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(54) **Title**: THERMALLY AND MECHANICALLY STABLE PRECIOUS METAL-LOADED CATALYSTS

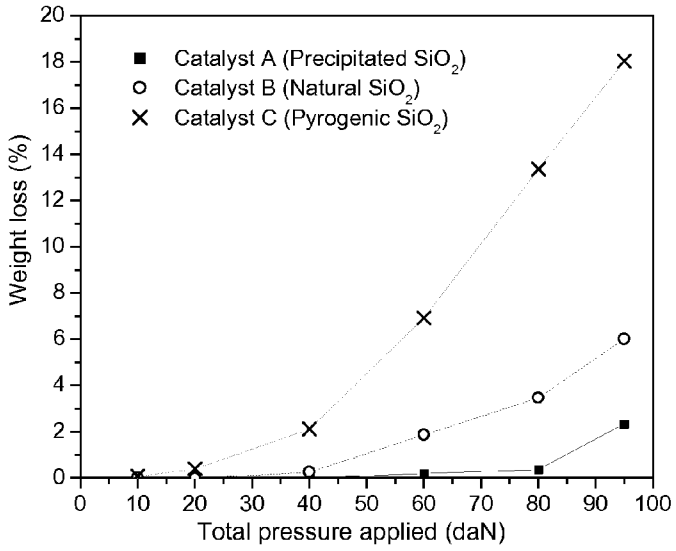

Figure 3 Bulk crush strength test results of finished catalysts

(57) **Abstract**: Catalyst comprising palladium, gold and alkali metal acetate as catalytically active components on an abrasion-resistant support, which is mechanically and thermally stable, shaped bodies that are produced from synthetically pure and mixed metal oxides which may be also modified by means of aluminum, calcium, cerium, iron, lanthanum, magnesium, molybdenum, titanium, yttrium and/or zirconium or oxides thereof. It can be used for preparing vinyl acetate monomer.

WO 2011/104170 A1

Title: Thermally and mechanically stable precious metal-loaded catalysts

Abstract

Catalyst comprising palladium, gold and alkali metal acetate as catalytically active components on an abrasion-resistant support, which is mechanically and thermally stable, shaped bodies that are produced from synthetically pure and mixed metal oxides which may be also modified by means of aluminum, calcium, cerium, iron, lanthanum, magnesium, molybdenum, titanium, yttrium and/or zirconium or oxides thereof. It can be used for preparing vinyl acetate monomer.

BACKGROUND OF INVENTION

The invention relates to a catalyst, a process for producing a catalyst which covers a catalyst form with an outer shell containing metal(s). Such catalysts are useful for example, for vinyl acetate monomers (VAM) production.

Processes for preparing vinyl acetate monomer are known from DE 16 68 088, EP-A 0 464 633, EP-A-0 519 435, EP-A 0 634 208, EP-A 0 723 810, EP-A 0 634 209, EP-A 0 632 214, EP-A 0 654 301, EP-A 0 723 810, U.S. Pat. No. 4,048,096, U.S. Pat. No. 5,185,308 and U.S. Pat. No. 5,371,277. These documents also describe processes for producing supported catalysts. Depending on the embodiment, supported catalysts having a homogeneous distribution of noble metal over the cross section of the support and catalyst having a more or less pronounced shell profile are produced.

DE-B 21 00 778, U.S. Pat. No. 4,902,823, U.S. Pat. No. 5,250,487, U.S. Pat. No. 5,292,931, U.S. Pat. No. 5,808,136, EP 0 807 615, EP 0 916 402, EP 0 997 192 A1, EP 1 323 469 A2 and EP 0 987 058 disclose the use of shaped bodies based

on pyrogenic silicon dioxides as catalyst supports in the preparation of vinyl acetate monomer.

These patent texts also disclose a process for producing the supported catalysts containing gold, palladium and alkali metal compounds. Depending on the embodiment, catalysts having a homogeneous noble metal distribution over the cross section of the support and catalysts having a more or less pronounced shell profile are obtained.

These catalysts are usually obtained by impregnating the support with a basic solution and a solution containing gold and palladium salts, with the impregnations occurring simultaneously or in succession, with or without intermediate drying. The support is subsequently washed to remove any chloride present. Before or after washing, the insoluble noble metal compounds precipitated on the support are reduced. The catalyst precursor obtained in this way is dried and impregnated with alkali metal acetates or alkali metal compounds which are converted completely or partly into alkali metal acetates under the reaction conditions in the production of vinyl acetate monomer in order to activate the catalyst. Preferred alkali metal compounds are potassium compounds, in particular potassium acetate.

