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(54) Benævnelse: **METALKATALYSTSAMMENSÆTNING**

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DESCRIPTION

[0001] This disclosure relates to metal catalyst compositions, methods of forming metal catalyst compositions, and in particular metal catalyst compositions that reduce coke formation during dehydrogenation reactions that produce olefins.

[0002] Dehydrogenation converts alkanes to alkenes (i.e., olefins) using metal catalysts, which increase the selectivity of the reaction. While metal catalysts increase the selectivity, they are vulnerable to carbon buildup, i.e., "coking." Coking deactivates the metal catalyst within minutes (e.g., 10 minutes (min)), after the dehydrogenation begins and blocks the flow of reactants, which results in higher pressure drops in the reactor.

[0003] To remove coke, the metal catalysts undergo an oxidation treatment at high temperatures (e.g, greater than 500 degrees Celsius (°C)). This adds cost to the olefin production, reduces carbon efficiency, and leads to sintering of metal particles of the metal catalyst, which causes catalyst degradation.

Figure (Fig.) 1 illustrates a high resolution transmission electron microscope (TEM) image of the metal catalyst composition Example (Ex) 1.

Fig. 2 illustrates diffuse reflectance infrared spectroscopy (DRIFTS) spectra of carbon monoxide (CO) chemisorption at saturation coverage on the metal catalyst composition of Ex 1 treated at different temperatures and of the uncoated metal catalyst of Comparative Example (Com Ex) 1.

Fig. 3 illustrates thermal gravimetric analysis (TGA) measurements of coke formation on the metal catalyst composition of Ex 1 and on the uncoated metal catalyst of Com Ex 1.

Fig. 4 illustrates TGA measurements of coke formation on the metal catalyst composition of Ex 2 and on the uncoated metal catalyst of Com Ex 2.

Fig. 5 illustrates scanning transmission electron microscopy (STEM) images for the over-coated catalyst of Ex 3.

Fig. 6 illustrates STEM images for the uncoated catalyst in Com Ex 1.

Fig. 7 illustrates STEM images for the uncoated catalyst in Com Ex 2.

Fig. 8 illustrates the dehydrogenation of ethane (DHE) reaction test using the metal catalyst composition of Ex 2.

Fig. 9 illustrates the pore size distribution of the metal catalyst composition of Ex 1 before and after activation.

Fig. 10A illustrates the nitrogen adsorption-desorption isotherms of the uncoated metal catalyst of Com Ex 1.

Fig. 10B illustrates the nitrogen adsorption-desorption isotherms of the metal catalyst composition of Ex 1 prior to activation.

Fig. 10C illustrates the nitrogen adsorption-desorption isotherms of the metal catalyst composition of Ex 1 after activation.

Fig. 10D illustrates the pore size distribution calculated from the adsorption branch of the isotherms for Fig. 10A-C.

[0004] "Over-coat" refers to a thin coating controlled to an atomic level that is deposited onto nano-size metal particles of a catalyst and the catalyst support.

[0005] "Alumina over-coat" refers to a coating of alumina controlled to an atomic level that is deposited onto nano-size metal particles of a catalyst and the catalyst support.

[0006] "Coking" refers to a solid carbonaceous buildup during the dehydrogenation reaction.

[0007] "Substrate" refers to a base and/or a support.

[0008] "Layer" refers to a coating. A layer can be a substrate and/or can be formed on a substrate or on another layer. A layer can be formed from the compounds of the present disclosure using an ALD process. Theoretically, an ALD cycle forms a layer that is uniformly one atom or molecule thick on an exposed surface. However, the layer may not occur on all portions of the exposed surface. Such a partial layer is understood to be a layer herein.

[0009] "Deposition", "deposition process" and "vapor deposition process" refer to a process in which a layer is formed on one or more surfaces of a substrate and/or a layer.

[0010] "Dehydrogenation" refers to a chemical reaction that involves the elimination of hydrogen (H_2) and can include dehydrogenation reactions that are oxidative or nonoxidative reaction.

[0011] "Atomic layer deposition" (ALD) is also meant to include the related terms "atomic layer epitaxy" (ALE), molecular beam epitaxy (MBE), gas source MBE, organometallic MBE, and chemical beam epitaxy when performed with alternating pulses of chemical components.

[0012] "As-prepared" refers to the metal catalyst composition prior to activation.

[0013] "Moieties" refers to any discrete unit of material structure, where the discrete units are comprised of atoms, molecules, ions or combinations thereof.

[0014] "Ligand" refers to refers to a nonmetallic ion, molecule, or atom that is attached to a central atom of a coordination compound.

[0015] A method of forming a metal catalyst composition includes performing a plurality of atomic layer deposition cycles to form an alumina over-coat on a supported metal catalyst, where one or more of the atomic layer deposition cycles include sequential steps: (a) contacting a supported metal catalyst surface with a ligand-containing alumina precursor for a predetermined contact time to form an intermediate layer having a plurality of aluminum moieties that chemically bond to the supported metal catalyst surface, (b) contacting the intermediate layer with an inert gas selected from the group consisting of helium, nitrogen, argon, neon, carbon dioxide and a combination thereof, for a predetermined intermediate stripping time that is from 1 s to 300 s, to remove unreacted ligand-containing alumina precursors, (c) reacting the aluminum moieties with water for a predetermined reaction time that is from 1 s to 300 s, to convert at least a portion of the ligands to hydroxyl groups thereby forming a layer of the alumina over-coat on the supported metal catalyst surface or a previously formed layer of the alumina over-coat, (d) prior to replicating the sequential steps (a), (b) and (c) to form an additional layer of the alumina over-coat, contacting the layer of the alumina over-coat formed in step (c) with an inert gas selected from the group consisting of helium, nitrogen, argon, neon, carbon dioxide and a combination thereof, for a predetermined final stripping time that is 1 s to 300 s, to remove unreacted water, and (e) activating the alumina over-coat, where said activating includes calcining the over-coat in the presence of a non-reducing gas selected from the group consisting of helium, nitrogen, argon, neon, oxygen, ozone, dry air and combinations thereof, at a temperature within a range from 500 °C to 800 °C for 60 minutes to 10 hours, after forming a final layer of the alumina over-coat having a thickness of from 1 nanometer to 100 nanometers, to form a plurality of pores therein. At least 80 percent (%) of the plurality of pores have a diameter within a range of from 0.3 nanometer (nm) to 5 nm, where the pore size distribution is determined using nitrogen BET. The metal catalyst composition reduces an amount of coke formed during a dehydrogenation or an oxidative dehydrogenation reaction, as compared to same supported metal catalysts without the alumina over-coat.

[0016] The metal catalyst composition includes the supported metal catalyst having the support with the plurality of metal particles, and an alumina over-coat deposited on a surface of the supported metal catalyst by atomic layer deposition followed by activating the alumina over-coat, according to the methods of the invention. Activating the alumina over-coat forms pores in the alumina over-coat, at least 80 percent (%) of the plurality of pores have a diameter within a range of from 0.3 nanometer (nm) to 5 nm, and where the alumina over-coat has a thickness within a range of from 1 nm to 100 nm. The disclosed metal catalyst compositions reduce an amount of coke formed during a dehydrogenation reaction, as compared to metal catalysts without the alumina over-coat.

[0017] ALD is a deposition technique in which vapors generated during each cycle can be sequentially directed to and/or sequentially contacted with a surface to form, for example, an alumina containing layer on the surface. The supported metal catalysts can be commercially purchased or formed with ALD. Forming supported metal catalysts with ALD is discussed in International Publication Number WO 2011/031288, titled "METAL CONTAINING

COMPOSITES".

[0018] WO 2010/135107 discloses that ultra-thin porous films are deposited on a substrate in a process that includes laying down an organic polymer, inorganic material or inorganic-organic material via an atomic layer deposition or molecular layer deposition technique, and then treating the resulting film to introduce pores. The films are characterized in having extremely small thicknesses of pores that are typically well less than 50 nm in size.

[0019] Supported metal catalysts include a substrate which supports a support, e.g., an oxide support, and metal particles that are chemically bonded to the support. Metal particles provide an activation site for the catalytic reaction.

