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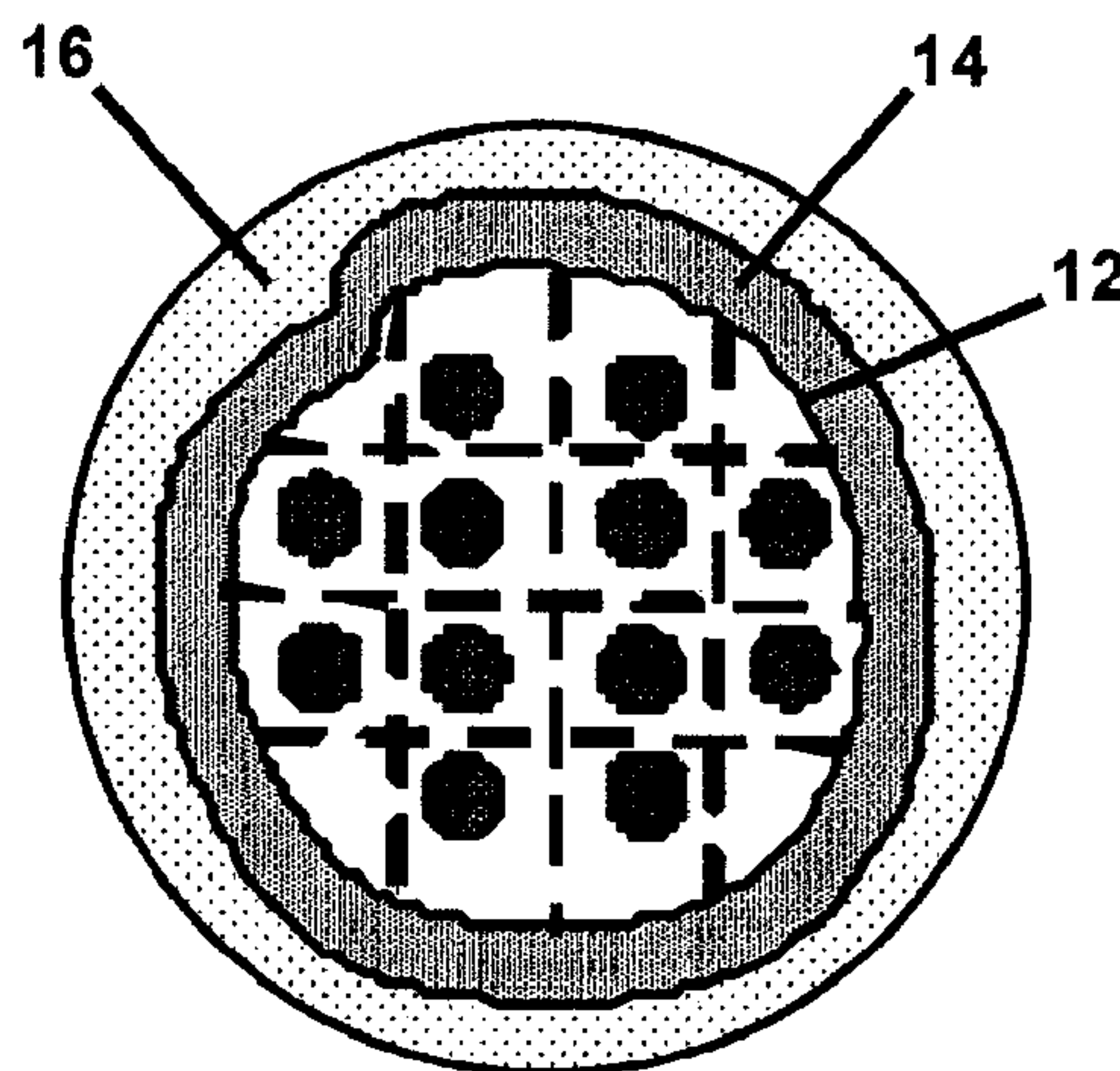
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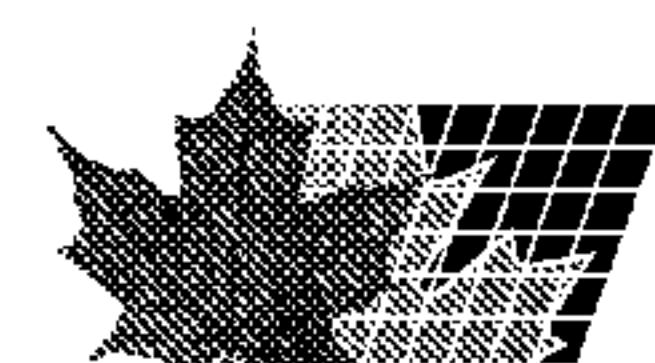
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(57) Abrégé/Abstract:

In various illustrative embodiments of the present invention there is provided a catalyst composition suitable for use in hydrocarbon refining. The catalyst composition comprises a core having a support and a first catalytic material dispersed in the support, a



(57) Abrégé(suite)/Abstract(continued):

permselective inner shell applied to the core, and an outer shell applied on the permselective inner shell. The outer shell may further comprise a second catalytic material. In various embodiments, there are also provided methods of making the catalyst composition and uses thereof. In various illustrative embodiments of the present invention, there is provided a catalyst composition described herein wherein the first and second catalytic materials comprise one or more metals or combinations thereof. In various other illustrative embodiments of the present invention, there is provided a method of using the catalyst composition for hydroprocessing a hydrocarbon feed.

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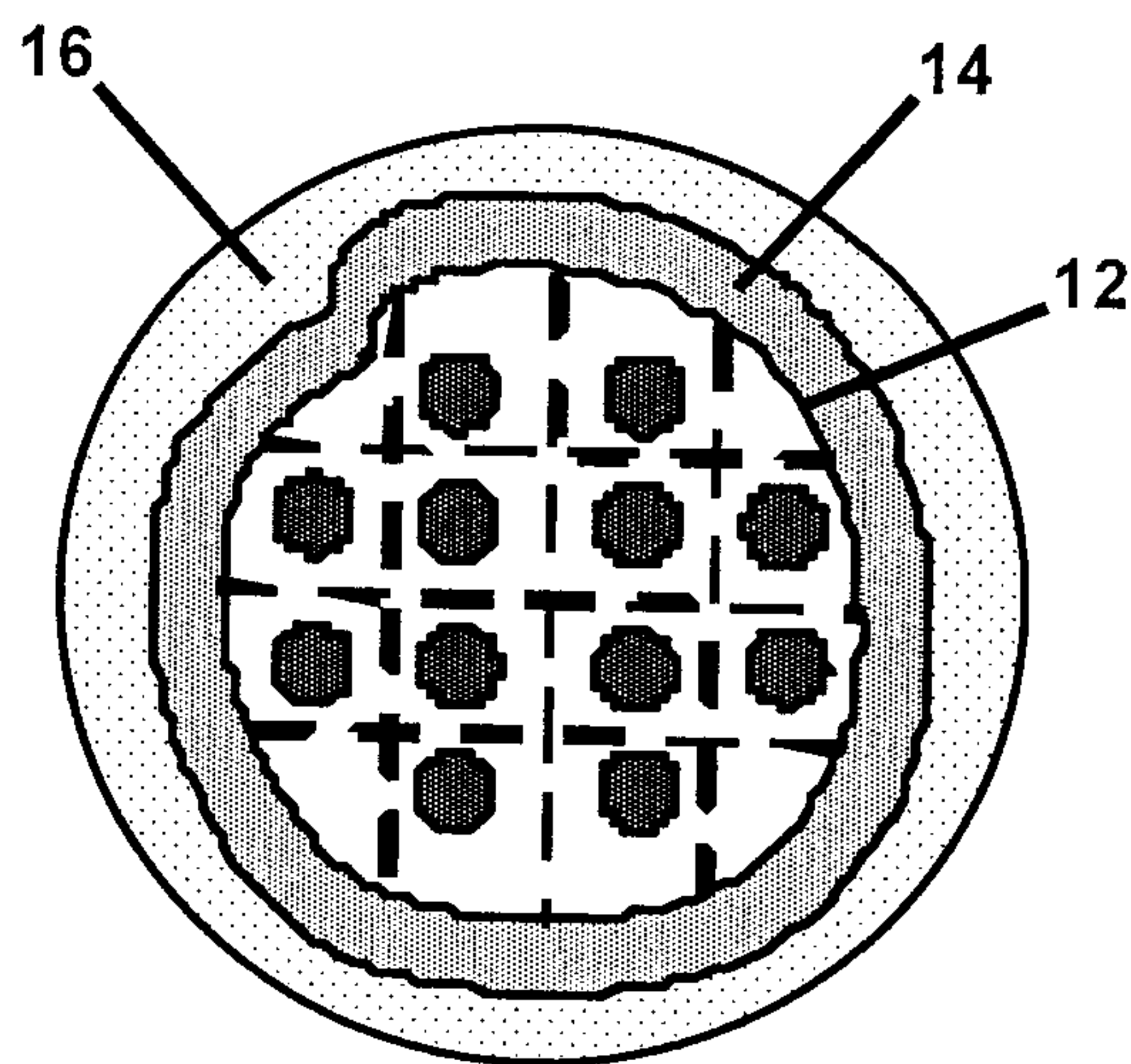