The reduction of the catalyst can be carried out in the aqueous phase or in the gas phase. To carry out the reduction in the aqueous phase, suitable reducing agents are, for example, formaldehyde or hydrazine. The reduction in the gas phase can be effected using hydrogen or a hydrogen/nitrogen mixture (95% by volume of N_2+5% by weight of H_2) or ethylene. According to EP 0 634 209, the reduction is carried out using hydrogen at temperatures in the range from 40 to 260 °C., preferably from 70 to 200 °C. However, the catalyst is frequently reduced by means of ethylene directly in the production reactor only after activation by means of alkali metal acetate.

In the production process, the catalyst is firstly supplied only slowly with the reactants. During this start-up phase, the activity of the catalyst increases and usually reaches its final level only after days or weeks.

The document EP 0 431 478 describes a process for preparing vinyl acetate in the gas phase from ethylene, acetic acid and oxygen over a catalyst containing palladium and gold on a support. The support comprises a SiO_2/Al_2O_3 mixture, with the support particles being pressed with the aid of Li, Mg, Al, Zn or Mn salts of a C_2-C_{20}-carboxylic acid as binder.

The document EP 0 723 810 A1 describes a supported catalyst for the production of vinyl acetate monomer, which contains palladium, gold, and alkali metal acetate as catalytically active components on a support composed of silicon dioxide, silicon dioxide gel, aluminosilicate or aluminium oxide, with the support additionally containing at least one element of groups I A, II A, III A and IV B of the Periodic Table.

Supported catalysts containing gold, palladium and alkali metal compounds are used for the production of vinyl acetate. For this purpose, ethylene, acetic acid and molecular oxygen or air are reacted in the gas phase, with or without addition of inert gases, at temperatures in the range from 100 to 250 °C and under ambient or super atmospheric pressure in the presence of the supported catalyst.

WO 2008145389, US 2003187293, US 6072078 and WO 9962634 disclose the use of shaped bodies based on natural silicon dioxide-based support for catalysts preparation. As described in US 6207610 B1, pyrogenic SiO_2-based support shows crush strength 10 – 250 Newton and abrasion < 5 wt%. According to WO 2008145389, crush strength is 20 – 40 Newton. Catalyst prepared using a

support based on synthetic material, especially spherical shape, gives rise to less abrasion problems when loading catalyst into a tubular reactor. Mechanical strength and thermal stability of a catalyst prepared on a synthetic-based material still remained a problem for prolonged operation stability using the existing technology.

SUMMARY OF INVENTION

The objective of this invention is to provide a catalyst that can maintain its performance after exposure to high abrasion or impact forces similar to those experienced when loading catalyst in a tubular reactor, said catalyst should also exhibit high thermal stability.

This objective is achieved by a catalyst according to claims 1 to 10. The catalysts according to the invention are particularly useful for vinyl acetate monomer production.

The catalyst according to the invention is a supported catalyst comprising a support molding and a catalytically active component,
wherein the catalytically active component comprises at least one member selected from the group consisting of palladium and palladium compounds, at least one alkali metal compounds and at least one member selected from the group consisting of gold, gold compounds, aluminum, alumina compounds, cadmium, barium, barium compounds, cadmium compounds, calcium, calcium compounds, cerium, cerium compounds, copper, copper compounds, iron, iron compounds, lanthanum, lanthanum compounds, magnesium, magnesium compounds, molybdenum, molybdenum compounds, titanium, titanium compounds, yttrium, yttrium compounds, zirconium and/or zirconium compounds,

and wherein the support molding comprises a synthetically produced precipitated pure or mixed oxide.
Precipitated pure or mixed oxide are oxides chosen from the group consisting of Aluminium, Zirconium, Titanium or Cerium or mixtures thereof.

The catalyst of the invention has the advantage to avoid the problem of catalyst abrasion and thermal stability while maintaining its maximum catalytic activity.

There is no prior art describing usage of precipitated pure or mixed oxide supports based on thermally and mechanically stable oxides for catalysts especially for such catalysts that can be used in vinyl acetate monomer production.

Depending on the embodiment, catalysts having a homogeneous noble metal distribution over the cross section of the support and catalysts having a more or less pronounced shell profile are obtained.

Preferably the supported catalyst according to the invention is a shell type catalyst.

A shell type catalyst is a catalyst comprising a support and a catalytcally active component that is deposited onto the support in the form of an outer shell which partially or completely encases the support.