[0020] Examples of the metal particles of the supported metal catalysts include, but are not limited to, palladium, platinum, rhodium, iridium, ruthenium, rhenium, gold, silver, copper, nickel, and combinations thereof. The metal particle is preferably palladium.

[0021] Examples of the support include, but are not limited to, aluminum oxide, titanium dioxide, silicon dioxide, niobium oxide, copper oxide, iron oxide, zinc oxide, cerium oxide, magnesium oxide, zirconium oxide, carbon aerogel, and combinations thereof. The support is preferably aluminum oxide. Additionally, the support of the supported metal catalyst can be porous or can be non-porous.

[0022] The substrate can have the same chemical composition or different chemical composition as the support. Examples of the substrate include, but are not limited to, silicon, glass, metals, polymers, porous host matrices (aerogels, silica gel, mesoporous silica), nitride, sulfide, carbon, nanowires, oxides, and combinations thereof.

[0023] The alumina over-coat is formed of sequential layers of the ligand-containing alumina precursors (also referred herein as "alumina precursors") and oxidizing reagents deposited via ALD. The deposition of each of the layers provides a consistently uniform layer growth rate for the alumina over-coat. There is an essentially constant growth rate of the alumina over-coat for each of the ALD cycles used in forming the alumina over-coat such that the thickness of the alumina over-coat is controlled to the atomic level.

[0024] ALD is performed in a viscous flow reactor system as discussed in J.W. Elam, M. D. Groner and S.M. George, "Viscous Flow Reactor with Quartz Crystal Microbalance for Thin Film Growth by Atomic Layer Deposition", Rev. Sci. Instrum. 73, 2981-2987 (2002). Other ALD systems are also suitable for embodiments of this disclosure. The ALD system maintains a temperature within a range of from 20 °C to 600 °C.

[0025] The alumina over-coat is formed on the supported metal catalyst by ALD, as described herein. For ALD, vapors used to form the alumina over-coat are sequentially pulsed into a reactor of the ALD system. "Vapors" include volatile and/or high vapor pressure liquids and/or solids.

[0026] Each ALD cycle of the present disclosure includes the following steps. An ALD cycle includes contacting a supported metal catalyst surface with a ligand-containing alumina precursor for a predetermined contact time to form an intermediate layer having a plurality of aluminum moieties that chemically bond to the supported metal catalyst surface. The predetermined contact time is from 1 second (s) to 300 s, preferably 60 s. Ligand-containing alumina precursors are selected from compounds having the formula $Al(R^1)_3$, where each R^1 is independently methyl, ethyl, propyl, chloride, bromide, dialkylamino, or alkoxide.

[0027] The ALD cycle includes contacting the intermediate layer with an inert gas for a predetermined intermediate stripping time to remove unreacted ligand-containing alumina precursors. The predetermined intermediate stripping time is from 1 s to 300 s, preferably 60 s. The inert gas is selected from the group consisting of helium, nitrogen, argon, neon, carbon dioxide and a combination thereof.

[0028] The ALD cycle includes reacting the aluminum moieties with an oxidation reagent for a predetermined reaction time to convert at least a portion of the ligands to hydroxyl groups thereby forming a layer of the alumina over-coat on the supported metal catalyst surface or a previously formed layer of the alumina over-coat. The predetermined reaction time is from 1 s to 300 s, preferably 60 s. The Oxidizing reagent is water.

[0029] Prior to forming an additional layer of the alumina over-coat, the ALD cycle includes contacting the layer of the alumina over-coat previously formed with an inert gas for a predetermined final stripping time to remove unreacted oxidation reagents. The predetermined final stripping time is from 1 s to 300 s, preferably 60 s.
Each ALD cycle can be performed two or more times. Different numbers of ALD cycles can be performed to obtain an optimal thickness for various applications. While a number of ALD cycles can be performed, the accessibility of the metal particles of the supported metal catalyst may contribute to determining the number of ALD cycles for particular applications. For example, if the thickness of the alumina over-coat is too small (e.g., less than 1 nm) the alumina over-coat may not minimize coking and sintering. On the other hand, if the thickness of the alumina over-coat is too large (e.g., greater than 15 nm) the metal particles may not be accessible by the reactants during the dehydrogenation or oxidative dehydrogenation reactions; thereby rendering the catalyst ineffective.

[0030] A thickness of the over-coat is dependent on the number of ALD cycles that deposited the over-coat and is controlled to the nanometer. The alumina over-coat has a thickness from 1 nm to 100 nm, preferably 1 nm to 15 nm, more preferably 9 nm.

[0031] The method includes activating the alumina over-coat. Activating forms pores in the alumina over-coat allowing the metal particles to become accessible by the reactants. During activation, the alumina over-coat undergoes a structural transformation from the surface of the alumina over-coat to the metal particles, and removes carbon residual that accumulated from the ALD process, which forms the pores and exposes the metal particle.

[0032] At least 80 % of the pores in the alumina over-coat have a diameter within a range of from 0.3 to 5 nm, preferably within a range of from 0.5 nm to 3 nm. In some embodiments, at least 90% of the pores in the alumina over-coat have a diameter within a range of from 0.3 nm to 5 nm, preferably within a range of from 0.5 nm to 3 nm. The small diameter minimizes an amount of produced olefins that can reach the metal particles and helps to prevent coke formation.

[0033] Activating includes calcining and optionally may also include reducing. Calcining, also referred to as calcination, is the heating of a solid to a temperature below its melting point that brings about a thermal decomposition and/or dissociation. Calcining in the methods of the inventionoccurs in the presence of a non-reducing gas at a temperature within a range of from 500 °C to 800 °C for 60 min to 10 hrs, and more preferably at 700 °C for 2 hrs. Suitable non-reducing gases are selected from the group consisting of helium, nitrogen, argon, neon, oxygen, ozone, dry air, and combinations thereof. Calcining can be performed in the ALD system or in a separate reactor, where the separate reactor produces and maintains the calcination conditions as discussed herein.

[0034] Reduction can occur in the presence of hydrogen, hydrocarbons, carbon monoxide, formalin, and combinations thereof. Reduction can occur in the presence of a non-oxidizing gas at a temperature within a range of from 30 °C to 1000 °C for a time interval within a range from 3 min to 5 days. For some applications, reduction occurs at a temperature within a range of from 500 °C to 800 °C for 60 min to 10 hrs, and more preferably at 700 °C for 2 hrs. Suitable non-oxidizing gases include helium, nitrogen, argon, neon, hydrogen, and combinations thereof.

[0035] A method for reducing coke formation during dehydrogenation or oxidative dehydrogenation is disclosed. The method includes contacting an alkane with the metal catalyst composition in the presence of inert gas, oxygen, and combinations thereof at a temperature within a range of 300 °C to 800°C, where the metal catalyst composition is formed by performing a plurality of ALD cycles on a supported metal catalyst surface, as described herein. The alkanes can include, but are not limited to, C2 to C20 carbon atom alkanes, either alone or in mixtures, preferably having two to eight carbon atoms. Suitable alkanes include, but are not limited to, ethane, propane, n-butane isobutane, n-pentane, isoamylenes, n-hexane, isohexanes, n-heptane, isoheptane, octane and isooctanes. The alkanes may include both linear and branched alkanes.

[0036] Problems that lead to coking include the migration of metal particles and produced olefins polymerizing on the metal particle. It is believed that the alumina over-coat inhibits the problems that lead to coking. For example, the over-coat acts as a barrier such that the migration of the metal particles is inhibited. Since larger metal particles are more likely to make coke than small metal particles, minimizing the growth of metal particles, by preventing migration, helps minimize coke formation. Additionally, the alumina over-coat restricts the access of the produced olefins to the metal particles. By having pores with a diameter of 2 nm or less, the access of produced olefins is restricted to the metal particle and prevents the required concentration of produced olefins needed to polymerize from collecting on the metal particle.

