et. al., J. Chem. Soc. Chem. Commun, page 1635, (1995), A. Corma, et. al., J. Chem. Soc. Chem Commun., page 147 (1994), and T. Blasco et. al., J. Catalysis, 156, 65-74, (1995).

According to the state-of-the-art understanding of TS-1 and Ti-MCM-41 synthesis, the presence of alkali ions must be avoided during the hydrolysis of the Ti and Si sources in order to prevent the formation of TiO_2. This is explicitly taught in for example US 4,410,501, US 5,401,486 and EP 631983-Al and other open published litterature such as for example A.J.H.P. van de Pol, Applied Catalysis A92, (1992),93; A.Tuel, Applied Catalysis A, 110 (1994) 137; and more recently in M.A. Ugina, et. al., Applied Catalysis A: General, 124, 391-408; and P. Serrano, et. al., Microporous Materials, 4, 273-282, (1995). This control is required according to the prior art irrespective of the nature of the hydrolysis and other synthesis parameters. Recently M. A. Camblor, et. al., Applied Catalysis A:

General. 133, L185-L189, (1995), and US5474754 have disclosed methods of preparing titanium containing zeolites which are able to utilise smaller amounts of expensive templating agents but the requirement is still observed that the templating agents should be free of alkali metal cations. Providing templates which have low levels of alkali metal cations is a costly operation. The use of such templates is a significant cost in the production of titanium containing zeolites.

We have now discovered a process for the production of catalytically active metal containing molecular sieves and in particular titanium containing molecular sieves such as for example TS-1 or TS-2 which differs from the known processes for preparing such molecular sieves. The process of the present invention provides a metal e.g titanium, isomorphous substituted molecular sieve which is free of unwanted impurities. In the case of a titanium molecular sieve it is free of significant quantities of polymeric TiO_2 species as detected by UV/Vis spectroscopy, even though the synthesis uses templating agents which hitherto have not been used due to TiO_2 formation.

Accordingly the present invention provides a method for the synthesis of a metal isomorphous substituted molecular sieve which method comprises:

a) forming a co-precipitate or co-gel comprising metal oxide in the absence of alkali metal, and

b) crystallising the co-precipitate or co-gel in the presence of an organic templating agent to form a the a metal isomorphous substituted molecular sieve,

wherein the level of alkali metal within the organic structure directing agent is at least 50 ppm.

The metal may be any metal which may be incorporated in the framework of a molecular sieve and includes for example titanium and chromium. The process of the present invention is applicable to any synthesis of a metal containing molecular sieve which is normally sensitive to the presence of alkali metal in the template during syntheses of the molecular sieve. Preferably the metal is titanium and the metal oxide is silica/titania. In the process of the present invention it has been found that the use of an intermediate silica titania co-precipitate or co-gel in the synthesis of zeolite isomorphous substituted molecular sieves enables the use of impure templating agents. In particular it is possible to use templating agents which contain relatively high levels of alkali metal species such as Na+ and K+ cations. This is particularly advantageous as the normal practice in the synthesis of molecular sieve materials using organic templating agents is to ensure as far as possible the total absence of alkali metal cations. Typically the levels of sodium are 20 ppm or less and the levels of potassium are 5 ppm or less. In the present invention therefore the templating agents do not have to be alkali metal free and may have 20ppm or higher levels of sodium and/or 5 ppm or higher levels of potassium. Preferably the sodium and/or potassium levels are greater than 50 ppm, preferably greater than 100 ppm and most preferably greater than 130 ppm. The levels may be greater than 500 ppm.

A number of titanium isomorphous substituted molecular sieves may be prepared by this method. Which molecular sieve is produced will depend on the templating agent used and the presence of other precursors for the particular zeolite desired. It is envisaged that the process will be particularly suitable for the production of titanium isomorphous substituted silicalite molecular sieves such as beta and MCM-41 molecular sieves.

The co-precipitate or co-gel may be made by any of the known processes in the art. As example suitable co-precipitates and co-gels may be made according to EP 0311 983 which describes the synthesis of a co-precipitate, WO95/03249, WO95/03250. and sol-gel methods as disclosed in M.A. Ugina, et. al., Applied Catalysis A: General. 124, 391-408; P. Serrano, et. al., Microporous Materials. 4, 273-282. and M. A. Camblor. et. al.. Applied Catalysis A: General. 133, L185-L189, (1995).