As support material, it is possible to use precipitated highly pure synthetic oxides and mixed synthetic oxide or carbide mixture, for example thermally and mechanically stable SiO_2 gel prepared with or without using binder.

The invention preferably provides a shell-type catalyst comprising e.g. palladium, gold and alkali metal acetate as catalytically active components on a

mechanically and thermally stable synthetic support, such as precipitated SiO_2, SiO_2 gel, ZrO_2, other metal oxides, SiC and metal oxide mixture, for example aluminosilicate.

The supported catalyst preferably comprises precipitated pure or mixed oxide which is selected from one or more of the group consisting of SiO_2, SiO_2 gel, Al_2O_3, TiO_2 and ZrO_2 in any desired combination but with the exception of SiO_2/Al_2O_3 mixed oxides, in which at least 75wt.% of SiO_2 is present.

More preferably at least 90 wt.% of the precipitated pure or mixed oxide is SiO_2. Even more preferably at least 95 wt.% of the precipitated pure or mixed oxide is SiO_2 and most preferably at least 98 wt.% of the precipitated pure or mixed oxide is SiO_2.

Precipitated oxides are known in the art. The synthesis process for e.g. precipitated silica is described in, JP 8-333112, JP 07196309 and JP 3658416 (& JP 2000169134: preparation of spherical SiO2 using the precipitated silica). Precipitated silica is prepared by pH swing precipitation of Na silicate.

The catalyst when charged into the tubular reactor, for example reactors for vinyl acetate production, causes catalyst abrasion due to the length of the reactor (generally 6-8 m long). Attrition and abrasion of mechanically unstable catalyst result in reduction of activity due to loss of outer layer which consists of metals especially for the shell-type catalyst. Mechanically stable catalysts can avoid losing active sites during catalyst loading. Similarly a catalyst with low crushing strength can break during loading causing high pressure drop across the catalyst bed.

The supported catalyst according to the invention thus preferably exhibits abrasion of less than 1 wt%. Abrasion is measured according to ASTM D 4058-96.
The crushing strength of a single bead of the supported catalyst according to the invention is preferably at least 100 N, more preferably at least 251 N and most preferably at least 260 N. The crushing strength is measured according to ASTM D 4179.

The bulk crush strength of the supported catalyst according to the invention is preferably less than 5 wt% at 950 N. The bulk crush strength of the supported catalyst is measured according to ASTM D 7084.

In yet another embodiment of the supported catalyst according to the invention the supported catalyst exhibits less than 10% reduction of the BET surface area at temperatures higher than 500 °C for at least 30 min. More preferably the supported catalyst exhibits less than 10% reduction of the BET surface area at temperatures higher than 500 °C for at least 120min.

It is also preferred that the average pore diameter of at least 50% of the pore volume of the supported catalyst is larger than 3 nm.

Preferably at least 50% of the pore volume of the supported catalyst according to the invention is contained in major mode of the pore size distribution.

BET surface area, pore volume and average pore diameter are determined by nitrogen adsorption-desorption method.

The invention further provides a process for producing the catalyst. Said process is characterized in that the support molding is impregnated with or without a salt of at least one doping component, calcined and subsequently impregnated with

the catalytically active component or the support material is mixed with an oxide of the doping component, shaped and subsequently impregnated with the catalytically active components. Calcination is a thermal treatment carried out at temperatures between 200°C and 1000°C, e.g. 450°C for 20min to 4h, e.g. 1h.

This precipitated silica support enables to achieve the aforementioned supported catalyst due to its excellent mechanical strength. Pyrogenic or natural SiO_2 have insufficient mechanical strength.

The precipitated pure or mixed oxide leads to a thermally stable and mechanically strong support that is used for the catalyst preparation with the catalytically active component.

The catalyst stability is maintained under exposure to high temperatures in the range from 100°C to 1000°C, preferably 300°C to 900°C during the catalyst preparation and of course when the catalyst is used in a reaction.

The present invention also encompasses a process for producing vinyl acetate monomer in the presence of the supported catalyst as described above. For this purpose, ethylene, acetic acid and molecular oxygen or air are reacted in the gas phase, with or without addition of inert gases, at temperatures in the range from 100°C to 250 °C and under ambient or super atmospheric pressure in the presence of the supported catalyst according to the present invention.