EXAMPLES

[0037] Materials include trimethylaluminum (TMA), $(CH3)_3Al$, assay 97%, Sigma-Aldrich ®; palladium on alumina (Pd/Al_2O_3)catalyst, Pd nanoparticles with an average size of 3.2 ± 0.67 nm and loading of 1.88%, synthesized by wet impregnation onto gamma Al_2O_3.; formalin (37% HCOH and 15% CH_3OH in aqueous solution), Sigma-Aldrich ®; ultrapure water (Millipore ™); palladium(II) hexafluoroacetylacetonate, $Pd(C_5HF_6O_2)_2$, (Sigma-Aldrich ®); silica gel S10040M, (SiliCycle ®); inert gas: nitrogen; Palladium nitrate ($Pd(NO_3)_2$), 10% solution, Johnson Matthey®; Citric acid; Gamma-alumina (180 m^2/g, 0.6 cc/g), Sasol®.

[0038] Equipment includes viscous flow reactor system (J.W. Elam and as discussed herein); mount quartz crystal microbalance (Maxtek Inc.), having thickness monitor model TM-400R and QCM sensors CCAT1BK-1007-000 (Colorado Crystal Corporation), in Maxtek BSH-150 bakeable sensor (INFICON) housing and seal with Epotek P1011 epoxy (Epoxy Technology, Inc.). Operate the reactor at a pressure of 1-2 Torr with the nitrogen flow at 360 standard cubic centimeters per minute (sccm). Monitor pressure by a 10 Torr Baratron capacitance manometer to maintain flow velocity of 2.5 meters/second. High resolution transmission electron microscope (TEM), (JEOL ® JEM-2100F FAST TEM); Thermal gravimetric analysis (TGA), (TA Instrument); Diffuse reflectance Infrared (IR) spectroscopy (DRIFTS), (Thermo Nicolet Nexus 870 instrument ® with an MCT detector), and Nitrogen BET (ASAP 2020, Micromeritics ®).

Ex 1: 45Al/Pd/Al_2O_3

[0039] Sequentially expose the Pd/Al_2O_3 catalyst to 45 ALD cycles including TMA and ultrapure water at 200 °C. Each ALD cycle includes a 60 s TMA exposure, and a 60 s ultrapure water exposure, follow each exposure by a 60 s inert gas purge with nitrogen. The resulting as-prepared metal catalyst composition has a loading of 1.03 %. TEM measurements showed that there is an approximately 9 nm alumina over-coat on the surface of the Pd/Al_2O_3 catalyst after the 45 ALD cycles, as seen in Fig. 1.

[0040] Activate the alumina over-coat by calcining the as-prepared metal catalyst composition at 700 °C for 2 hrs in 10 % oxygen in helium and then reducing in 5 % hydrogen in helium at 300 °C for 30 min.

Ex 2: 45Al/Pd/Al_2O_3-ALD

[0041] Synthesize a Pd/Al_2O_3 catalyst by ALD using $Pd(C_5HF_6O_2)$ and formalin at 80 °C for one ALD cycle. The particle size of the Pd nanoparticles was 1.1 ± 0.5 nm and has a loading of 0.41%. Sequentially expose the synthesized Pd/Al_2O_3 catalyst to 45 ALD cycles as described in Ex 1. The resulting as-prepared metal catalyst composition has a loading of 0.23%.

[0042] Activate the alumina over-coat by calcining the as-prepared metal catalyst composition at 700 °C for 2 hrs in 10 % oxygen in helium and then reducing in 5 % hydrogen in helium at 300 °C for 30 min.

Ex 3: 30Al/Pd/Al_2O_3-ALD

[0043] Repeat Ex 2, but with changes. Perform 30 ALD cycles instead of 45 cycles.

Com Ex 1: Pd/Al_2O_3

[0044] Dissolve 3.0 g of citric acid in 2 mL water. Add 7 mL of 10% $Pd(NO_3)_2$ solution to the citric acid to form a Pd-citric acid solution. The Pd-citric acid solution was added drop wise to 15 g of gamma-alumina and dried for 1 hr at approximately 20 °C and then overnight at 125 °C to form the catalyst. Calcine 5 g of catalyst in flowing air at 300 °C for 5 hrs. Reduce the calcined catalyst in flowing hydrogen (200 sccm/min) by heating to 100 °C for 30 min then increasing the temperature to 175 °C for 30 min and finally 250 °C for 30 min, purge with He and cool to approximately 20 °C .

Com Ex 2: Pd/Al_2O_3-ALD

[0045] Synthesize a Pd/Al_2O_3 catalyst by ALD using $Pd(C_5HF_6O_2)$ and formalin at 80 °C for one ALD cycle.

Accessibility of Ex 1 (45Al/Pd/Al_2O_3) at 200 °C

[0046] Determine the accessibility of the as-prepared 45Al/Pd/Al_2O_3 from Ex 1 using DRIFTS with CO as a probe molecule after reducing in 5% hydrogen at 200 °C for 30 min. DRIFTS measurements of CO chemisorption were performed at 20 °C using a Thermo Nicolet Nexus 870 instrument with an MCT detector. A cold trap at approximately negative (-) 80 °C was used in the gas inlet line to remove all the iron carbonyls. The background spectra was taken after purging the sample with ultrahigh purity (99.999%) helium for 30 min at a flow rate of approximately 80 sccm. Pure CO (Airgas, research grade) at a flow rate of approximately 40 sccm was then introduced to the DRFITS cell for 20 min to saturate the Pd surface. After the CO saturation, another 5 min of helium purge at a flow rate of approximately 70 sccm was performed to remove gas phase CO in the DRIFTS cell. The spectrum was recorded (512 scans, a resolution of 4 cm^{-1}) after the helium purge.) The DRIFT spectra of CO chemsorption for 45Al/Pd/Al_2O_3-200 °C at saturation coverage is shown in Fig. 2.

Accessibility of Ex 1 (45Al/Pd/Al_2O_3) at 500 °C

[0047] Activate the alumina over-coat by calcining the as-prepared 45Al/Pd/Al_2O_3 from Ex 1 at 500 °C for 2 hrs in 10 % oxygen in helium and then reduce in 5 % hydrogen in helium at 300 °C for 30 min. Repeat the accessibility of Ex 1 (45Al/Pd/Al_2O_3) at 200 °C with changes. The Ex 1 (45Al/Pd/Al_2O_3) at 500 °C replaces the metal catalyst composition from of Ex 1 (45Al/Pd/Al_2O_3) at 200 °C. The DRIFT spectra of CO chemsorption for 45Al/Pd/Al_2O_3-500 °C at saturation coverage is shown in Fig. 2.

Accessibility of Ex 1 (45Al/Pd/Al_2O_3) at 700 °C

[0048] Activate the alumina over-coat by calcining the 45Al/Pd/Al_2O_3 from Ex 1 at 700 °C for 2 hrs in 10 % oxygen in helium and then reduce in 5 % hydrogen in helium at 300 °C for 30 min. Then repeat Accessibility of Ex 1 (45Al/Pd/Al_2O_3) at 200 °C with changes. The Ex 1 (45Al/Pd/Al_2O_3) at 700 °C replaces the metal catalyst composition from of Ex 1 (45Al/Pd/Al_2O_3) at 200 °C. The DRIFT spectra of CO chemsorption for 45Al/Pd/Al_2O_3-700 °C at saturation coverage is shown in Fig. 2.

Accessibility of Com Ex 1 (Pd/Al_2O_3)

[0049] Determine the accessibility of the uncoated metal catalyst of Com Ex 1. Repeat Accessibility of Ex 1 (45A1/Pd/Al_2O_3) at 200 °C with changes. The uncoated metal catalyst of Com Ex 1 replaces the metal catalyst composition from of Ex 1 (45Al/Pd/Al_2O_3) at 200 °C. The DRIFT spectra of CO chemsorption for Pd/Al_2O_3 at saturation coverage is shown in Fig. 2.

Accessibility Analysis

[0050] As seen in Fig. 2, the results indicate that the 45Al/Pd/Al_2O_3-200 °C catalyst was completely covered by the alumina over-coat, thereby, minimizing the accessibility of the CO molecule. The results for the 45Al/Pd/Al_2O_3-500 °C and 45Al/Pd/Al_2O_3-700 °C indicate that as the temperature during calcining increases, the accessibility of the CO molecule also increases. The capacity of the CO peak of 45Al/Pd/Al_2O_3-700 °C is in the same order of the uncoated sample Pd/Al_2O_3, indicating that the alumina over-coat became porous to allow Pd nanoparticles to become reaccessible after the calincation treatments.