The desired titanium isomorphous substituted molecular sieve may be derived from the co-precipitate or the co-gel using organic templating agents containing high levels of alkali metal cations via either the hydrothermal crystallization of a liquid gel produced by the complete dissolution of either a co-precipitate or a co-gel; by the formation of a liquid gel with incomplete dissolution of the co-gel or co-precipitate or by incipient wetness impregnation of the co-precipitate or co-gel as described in M. A. Camblor. et. al., Applied Catalysis A: General, 133, L185-L189, (1995), and US5474754

TS-1 may be made by the following process. The silica titania co-precipitate may be formed by mixing any suitable silica source together with a source of titanium to form a co-solution which may then be subject to the appropriate conditions for coprecipitation. In a preferred embodiment the silica source such as for example tetra ethyl ortho silicate (TEOS) is hydrolysed in an acid environment preferably a nitric acid environment followed by addition of a solution of a titanate such as for example tetrapropyl ortho titanate (TPOTi) in a suitable solvent such as for example isopropanol. The titanate is not hydrolysed before mixing with the silica source. The silica source solution is free of alkali metal ions such as K+ or Na+ and is either neutral (pH=7) or is acidic (pH< 7). This careful control of the hydrolysis environment ensures that there are no significant amounts of polymeric TiO_2 species formed in the co-solution and in the resulting co-precipitate. The silica source solution and the titania source solution are free of organic templating agents.

Once the co-solution is produced the silica titania may be co-precipitated by removal of water and the solvent used to prepare the co-solution. The water and solvent may be removed by evaporation at ambient temperatures or may be removed by heating or by supercritical CO_2. We have found that heating to a temperature in the range of room temperature to 200°C is particularly suitable, preferably it is in the range 80 to 120°C.

The silica titania co-precipitate may then be used for the production of titanium isomorphous substituted molecular sieves, such as silicalite-1, by dissolution in an appropriate templating agent e.g. tetra propyl ammonium hydroxide (TPAOH). The resultant solution may then optionally be seeded with colloidal molecular sieve such as colloidal silicalite which may be prepared according to the procedure described in for example WO93/08125 the disclosure of which is incorporated by reference. Once seeded the titanium containing molecular sieve e.g. silicalite-1 may be obtained by crystallisation whilst stirring at an appropriate temperature and over an appropriate period of time. For example we found 1 to 30 days preferably 1 to 10 days and most preferably is at least 3 days at 50 to 200 C preferably 130 to 180°C to be particularly suitable for the formation of isomorphous titanium silicalite-1.

The crystallised product obtained may be removed from the crystallisation medium by filtration and the washed.

Templating agent may be used in the formation of the co-precipitate or co-gel. In this aspect the templating agent will need to be substantially free of alkali metal cations. Typical templating agents include for example TEAOH. TPAOH. TMAOH and dibenzyldimethyl ammonium hydroxide.

The titanium containing catalysts of the present invention are useful catalysts, particularly for hydrocarbon oxidation. The direct oxidation of saturates to introduce functional groups such as ketones and alcohols using a heterogeneous catalyst system would be extremely attractive especially if there is high conversions and selectivity for either alcohol or ketone or even if conversion is low there is relatively high selectivity for one of the products.

The titanium isomorphous substituted molecular sieve catalysts of the present invention and in particular titanium silicalite-1 have been found to be an active oxidation catalyst especially for reactions involving hydrogen peroxide as oxidant. The new catalysts may also be effective with organic hydroperoxide oxidants.

When aqueous hydrogen peroxide is used the solution contains from 10-100, preferably 10 to 70 wt % hydrogen peroxide for example diluted hydrogen peroxide (30 to 40% by weight in water). It is also preferred that a polar solvent be present when aqueous hydrogen peroxide is used to increase the solubility of the organic compound in the H2O2 aqueous phase. Examples of suitable solvents include acetone and methanol.