DETAILED EMBODIMENTS OF THE INVENTION

EXAMPLES

The support material of example catalyst A comprises high purity precipitated silicon dioxide support with a particle diameter of about 5 mm. The high purity

SiO_2 is made by Fuji silysia. Catalytically active components are palladium, gold and potassium acetate.
Comparative catalyst B also comprises the active components palladium, gold and potassium acetate applied to a spherical natural silica support with diameters of about 5 mm (Süd Chemie KA-160).

In the case of example catalyst C, the active components palladium, gold and potassium acetate were applied to a support material comprising 100% of pyrogenic silicon dioxide (Degussa Aerolyst 3045).

METHOD
The test results of physical properties of catalyst support example A, B and C are disclosed in Table 1 and Table 2. BET surface area, pore volume and average pore diameter were determined by nitrogen adsorption-desorption method. The resistance of the support and the supported catalyst to abrasion was quantified by weighing the material before and after a period of abrasion in an apparatus, which complies to ASTM D 4058-96. Crushing strength of the individual catalyst support and supported catalyst particle was implemented by following ASTM D 4179. The bulk crush strength of the supported catalyst was measured by complying ASTM D 7084.

The results show that Example A is mechanically stronger than others. Fine powder was found at the end of the abrasion test for Example B and C. It is often reported that similar fine powder has been typically observed when loading catalyst in a tubular reactor. Fine powder was not observed after the abrasion test of Example A for 60 hours.

Table 2 reports the space time yield of vinyl acetate monomer as measure of the activity of the catalysts in gram of vinyl acetate monomer per hour at 150 ^{o}C, a pressure of 5 bar and a GHSV of 5000 h^{-1}:

The results of the catalyst evaluation are shown in Table 2. The results show that space time yield (STY) of a catalyst comprising precipitated SiO_2 support is superior to catalysts comprising natural SiO_2 and pyrogenic SiO_2. The catalyst evaluation after the attrition test show a distinct lessening of the STY to the catalyst comprising spherical natural SiO_2 when compared to the catalyst prepared using spherical precipitated SiO_2.

Table 1 Properties of support materials of example catalyst A and catalyst B

Catalyst support	BET Surface Area, m^2/g	Pore volume, mL/g	Average Pore Diameter nm	Average crushing strength Newton	Abrasion loss, wt%
Example A	113.3	0.75	20.3	> 275	< 0.0
Example B	156.9	0.48	10.1	42.5	1.9
Example C	149.7	0.93	20.1	-	-

Table 2 Catalyst activity, attrition test results and metal content of catalysts.

Attrition time	0 hr				6 hrs				24 hrs			
	STY (g/L-hr)	wt loss (%)	Pd (g/L)	Au (g/L)	STY (g/L-hr)	wt loss (%)	Pd (g/L)	Au (g/L)	STY (g/L-hr)	wt loss (%)	Pd (g/L)	Au (g/L)
Catalyst A	633	-	3.3	1.5	-	0.00%	3.3	1.5	672	0.0%	3.3	1.5
Catalyst B	601	-	3.3	1.5	-	0.22%	3.2	1.5	474	2.2%	3.1	1.5
Catalyst C	503	-	3.3	1.5	-	-	-	-	-	14.3%	-	-

STY-space time yield

What we claim is:

1. A supported catalyst comprising a support molding and a catalytically active component,
   wherein the catalytically active component comprises at least one member selected from the group consisting of palladium and palladium compounds, at least one alkali metal compounds and at least one member selected from the group consisting of gold, gold compounds, aluminum, alumina compounds, cadmium, barium, barium compounds, cadmium compounds, calcium, calcium compounds, cerium, cerium compounds, copper, copper compounds, iron, iron compounds, lanthanum, lanthanum compounds, magnesium, magnesium compounds, molybdenum, molybdenum compounds, titanium, titanium compounds, yttrium, yttrium compounds, zirconium and/or zirconium compounds,
   and wherein the support molding comprises a synthetically produced precipitated pure or mixed oxide.

2. A supported catalyst according to claim 1, wherein the supported catalyst is a shell type catalyst.

3. A supported catalyst according to claim 1 or 2, wherein the precipitated pure or mixed oxide is selected from one or more of the group consisting of SiO_2, SiO_2 gel, Al_2O_3, TiO_2 and ZrO_2 in any desired combination but with the exception of SiO_2/Al_2O_3 mixed oxides, in which > 75wt.% of SiO_2 is present.