Reduction of Coke Formation: Using Ex 1 (45Al/Pd/Al_2O_3)

[0051] Perform in situ TGA to quantify the reduction of coke formation using 20 milligrams (mg) of the metal catalyst composition from Ex 1 during an oxidative dehydrogenation of ethane (ODHE) reaction at 650 °C for 90 min. The flow rates of ethane, oxygen, and diluent helium are 10.5, 3.5, and 66.5 sccm, respectively. Prior to ODHE reaction, the sample was heated with a heating rate of 5 °C/min in 10% oxygen/helium (80 sccm) to 700 °C and then maintain isothermal for 2 hrs. Cool the sample to 650 °C in helium (80 sccm) and then maintain isothermal for 1 hr. After the treatment, the mixture of reactants was introduced to the sample for 90 min at 650 °C. The result is illustrated in Fig. 3.

Comparative Coke Formation: Using Com Ex 1 (Pd/Al_2O_3)

[0052] Repeat Reduction of Coke Formation: Using Ex 1 with changes. The uncoated metal catalyst of Com Ex 1 replaces the metal catalyst composition from Ex 1. The result is illustrated in Fig. 3.

Analysis

[0053] As seen in Fig. 3, the TGA results illustrate that there was 11.83 mg of coke formation on the 20 mg uncoated metal catalyst of Com Ex 1 after 60 min of the reaction at 650 °C. For the metal catalyst composition of Ex 1, there was 0.40 mg of coke formation on the 20 mg metal catalyst composition of Ex 1 after 1 hr of the reaction at 650 °C. The amount of coke formation on the metal catalyst composition from Ex 1 after 60 min was approximately 6.2% of the coke formation on the uncoated catalyst of Com Ex 1. The amount of coke formation on the metal catalyst composition of Ex 1 slowly increased during the reaction period of 90 minutes but is still significantly lower than the coke formation on the uncoated metal catalyst of Com Ex 1.

Reduction of Coke Formation: Using Ex 2 (45Al/Pd/Al_2O_3-ALD)

[0054] Repeat Reduction of Coke Formation: Using Ex 1 with changes. The metal catalyst composition from Ex 2 replaces the metal catalyst composition from Ex 1. The result is illustrated in Fig. 4.

Comparative Coke Formation 1: Using Com Ex 2 (Pd/Al_2O_3-ALD)

[0055] Repeat Reduction of Coke Formation: Using Ex 1 with changes. The uncoated metal catalyst of Com Ex 2 replaces the metal catalyst composition from Ex 1. The result is illustrated in Fig. 4.

Analysis

[0056] As seen in Fig. 4, the TGA results illustrate that there was 4.36 mg of coke formation on the 20 mg uncoated metal catalyst of Com Ex 2 after 1 hr of the reaction at 650 °C. For the metal catalyst composition of Ex 2, there was 0.05 mg of coke formation on the 20 mg metal catalyst composition of Ex 1 after 1 hr of the reaction at 650 °C. The amount of coke formation on the metal catalyst composition from Ex 2 was approximately 2.0 % of the coke formation on the uncoated catalyst from Com Ex 2. The amount of coke formation on the metal catalyst composition of Ex 2 slowly increased during the reaction period of 180 minutes but is still significantly lower than the coke formation on the uncoated metal catalyst of Com Ex 2.

Thermal Stability: Using Ex 1 (45Al/Pd/Al_2O_3)

[0057] Dilute the as-prepared metal catalyst composition of Ex 1 with fine quartz chips and slowly heat up with a heating rate of 2 °C/min. Calcine in 10 % oxygen at 700 °C for 2 hrs. Perform an oxidative dehydrogenation of ethane (ODHE) at 675 °C for 28 hrs. The flow rates of ethane, oxygen, and diluent helium are 9, 3, and 48 sccm, respectively. Use STEM measurements to determine any morphology changes of the Pd nanoparticles. No visible morphology changes of the Pd nanoparticles were observed on the used catalyst.

Thermal Stability: Using Ex 2 (45Al/Pd/Al_2O_3-ALD)

[0058] Repeat Thermal Stability: Using Ex 1 with changes. The metal catalyst composition of Ex 2 replaces the metal catalyst composition of Ex 1. No visible morphology changes of the Pd nanoparticles were observed on the used catalyst.

Thermal Stability: Using Ex 3 (30 Al/Pd/Al_2O_3-ALD)

[0059] Repeat Thermal Stability: Using Ex 1 with changes. The metal catalyst composition of Ex 3 replaces the metal catalyst composition of Ex 1. The results are illustrated in Table 1 and the STEM images are shown in Fig. 5. Considerable morphology changes were observed, the STEM images are shown in Fig. 5.

[0060] As seen in Fig. 5, (A) illustrates the 30Al/Pd/Al_2O_3-ALD catalyst after the ODHE reaction with low magnification and (B) illustrates the 30Al/Pd/Al_2O_3-ALD catalyst after the ODHE reaction with high magnification.

Thermal Stability: Using Com Ex 1 (Pd/Al_2O_3)

[0061] Repeat Thermal Stability: Using Ex 1 with changes. The uncoated metal catalyst of Com Ex 1 replaces the metal catalyst composition of Ex 1 and the ODHE reaction was run for 30 min because the coke formation blocked the reactor and shut down the reaction. STEM measurements demonstrated that there was nanowire formation and considerable sintering on the used catalyst. The STEM images are shown in Fig. 6.

[0062] As seen in Fig. 6, (A) illustrates fresh unused Pd/Al_2O_3 catalyst and (B) and (C) illustrate the used Pd/Al_2O_3 catalyst after the ODHE reaction with different magnification.

Thermal Stability: Using Com Ex 2(Pd/Al_2O_3-ALD)

[0063] Repeat Thermal Stability: Using Ex 1 with changes. The uncoated metal catalyst of Com Ex 2 replaces the metal catalyst composition of Ex 1 and the ODHE reaction was run for 30 min because of the coke formation. STEM measurements demonstrated that there was nanowire formation and considerable sintering on the used catalyst. The STEM images are shown in Fig. 7.

[0064] As seen in Fig. 7, (A) illustrates fresh unused Pd/Al_2O_3-ALD catalyst and (B) and (C) illustrate the used Pd/Al_2O_3-ALD catalyst after the ODHE reaction with different magnification.

Dehydrogenation of Ethane (DHE): Using Ex 2 (45Al/Pd/Al_2O_3-ALD)

[0065] Perform a DHE reaction with the metal catalyst composition at 675 °C for 5 hrs with a flow of ethane at 9 sccm and N_2 at 41 sccm. The conversion of ethane was found to be 4.9 %, with an ethylene selectivity of 97.6 %, which is shown in Fig. 8. There was no visible decrease in activity in the period of 5 hrs during the DHE reaction and the selectivity of ethylene only slightly dropped from 100 % to 97.6 % after 2 hrs. This long term of DHE reaction test suggests that the metal catalyst compositions inhibit coke formation in DHE reactions, as compared to reaction using catalysts that do not have the over-coat normally deactivate in a few minutes due to large coke deposition.

Porosity of ALD Applied Over-Coat

[0066] Use silicycle S10040M SiO_2 having a surface area of approximately 100 meters squared per gram (m^2/g), a primary particle size of 75-200 micrometers (μm) as a support. Load 500 mg of the support onto a powder holder and hold in the ALD system at 200 °C. Sequentially expose the support to TMA and ultrapure water at 200 °C for 45 ALD cycles. Each ALD cycle includes a 60 s TMA exposure, and a 60 s ultrapure water exposure, and follow each exposure by a 60 s inert gas purge with nitrogen. Use nitrogen BET to determine the pore size distribution of the alumina over-coat as-prepared and after calcination at 700 °C in air for 2 hrs. The results are shown in Fig. 9.