The oxidising agent may be an organic hydroperoxide, examples of suitable organic hydroperoxides include di-isopropyl benzene monohydroperoxide, cumene hydroperoxide, tert. butyl hydroperoxide, cyclohexylhydroperoxide, ethylbenzene hydroperoxide, tert. amyl hydroperoxide, tetraline hydroperoxide and the compound containing the saturated organic group is liquid or in the dense phase at the conditions used for the reaction. When the oxidant is a an organic hydroperoxide then tertiary butyl hydroperoxide is particularly beneficial since the tertiary butyl alcohol produced can readily be converted to the valuable isobutylene molecule. The preferred oxidising agent is hydrogen peroxide.

It is possible to oxidise saturated aliphatic compounds including aliphatic substituents of aliphatic/aromatic compounds by the process of the invention. The saturated groups which may be oxidised by the process of this invention include long or short, branched or linear alkanes containing 3 or more, preferably 3 to 30, more preferably 3 to 12 carbon atoms, cyclic alkanes and mono- and poly- alkyl aromatics in which at least one of the alkyl groups contain at least two preferably at least three, more preferably 3 to 18, most preferably 3 to 12 carbon atoms and mono- and poly-alkyl cyclic alkanes. The process of the invention is equally applicable to the epoxidation of olefins, dienes, the production of ether glycols, diols, the oxidation of alcohols or ketones, aldehydes, to acids and the hydroxylation of aromatics. We have surprisingly found that by the selection of appropriate conditions saturated groups may be oxidised with high selectivity to alcohols and ketones under relatively mild conditions. One particularly useful application is in the oxidation of linear and branched paraffins to secondary alcohols and ketones. The process is especially useful in the lower carbon number range to enable use of low-cost propane and butane feedstock in the manufacture of isopropanol alcohol, acetone, secondary butyl alcohol and methyl ethyl ketone. The aliphatic substituent may be a part of a totally aliphatic compound, an aryl compound (alkyl aromatic) or an alkylnaphthene compound. Furthermore, said compound may contain other functional groups providing they do not prevent the desired oxidation reaction taking place.

The reactivity sequence for the aliphatic compounds slows down from tertiary to secondary and to primary compounds.

Particular advantages of the present invention are that the process uses mild temperature and pressure conditions and the conversion and yield are high and by-product formation is small. In particular the oxidant conversion is high. The optimum reaction temperature is between 50 and 150°C, preferably about 100°C when using hydrogen peroxide. The oxidation reaction may be in the liquid or dense phase or in the gaseous phase, preferably the reactions are in the liquid phase.

The reaction can be carried out at room temperature but higher reaction rates may be involved at higher temperatures, for example under reflux conditions. Through increase of the pressure either due to the autogeneous pressure created by the heated reactants or by use of a pressurised reactor still higher temperatures can be reached. Use of higher pressures in the range of 1 to 100 bars (105 to 107Pa) can increase the conversion and selectivity of the reaction.

The oxidation reaction can be carried out under batch conditions or in a fixed bed, and the use of the heterogeneous catalyst enables a continuous reaction in system. The catalyst is stable under the reaction conditions, and can be totally recovered and reused.

The oxidation process of the present invention is preferably carried out in the presence of a solvent. Choice of solvent is important since it should dissolve the organic phase and the aqueous phase when hydrogen peroxide is used which is generally present due to the use of aqueous hydrogen peroxide as the oxidising agent. where organic hydroperoxides are used suitable organic solvents should be used. Polar compounds are preferred which are inert under reaction conditions, and examples of preferred solvents are alcohols, ketones and ethers, with a number of carbon atoms which is not too high, preferably less than or equal to 6. Methanol or tertiary butanol is the most preferred of the alcohols, acetone and butanone are the most preferred of the ketones. The amount of solvent may influence the reaction product and the conversion, the choice of solvent and the amount depending on the material to be oxidised. We have found, for example, that when oxidising normal hexane with aqueous hydrogen peroxide yields are improved when the ratio of acetone to hexane is in the range 1:1 to 4:1. The solvent improves the miscibility of the hydrocarbon phase and the aqueous phase which is generally present due to the use of aqueous hydrogen peroxide as the oxidising agent. If, however, the peroxide is supplied as a solution, such as tertiary butyl hydroperoxide which is frequently dissolved in ditertiary butyl peroxide, and the substrate is soluble in the solvent then no additional solvent is required.

The invention will be described with further details including a preparation of the catalyst and several examples of oxidation reactions.