4. A supported catalyst according to claim 3, wherein at least 90 wt.% of the precipitated pure or mixed oxide is SiO_2.

5. A supported catalyst according to any one of claims 1 to 4, wherein abrasion of the catalyst is less than 1 wt%.

6. A supported catalyst according to any one of claims 1 to 5, wherein the bulk crush strength of the supported catalyst is less than 5 wt% at 950 N.

7. A supported catalyst according to any one of claims 1 to 6, wherein the average crushing strength of a single bead is at least 251 N.

8. A supported catalyst according to any one of claims 1 to 7, wherein the supported catalyst exhibits less than 10% reduction of the BET surface area at >500 ^{o}C.

9. A supported catalyst according to any one of claims 1 to 8, wherein at least 50% of the pore volume of the supported catalyst is larger than 3 nm.

10. A supported catalyst according to any one of claims 1 to 9, wherein at least 50% of the pore volume of the supported catalyst is contained in major mode of the pore size distribution.

11. Process for producing a supported catalyst according to any one of claims 1 to 9, wherein the support molding is impregnated with or without a salt of at least one doping component, calcined and subsequently impregnated with the catalytically active component or the support material is mixed with an oxide of the doping component, shaped and subsequently impregnated with the catalytically active components.

12. Process for producing vinyl acetate monomer in the presence of supported catalyst according to any one of claims 1 to 10.

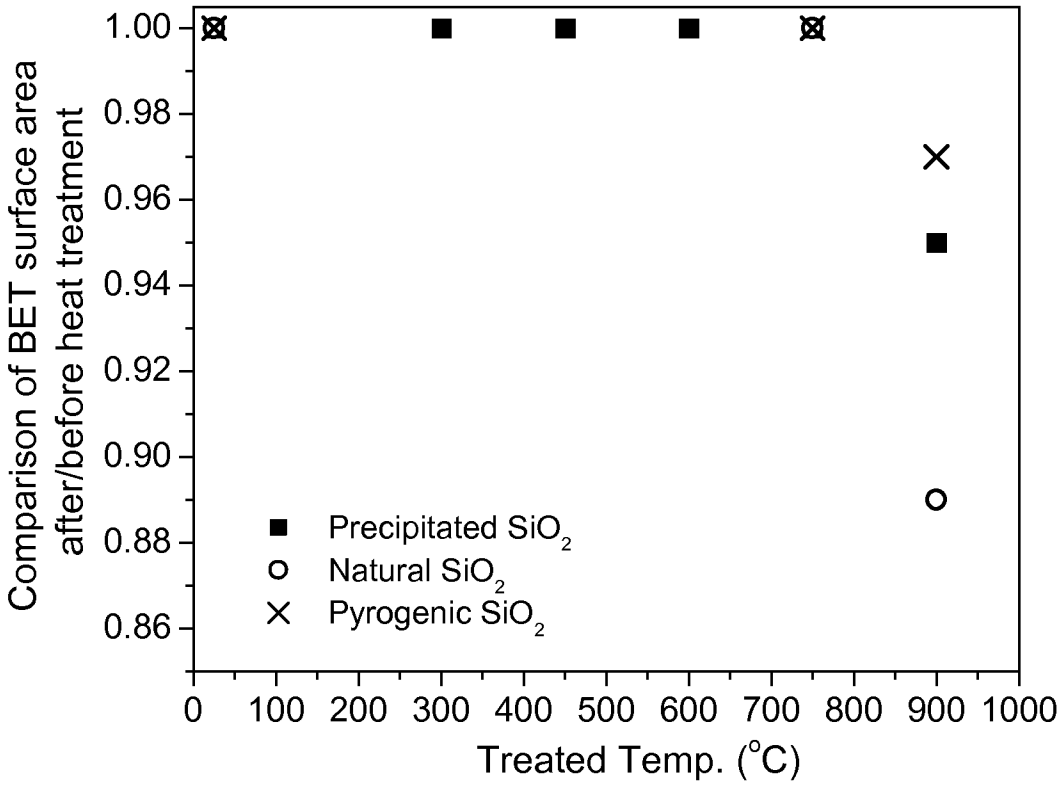

Figure 1: BET surface area of support A treated at different temperature for 2 hours in muffle furnace.