[0067] As seen in Fig. 9, the pore size distribution of the as-prepared over-coated support and the over-coated support after calcinations illustrate that the population of the pores at the size of approximately 2 nm significantly increased after high temperature treatment, which was evidentially identical to the size of the pores formed on the 45Al/Pd/Al_2O_3 catalysts after the same treatment. Therefore the formation of the pores within the ALD Al_2O_3 over-coats is most likely due to removal of carbon residues from the ALD process. Certainly, the structural changes in the amorphous Al_2O_3 over-coats could also contribute the pore formation by the thermal treatment.

Porosity of Over-Coated Metal Catalyst: Using Ex 1(45Al/Pd/Al_2O_3)

[0068] Determine the porosity of the alumina over-coat by nitrogen BET. In order to address the changes in surface area and pore size distribution, the quantity of adsorbed nitrogen and surface area were normalized based on the weight of an uncoated catalyst (Pd/Al_2O_3). The BET surface area, as deduced from the adsorption-desorption isotherms of the uncoated catalyst (Pd/Al_2O_3), the as-prepared metal catalyst composition of Ex 1, and the metal catalyst composition of Ex 1 after activating the over-coat are shown in Figs 10A, 10B, and 10C, respectively. As seen in Figs 10A and 10B, the surface area decreased from 253 m^2/gram to 30 m^2/gram as a consequence of applying 45 ALD cycles. The large hysteresis loop observed in Fig. 10B indicates that slit-shaped pores were formed after the ALD cycles.

[0069] However, after activating the alumina over-coat by calcining at 700°C for 2 hr under 10% oxygen in helium followed by reduction under 5% hydrogen in helium at 300°C for 30 min (45Al/Pd/Al_2O_3-700C), the BET surface area returned to 213 m^2/gram, shown in Fig. 10C.

[0070] Fig. 10D illustrates the pore size distribution calculated from the absorption branch of the isotherms of the samples in Figs 10A-10C. Fig. 10D illustrates the Al_2O_3 support of the uncoated Pd/Al_2O_3 catalyst was mesoporous with an average pore size of 6.6 nm. After 45 cycles of ALD Al_2O_3 over-coating, the mesopores disappeared, revealing the dramatic BET surface area decrease. This is not surprising, since the thickness of ALD Al_2O_3 over-coat (apprximately 9 nm, as shown in Fig. 1) is greater than the characteristic diameter of the mesopores. After high temperature treatment, the mesopores with a diameter of 6.6 nm were restored, and new pores were formed at approximately 2 nm (Fig. 10D). The pores were formed by structural changes in the amorphous Al_2O_3 over-coat caused by the thermal treatment, removal of carbon residues from the ALD process, and dewetting of the Al_2O_3 over-coat from the surface of the Pd nanoparticles caused by the large lattice mismatch between palladium and alumina. These pores made it possible for the embedded Pd nanoparticles to become accessible while the overlayer imparts high thermal stability.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO2011031288A [0017]
- WO2010135107A [0018]

Non-patent literature cited in the description

- **J.W. ELAMM. D. GRONERS.M. GEORGE**Viscous Flow Reactor with Quartz Crystal Microbalance for Thin Film Growth by Atomic Layer DepositionRev. Sci. Instrum., 2002, vol. 73, 2981-2987 [0024]

Patentkrav

1. En fremgangsmåde til formning af en metalkatalystsammensætning:

gennemførelse af en pluralitet af atomlagsdeponeringscyklusser for at danne metaloxid overbelægning på en understøttet metalkatalyst, hvor en eller flere af atomlagsdeponeringscyklusserne omfatter sekventielle trin:

(a) skabelse af kontakt mellem en understøttet metalkatalystflade med et ligandindeholdende metaloxidforstadie i en forudbestemt kontaktperiode for at danne et mellemliggende lag, der har en pluralitet af metalandele, der binder kemisk til den understøttede metalkatalystflade;
(b) skabelse af kontakt mellem det mellemliggende lag og en inaktiv gas, der er valgt ud fra den gruppe, der består af helium, nitrogen, argon, neon, kuldioxid og en kombination deraf, i en forudbestemt mellemliggende strippingperiode, der er fra 1 s til 300 s, for at fjerne ureageret ligandindeholdende metaloxidforstadie;
(c) skabelse af en reaktion mellem metalandelene og vand i en forudbestemt reaktionstid, der er fra 1 s til 300 s, for at konvertere mindst en del af liganderne til hydroxylgrupper og derved danne et lag af metaloxid-, metalhydroxid- eller metaloxyhydroxidoverbelægning på den understøttede metalkatalystflade eller et tidligere dannet lag af metaloxid-, metalhydroxid- eller metaloxyhydroxidoverbelægning;
(d) før replikering af sekventielle trin (a) og (b) og (c) for at danne et yderligere lag af metaloxidoverbelægningen, skabelse af kontakt mellem laget af metaloxid-, hydroxid-, oxyhydroxidoverbelægning, der blev dannet i trin c), og en inaktiv gas, der er valgt fra gruppen, der består af helium, nitrogen, argon, neon, kuldioxid og en kombination deraf, i en forudbestemt endelig strippingtid, der er fra 1 s til 300 s for at fjerne ureageret vand; og (e) aktivering af laget af metaloxid-, metalhydroxid- eller metaloxyhydroxidoverbelægning, hvor nævnte aktivering omfatter udglødning af overbelægningen ved forekomst af en ikke-reducerende gas, der er valgt ud fra den gruppe, der består af helium, nitrogen,

argon, neon, oxygen, ozon, tør luft og kombinationer deraf, ved en temperatur inden for et område fra 500 °C til 800 °C i 60 minutter til 10 timer, efter dannelse af et endeligt lag af nævnte overbelægning, der har en tykkelse på fra 1 nanometer til 100 nanometer, for at danne en pluralitet af porer deri, hvor mindst 80 procent af pluraliteten af porer har en diameter inden for et område på 0,3 nanometer til 5 nanometer, hvor fordelingen af porestørrelse bestemmes ved brug af nitrogen BET;
og hvor metalkatalystsammensætningen reducerer en mængde koks, der blev dannet under en dehydrogenering eller en oxidativ dehydrogeneringsreaktion, til sammenligning med samme understøttede metalkatalyster uden metaloxidoverbelægningen;
og hvor metaloxidet er aluminiumoxid.

2. Fremgangsmåden i ethvert af de forrige krav, hvor det ligandindeholdende metaloxidforstadie er valgt fra den gruppe, der består af M(R1)3, hvor M er metallet, og hvor hvert R1 er uafhængigt methyl, ethyl, propyl, klorid, bromid, dialkylamino eller alkoxid.

3. Fremgangsmåden i ethvert af de forrige krav, hvor den understøttede metalkatalyst omfatter en støtte, der har metalpartikler.

4. En metalkatalystsammensætning, der er forberedt i henhold til fremgangsmåden i krav 1, og hvor metalkatalystsammensætningen reducerer en mængde koksdannelse under en dehydrogenering eller en oxidativ dehydrogeneringsreaktion, til sammenligning med understøttede metalkatalyster uden aluminiumoxidoverbelægningen.

5. Metalkatalysten i krav 4, hvor aluminiumoxidoverbelægningen har en tykkelse inden for et område på fra 1 nanometer til 15 nanometer.

6. Metalkatalysten i ethvert af kravene 4 til 5, hvor det ligandindeholdende aluminiumoxidforstadie er trimethylaluminium.