FIG. 1

(57) Abstract: In various illustrative embodiments of the present invention there is provided a catalyst composition suitable for use in hydrocarbon refining. The catalyst composition comprises a core having a support and a first catalytic material dispersed in the support, a permselective inner shell applied to the core, and an outer shell applied on the permselective inner shell. The outer shell may further comprise a second catalytic material. In various embodiments, there are also provided methods of making the catalyst composition and uses thereof. In various illustrative embodiments of the present invention, there is provided a catalyst composition described herein wherein the first and second catalytic materials comprise one or more metals or combinations thereof. In various other illustrative embodiments of the present invention, there is provided a method of using the catalyst composition for hydroprocessing a hydrocarbon feed.

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CATALYST COMPOSITIONS WITH PERMSELECTIVE COATINGS, METHODS OF MAKING SAME, AND USES THEREOF

FIELD OF THE INVENTION

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The present invention relates generally to catalyst compositions, and more particularly to catalyst compositions with permselective coatings suitable for use in hydrocarbon refining.

10 BACKGROUND OF THE INVENTION

The world-wide reserves of conventional crude oil are decreasing and heavy oil, such as that obtained from oil sands, is increasingly becoming an important source for producing oil and oil-derived products. Heavy oil has different properties than those of
15 conventional crude oil. In particular, heavy gas oil (HGO) produced from the oil sands contains about 50% more cyclic aromatic compounds and significantly higher concentrations of sulfur and nitrogen than conventional crude-derived HGO.

Hydroprocessing processes have been used to improve poor quality feeds such as
20 those, for example, comprising a high concentration of sulfur or high aromatic content. For example, hydroprocessing has been used to improve resids, vacuum gas oils, coker gas oils, and middle distillate and recycle streams. Various hydroprocessing processes generally use a catalyst to remove sulfur and/or to at least partially hydrogenate multi-ring aromatics or naphtheno-aromatics to compounds that are more
25 easily processed in subsequent operations. Current hydrodearomatization (HDA) catalysts, for example, used in reduction of the aromatic content of oil comprise non-noble metal sulfide catalysts. Noble metal catalysts are also known, but are sensitive to sulfur poisoning.

30 Therefore, there still exists a need for catalyst compositions suitable for use in hydrocarbon refining, in particular for treating poor quality feeds.

SUMMARY OF THE INVENTION

In various illustrative embodiments of the present invention, there is provided a catalyst composition comprising a core having a porous support and a first catalytic material dispersed in the support, a permselective inner shell applied to the core, and an outer shell applied to the permselective inner shell. In various embodiments, the porous support comprises porous support pores sized to permit hydrogen sulfide diffusion into the pores. The permselective inner shell forms an interface between the outer shell and the core. The permselective inner shell comprises permselective inner shell pores sized to exclude hydrogen sulfide from entering the core while allowing hydrogen and activated hydrogen to pass from the outer shell into the core and *vice versa*. The first catalytic material in the support activates hydrogen entering the core into highly reactive hydrogen that can migrate from the core onto the outer shell for reacting with the feed (e.g., hydrogenation reactions). The outer shell supports the feed to be treated and receives the activated hydrogen species. In various embodiments, the outer shell may also have catalytic activity.