EXAMPLE 1

TS-1 (Euro Cat.) was made following the Enichem procedure (U.S. patent 4.410.501)

The composition ratio Si:Ti:OH: H_2O 1:0.03:0.43:30
25.8 g of TEOS was transfered to a Teflon beaker and vigorously stirred; 0.8 ml of TEOT was carefully dripped into this TEOS, whilst nitrogen was flushed over it to prevent carbon dioxide absorption. The temperature was raised to 35°C and the reactants were mixed homogeneously for half an hour. Then the mixture was cooled to 0°C. 53.3 g of a 20 % aqueuos solution of TPAOH (low levels of alkali metal) .was added very slowly into the mixture of TEOS and TEOT. After addition of all TPAOH. the mixture was heated in about one hour to a temperature in the range 80 - 90°C.The mixture was kept for 3 to 5 h at this temperature. Distilled

water was added to increase the volume of the mixture to its original value of about 0.085 l. The hydrothermal synthesis was done at 175° C for 3 days.

The catalyst was characterized by XRD, UV-Vis, IR, ICP and its catalytic performance in n-heptane oxidation with 30% H_2O_2. The catalytic test results are summarized in Table 1.

TEOS = Tetra Ethyl ortho Silicate
TEOT = Tetra Ethyl ortho Titanate
TPAOH = Tetra Propylammonium Hydroxide

Example 2

TS - 1 made by using Grace coprecipitated TiO_2- SiO_2 (European patent 0311983)

32.6 g TiO_2 - SiO_2 Grace (TiO_2 4.3% 0.52 mol. 50 micron) was dissolved in 158.3 g aqueous TPAOH 40% (containing 26 ppm K^+,630 ppm Na^+)· Then 183.46 g H_2O was added at once. The reaction mixture was charged into Teflon-lined autoclave and heated to 175°C under stirring 350 rpm. for 2 days. After cooling the material was centrifuged and washed with water several times. The calcination was done at 550° C for 16 h in an air flow .The catalyst was characterized by XRD to indicate a solid highly crystaline titanium zeolite, and ICP to indiate the presence of high levels of titanium. Its catalytic perfomance in n-heptane oxidation with 30% H_2O_2 was evaluated.

The catalytic test shows the following results (Table 1)

Example 3

TS-1 was synthesized using a freshly prepared silica -titania coprecipitate. The silica-titania coprecipitate was made by hydrolizing TEOS and TEOT in a 0.05M HNO_3 solution. The resulting clear solution was heated at 100°C under stirring until a white solid material formed. This material was then dried overnight at 120°C to remove the remaining water and alcohol. The coprecipetate was found to be amorphous by X-ray powder diffraction. Typical procedure is as follows: 300g TEOS (1.44 mol) was added slowly to 1460 g 0.05M HNO_3 (7.26 g HNO_3 65%). 16.22g TEOT(0.048 mol) was disolved in 162g isopropanol and was added dropwise to the silicen solution (addition time 5h) Si: Ti ratio 30:1

Example 4

23 g TiO_2/SiO_2 (freshly made following example 3) was dissolved in 116.8 g TPAOH 40% (26 ppm K^+,630 ppm Na^+), then 112 H_2O was added. The TS-1 mixture was charged into Teflon-lined autoclave and heated at 175° C under stirring conditions for 5 days. The mixture was cooled, centrifuged and washed with water several times. The solid material was dried at 120°C overnight, then calcined at 550° C for 16 h in air. The catalyst was characterized by XRD, UV-VIS, ICP, and its catalytic performance in n-heptane oxidation with 30 % H_2O_2.

The catalytic test shows the following results (table 1)

Example 5

The composition ratio Si : Ti : HO^-: Q^+ : H_2O 1: 0.03 : 0.132:0.09 :27

35 g TiO_2-SiO_2 was dissolved in a solution of 26.6 g TPAOH 40 %, 269 g H_2O, 0.1 g NaOH, subsequently 5 g of colloidal seed, which are 0.16 wt %, was added to the mixture. The mixture was charged into Teflon-lined autoclave, then it was stirred at 350 rpm and heated to 180°C for 3 days. The mixture was cooled, centrifuged and washed with water several times. The solid material was dried at 120° C overnight and calcined at 550°C for 16 h in air.