7. En fremgangsmåde til reduktion af koksdannelse under en dehydrogeneringsreaktion, som omfatter:

skabelse af en alkan med en metalkatalystsammensætning ved tilstedeværelse af inaktiv gas, oxygen og kombinationer deraf og ved en temperatur inden for et område på 300 grader Celsius til 800 grader Celsius, hvor metalkatalystsammensætningen er dannet ved at udføre en pluralitet af atomlagsdeponeringscyklusser for at danne en aluminiumoxidoverbelægning på en understøttet metalkatalyst, hvor én eller flere af atomlagsdeponeringscyklusserne omfatter sekventiel; skabelse af kontakt mellem en understøttet metalkatalystflade med et ligandindeholdende aluminiumoxidforstadie i en forudbestemt kontakttid for at danne et mellemliggende lag, der har en pluralitet af aluminiumsandele, der binder kemisk til den understøttede metalkatalystflade;
skabelse af kontakt mellem det mellemliggende lag og en inaktiv gas i en forudbestemt mellemliggende strippingtid for at fjerne ureagerede ligandindeholdende aluminiumoxidforstadier;
skabelse af en reaktion mellem aluminiumsandelene og vand i en forudbestemt reaktionstid for at konvertere mindst en del af liganderne til hydroxylgrupper og derved danne et lag af aluminiumoxidenoverbelægning på den understøttede metalkatalystflade eller et tidligere dannet lag af aluminiumoxidoverbelægningen;
skabelse af kontakt mellem laget af aluminiumoxidoverbelægning og en inaktiv gas i en forudbestemt endelig strippingtid for at fjerne ureageret vand;
og
aktivering af aluminiumoxidoverbelægningen, hvor nævnte aktivering omfatter kalcinering af overbelægningen ved tilstedeværelse af en ikke-reducerende gas, der er valgt ud fra den gruppe, der består afhelium, nitrogen, argon, neon, oxygen, ozon, tør luft og kombinationer deraf, ved en temperatur inden for et område, der går fra 500 ℃ til 800 ℃, i 60 minutter til 10 timer efter dannelse af et endeligt lag af aluminiumoxidoverbelægningen, der har en tykkelse på fra 1

nanometer til 100 nanometer, for at danne en pluralitet af porer i aluminiumoxidoverbelægningen, hvor mindst 80 procent af pluraliteten af porer har en diameter inden for et område på fra 0,3 nm til 5 nanometer, hvor porestørrelsesfordelingen bestemmes ved hjælp af BET; og hvor metalkatalystsammensætningen reducerer en mængde koks, der blev dannet under en dehydrogeneringsreaktion eller en oxidativ dehydrogeneringsreaktion, til sammenligning med understøttede metalkatalyster uden aluminiumoxidoverbelægningen.

8. Fremgangsmåden i krav 7, hvor alkanen er valgt fra den gruppe, der består af en C2-alkan og en C3-alkan.

9. Fremgangsmåden i ethvert af kravene 1 til 3, hvori aktiveringen udføres gennem opvarmning ved 700 C i to timer under 10 % oxygen i helium efterfulgt af reduktion under 5 % hydrogen i helium ved 300 C i 30 minutter.

10. Metalkatalysten i ethvert af kravene 4 og 6, hvori aktiveringen udføres gennem opvarmning ved 700 C i og timer under 10 % oxygen i helium efterfulgt af reduktion under 5 % hydrogen i helium ved 300 C i 30 minutter.

11. Fremgangsmåden i ethvert af kravene 7 og 8, hvori aktiveringen udføres gennem opvarmning ved 700 C i og timer under 10 % oxygen i helium efterfulgt af reduktion under 5 % hydrogen i helium ved 300 C i 30 minutter.

DRAWINGS

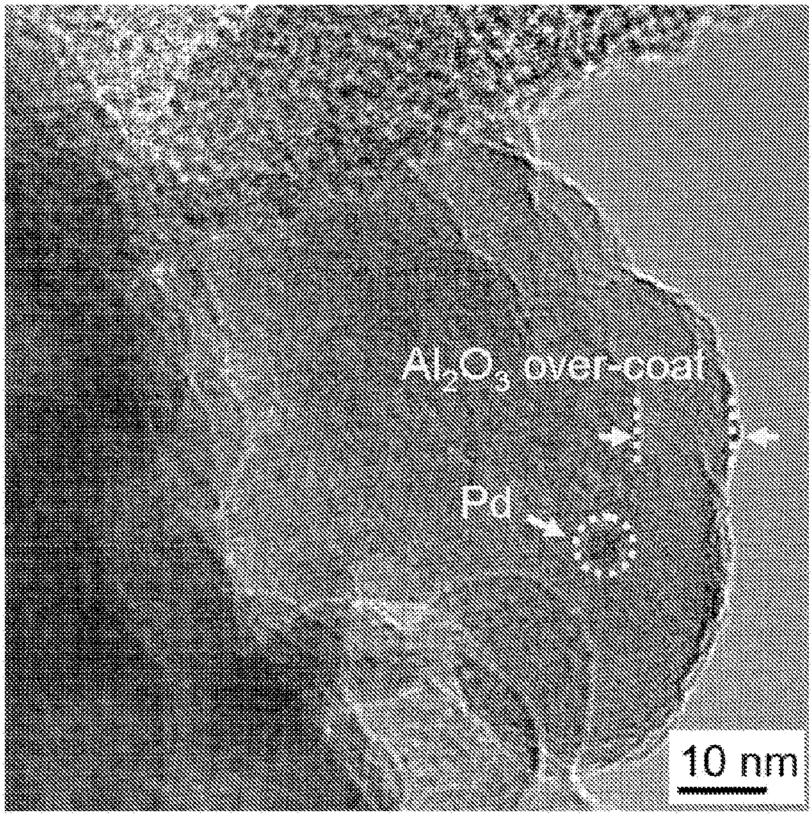


Fig. 1

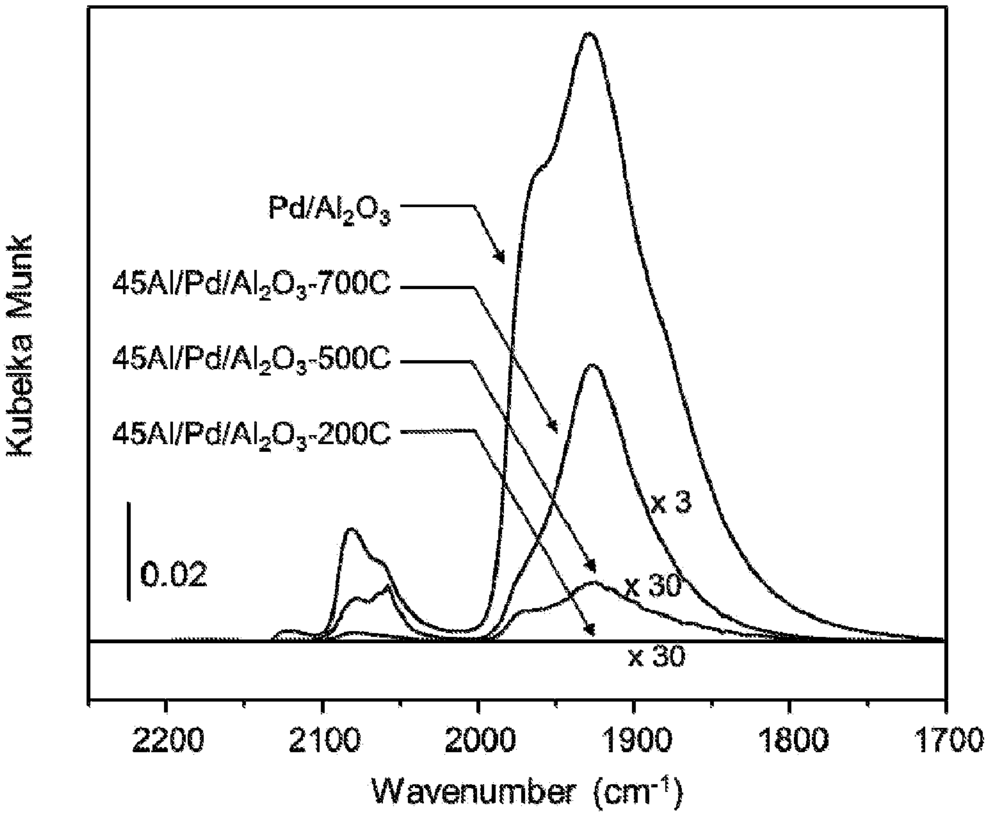

Pd/Al2O3
45Al/Pd/Al2O3-700C
45Al/Pd/Al2O3-500C
45Al/Pd/Al2O3-200C
Kubelka Munk
0.02
x 3
x 30
x 30
2200
2100
2000
1900
1800
1700
Wavenumber (cm-1)