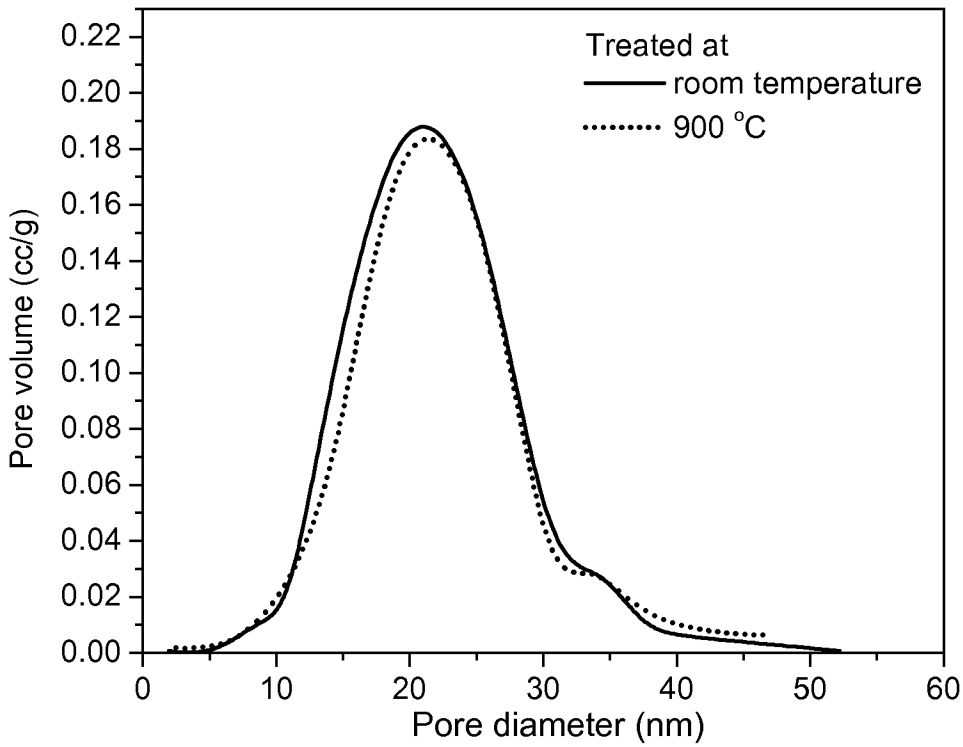

Figure 2: Pore size distribution of support A treated at different temperature for 2 hours in muffle furnace

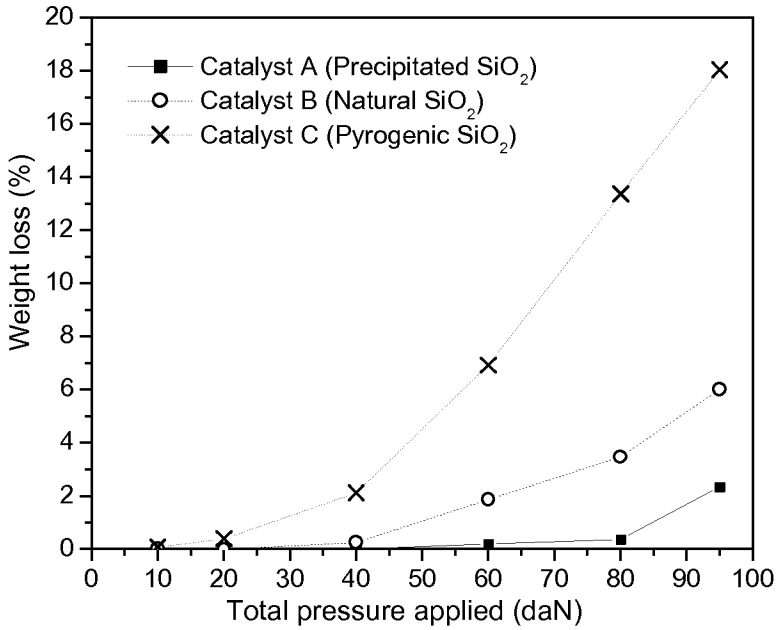

Figure 3 Bulk crush strength test results of finished catalysts

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/052396

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/58 B01J23/60 B01J23/63 B01J23/652 B01J23/66
B01J23/89 C07C67/055 B01J21/08 B01J37/03
ADD.
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)
B01J C07C

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 808 136 A (TACKE THOMAS [DE] ET AL) 15 September 1998 (1998-09-15) lines 31-34 - column 2 lines 6-11 - column 1; claims	1-12
X	EP 1 205 246 A1 (DAIREN CHEMICAL CORP [TW]) 15 May 2002 (2002-05-15) paragraph [0008]; claims	1-12
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X	US 5 225 388 A (WUNDER FRIEDRICH [DE] ET AL) 6 July 1993 (1993-07-06) claims; examples	1-12

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 May 2011	25/05/2011

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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