The catalyst was characterized by XRD and its catalytic performance. The catalytic test results are summarized in table I

Example 6

Molar ratio : Si : Ti : HO^- : Q^+ : H_2O 1:0.03 : 0.57 : 0.51 : 30.

27 g TiO_2-SiO_2 was added to solution of 114.2 g TPAOH 40 % 174 g H_2O, O.13 g NaOH, subsequently 5 g colloidal seed, which are 0.16 wt %, was added. The mixture was stirred for 2 h, then transfered to Teflon-lined autoclave. The hydrothermal synthesis was done at180° C for 3 days under stirring conditions (350 ppm). The mixture was cooled, centrifuged and washed with water several times. The solid material was dried at 120° C overnight and calcined at 550° C for

16 h. The catalyst was characterized by XRD and its catalytic performance. The catalytic oxidation results are summarized in table 1.

Example 7

The composition molar ratio: Si : Ti : HO^- : Q^+: H_2O 1: 0.03 : 0.05 : 0.023 : 31

31 g TiO_2-SiO_2 was added to a solution of 11.678 g TPAOH 40 % 0.088 g NaOH. 272 g water. subsequently 5 g colloidal seed, which are 0.16 w %. was added. Then the mixture was charged into Teflon-lined autoclave, stirred at 350 rpm and heated to 160°C for 3 days. After cooling the mixture was centrifuged and washed with water several times. The solid material was dried at 120°C overnight and calcined at 550°C for 16 h. The solid material was characterized by XRD and its catalytic performance. The catalytic oxidation results are summarized in table I.

Example 8

The composition molar ratio: Si : Ti : HO^- : Q^+: H_2O I: 0.03 : 0.05 : 0.023 : 31

31 g TiO2-SiO_2 was added to a solution of 11.678 g TPABr , 0.088 g NaOH, 272 g water. subsequently 5 g colloidal seed. which are 0.16 wt %, was added. Then the mixture was charged into Teflon-lined autoclave, stirred at 350 rpm and heated to 160°C for 3 days. After cooling the mixture was centrifuged and washed with water several times. The solid material was dried at 120°C overnight and calcined at 550°C for 16 h. The catalytic test in n -heptane oxidation gives the following results Table 1

Example 9

22.7 g TiO_2-SiO_2 was dissolved in a solution of 73.588 g NH_4OH 25 %. 8.67 g TPABr. 151.75 g H_2O, subsequently 5 g colloidal seed, which are 0.16 wt %, was added. The mixture was charged intoTeflon-lined autodave, which was heated to 175°C for 5 days. The hydrothermal synthesis was performed under stirring conditions. The mixture was cooled. centrifuged and washed with water several times. The solid material was dried at 120°C overnight and calcined at 550°C for 16 h. The solid material was characterized by XRD and its catalytic performance. which shows the following results(table I).

Oxidation Examples

The catalyst were tested in n-heptane oxidation with aqueous H_2O_2 30 %. The reaction conditions are 20.4 g n-heptane (0.204 mol), 44.4 g H_2O_2 30 % (0.39 mole), 1 g catalyst. 71.1 g acetone. 100° C, under magnetic stirring.
The results are summarized in the following table.

Table 1

oxidation of n-heptane with H_2O_2 30 % over TS-I			
catalyst (made) following	conversion mole%	Selectivity mol %	
		alcohols	ketones
EXAMPLE 1	57	39	61
EXAMPLE 2	30	48	51
EXAMPLE 3/4	72	36	63
EXAMPLE 5*	48	44	56
EXAMPLE 6*	47	49	51
EXAMPLE 7	30	45	55
EXAMPLE 8	23	76	24
EXAMPLE 9	23	52	48
EXAMPLE 9*	41	35	64
comparitive sample	0.2	100	-

*The catalyst was treated with a solution of H_2SO_4 as described in the following procedure: 3 g. calcined catalyst was stirred with 1M H_2SO_4 overnight at room temperature. The mixture was centrifuged and washed with water several times till pH 7 was obtained. The solid material was dried at 120° C overnight.