Fig. 2

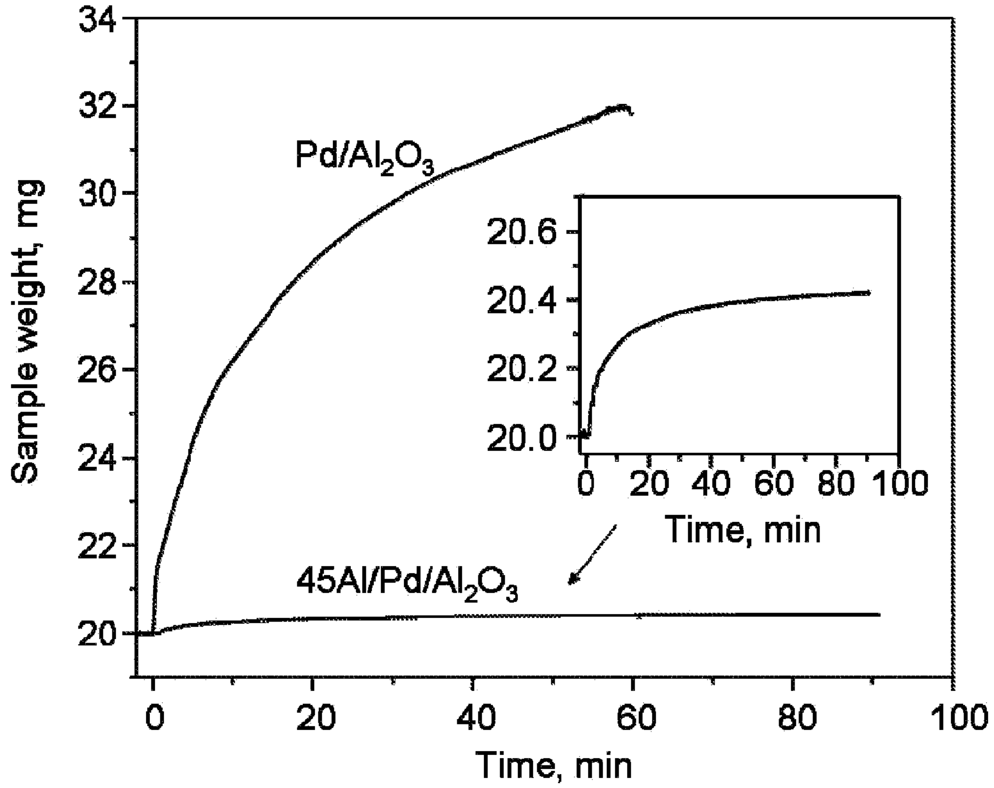
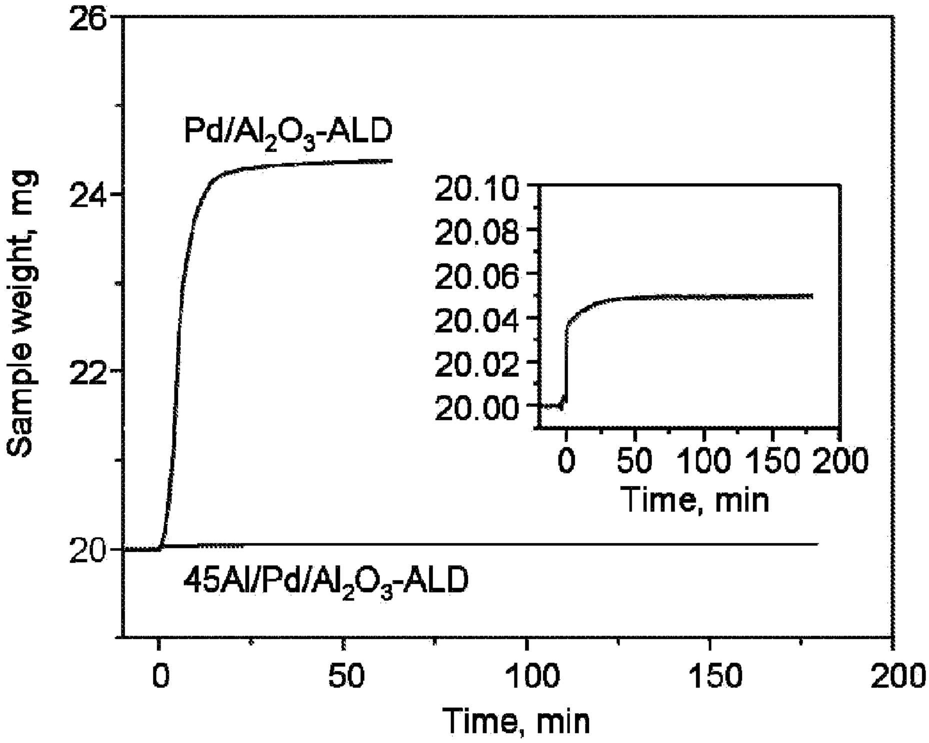

34
32
30
28
26
24
22
20
Sample weight, mg
Pd/Al2O3
45Al/Pd/Al2O3
20.6
20.4
20.2
20.0
0 20 40 60 80 100
Time, min
0
20
40
60
80
100
Time, min

Fig. 3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45Al/Pd/Al2O3-ALD
Sample weight, mg
26
24
22
20
0
50
100
150
200
Time, min
20.10
20.08
20.06
20.04
20.02
20.00
0
50
100
150
200
Time, min