As Table 1 shows, our synthesis' method (Examples 2, and 3/4) in the presence of Na^+ or even with deliberatly added Na^+ (Examples 5:6,7,8) give a catalyst which does not contain anatase at all as verified by UV-VIS, and this are very active in oxidation of hydrocarbons with H_2O_2.

CLAIMS

1. A method for the synthesis of a metal isomorphous substituted molecular sieve which method comprises;

a) forming a co-precipitate or co-gel comprising metal oxide in the absence of alkali metal. and

b) crystallising the co-precipitate or co-gel in the presence of an organic templating agent to form a the a metal isomorphous substituted molecular sieve.

wherein the level of alkali metal within the organic structure directing agent is at least 50 ppm.

2. A method as claimed in claim 1 wherein the metal is titanium and the metal oxide comprises silica titania

3. A method as claimed in claim 2 wherein the titanium isomorphous molecular sieve is a titanium silicalite.

4. A method as claimed in any of claims 2 to 3 wherein the titanium isomorphous molecular sieve comprises at least 1mole % of Ti.

5 A method as claimed in any of claims 2 to 4 which further comprises:

(a) dissolving a co-precipitate or co-gel or silica titania , which is substantially free of polymeric TiO_2 and alkali metal cations. in a solvent to form a gel,

(b) seeding the resultant gel with colloidal molecular sieve seeds to form a crystallisation mixture,

(c) allowing the titanium isomorphous substituted molecular sieve to crystallise from the crystallisation mixture, and

(d) separating the crystallised molecular sieve from the crystallisation mixture.

6 A method as claimed in any of claims 1 to 4 wherein the organic templating agent is a tetraalkyl ammonium hydroxide or halide.

7. A method as claimed in any of claims 2 to 5 wherein the silica titania co-precipitate is made by the process of any of claims 8 to 13.

8. A method for manufacturing a silica titania co-precipitate which is substantially free of alkali metal cations which method comprises;

(a) preparing a titania source solution substantially free of alkali metal cations and which comprises an organometallic titanium precursor which is not hydrolysed,
(b) preparing a silica source solution substantially free of alkali metal cations which solution comprises the hydrolysis product of an organometallic silica precursor and wherein the solution is at pH 7 or less,
(c) addition of solution (a) to solution (b) to produce a co-solution, and
(d) removing the solution solvent and any water from the co-solution to provide a co-precipitate which is substantially free of alkali metal cations.

9. A method as claimed in claim 8 wherein the organometallic titanium precursor is a titanate.

10. A method as claimed in either claim 8 or claim 9 wherein the co-precipitate is formed from an alcoholic co-solution.

11. A method as claimed in any of claims 8 to 10 wherein the co-solution is heated in the range 70°C to 250°C.

12. A method as claimed in any of claims 8 to 11 wherein the silica source solution has a pH of less than 7.

13. A method as claimed in any of claims 8 to 12 wherein the silica source solution is acidified with a mineral acid.

14. A method as claimed in claim 13 wherein the mineral acid is nitric acid.

15. A method for the oxidation of an aliphatic hydrocarbon or an alkylaromatic hydrocarbon to an alcohol which method comprises oxidising the hydrocarbon in the presence of a titanium silicalite-1 isomorphous substituted molecular sieve as prepared by example ?.

16 A method as claimed in claim 15 wherein the oxidation is undertaken in the

presence of hydrogen peroxide.

17 A method as claimed in either of claims 15 or 16 wherein the hydrocarbon is a saturated aliphatic hydrocarbon.

18. A titanium isomorphous substituted molecular sieve obtainable by the process of any one of claims 2 to 14.

INTERNATIONAL SEARCH REPORT

Int ational Application No
PCT/EP 98/00765

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B37/00 B01J29/04

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MIGUEL A. CAMBLOR: "Large pore Ti-Beta zeolite with very low aluminium content: an active and selective catalyst for oxidations using hydrogen peroxide" INDUSTRIAL CHEMISTRY LIBRARY, vol. 8, 1996, pages 391-404, XP002067432 see page 393, line 5 - page 395, line 6	8-13,18
A	---	1-3,5-7, 14-17

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of theinternational search 18 June 1998	Date of mailing of the international search report 03/07/1998
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Rigondaud, B

2

INTERNATIONAL SEARCH REPORT

Int. ational Application No
PCT/EP 98/00765

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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