Fig. 4

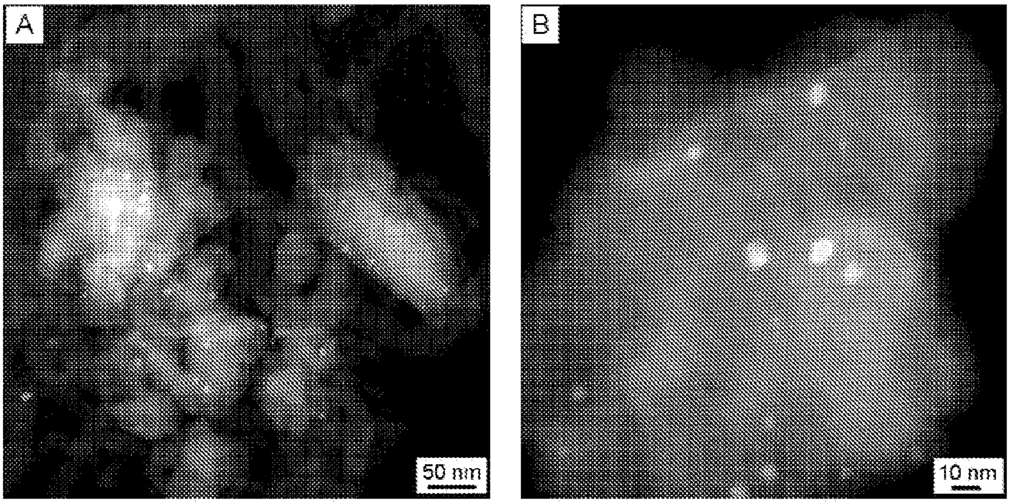

Fig. 5

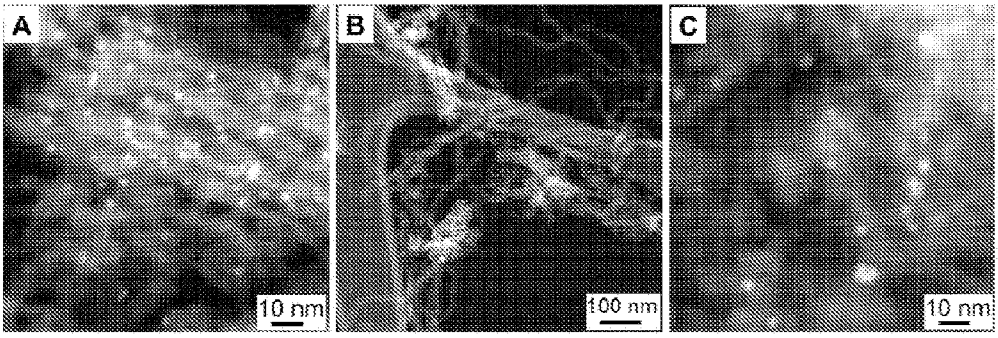

Fig. 6

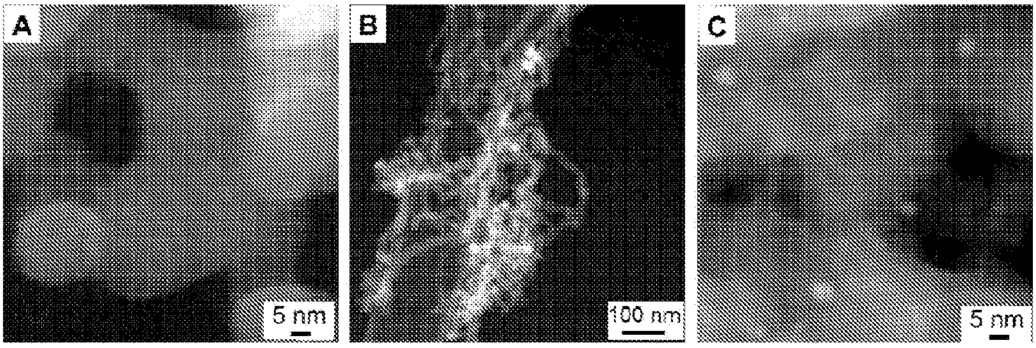

Fig. 7

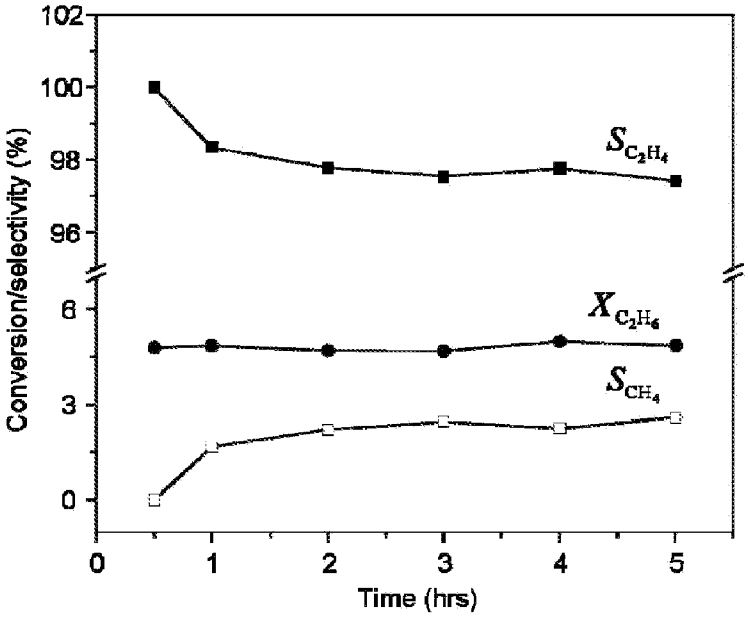
Conversion/selectivity (%)
Time (hrs)
$S_{C_2H_4}$
$X_{C_2H_6}$
S_{CH_4}
102
100
98
96
6
3
0
0
1
2
3
4
5

Fig. 8

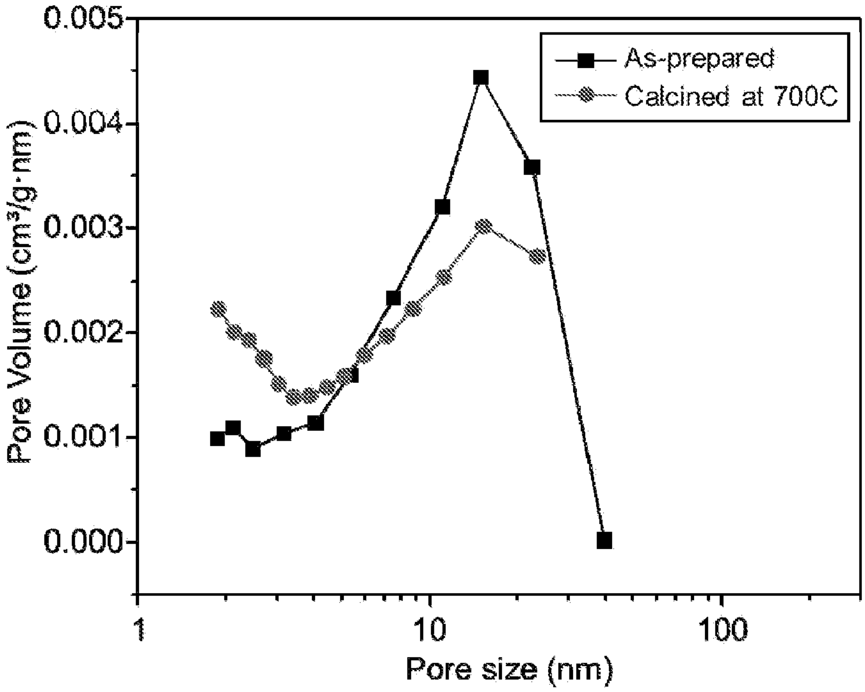
0.005
0.004
0.003
0.002
0.001
0.000
Pore Volume (cm³/g·nm)
1
10
100
Pore size (nm)
As-prepared
Calcined at 700C

Fig. 9

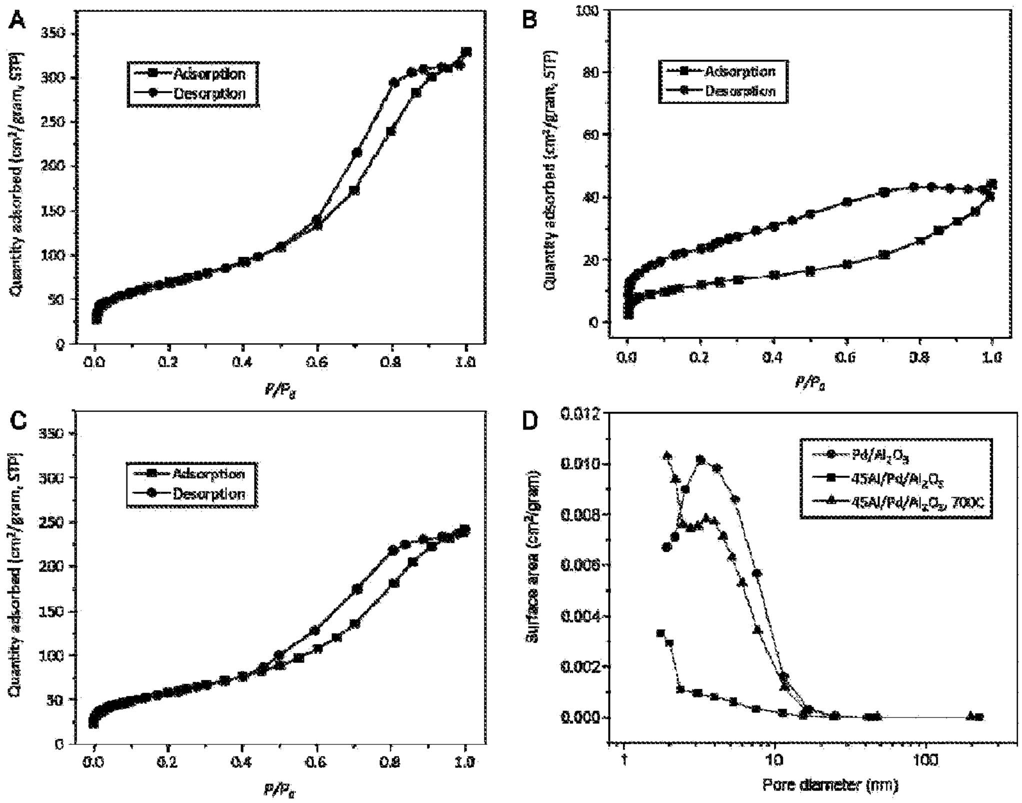
A
Adsorption
Desorption
Quantity adsorbed (cm³/gram, STP)
P/P0
B
Adsorption
Desorption
Quantity adsorbed (cm³/gram, STP)
P/P0
C
Adsorption
Desorption
Quantity adsorbed (cm³/gram, STP)
P/P0
D
Pd/Al2O3
45Al/Pd/Al2O3
45Al/Pd/Al2O3, 700C
Surface area (cm²/gram)
Pore diameter (nm)

Fig. 10