In various other illustrative embodiments of the present invention, there is provided the catalyst composition as described herein further comprising a second catalytic material dispersed in the outer shell. The second catalytic material catalyses the reactions of the feed with the activated hydrogen species from the core occurring on the outer shell.

In various other illustrative embodiments of the present invention, there is provided a catalyst composition described herein wherein the first catalytic material is a noble metal.

In various other illustrative embodiments of the present invention, there is provided a catalyst composition described herein wherein the second catalytic material is at least one metal from Group 6B mixed with at least one metal from Group 8.

In various other illustrative embodiments of the present invention, there are provided methods of hydroprocessing hydrocarbons using the catalyst composition described

herein (e.g., hydrogenation, hydrocracking, hydrotreating reactions or combinations thereof).

BRIEF DESCRIPTION OF THE DRAWINGS

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In accompanying drawings which illustrate embodiments of the invention,

FIG. 1 illustrates a catalyst composition with a core and a permselective inner shell on the core according to a first embodiment of the invention;

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FIG. 2 illustrates the core of the catalyst composition in FIG. 1 comprising a support and a first catalytic material dispersed on the support;

15

FIG. 3 illustrates the core of the composition in FIG. 1 coated with the inner shell, and the permselective properties of the inner shell of the composition in FIG. 1;

20

FIG. 4 illustrates the catalyst composition according to another embodiment of the invention;

FIG. 5 illustrates the catalyst composition of FIG. 4 further comprising a second catalytic material in the outer shell;

25

FIG. 6 illustrates pore size distribution and adsorption isotherms of samples Al-1 and commercial γ -Al₂O₃ shown in Table 1;

FIG. 7 illustrates XRD patterns of selected samples of the core shown in Tables 1 and 2 and commercial γ -Al₂O₃. The core samples were calcinated and reduced at 300°C for 2 h with flowing H₂;

30

FIG. 8 illustrates the effect of platinum precursors of the first catalytic material on dispersion in the Al₂O₃ support of the core. The dry gels were calcinated in a muffle furnace at 550 °C for 2 h with a heating rate of 2 °C/min, and reduced to 300 °C for 2 h

in flowing H₂;

FIG. 9 illustrates Transmission Electron Microscopy (TEM) images of the core sample BA-1 in Table 2;

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FIG. 10 illustrates the effect of heating rate during calcination on the dispersion of the first catalytic material in the support of selected core samples shown in Table 2. The dry gel was calcinated in flowing gas at a heating rate of 2 or 10 °C/min;

10 FIG. 11 illustrates the effect of gas flow during calcination on the dispersion of the first catalytic material in the support of selected core samples shown in Table 2. All the catalysts were calcinated in flowing air or in static air in a muffle furnace at a heating rate of 2 °C/min;

15 FIG. 12 illustrates toluene hydrogenation activity of core samples N-4, Py-4, MA-1, and BA-1 shown in Table 2 at 240 °C for three different runs. The numbers in brackets on the x-axis indicate approximate dispersions of the first catalytic material in the core;

20 FIG. 13 illustrates the apparatus used for chemical vapour deposition of the permselective inner shell on the core;

FIG. 14 illustrates the effect of deposition temperature on measured surface area of the Al₂O₃ core for a deposition time of 1 h;

25

FIG. 15 illustrates the amount of the SiO₂ permselective shell applied to the Ni/Al₂O₃ core as a function of deposition time at a deposition temperature of 350°C;

FIG. 16 illustrates XRD spectra for the Ni/Al₂O₃ core as a function of various
30 deposition times of the permselective inner shell: (a) reduced, with no deposition, (b) 3-h deposition at 350°C, before reduction, and (c) 3-h deposition at 350 °C, after calcination and reduction;

FIG. 17 illustrates temperature-programmed desorption (10 °C/min) of NH_3 on the $\text{Ni}/\text{Al}_2\text{O}_3$ core as a function of various deposition times of the permselective inner shell: (a) no deposition, (b) 1-h deposition, (c) 1.5-h deposition, (d) 2-h deposition, (e) 2.5-h deposition, and (f) 3-h deposition. All at a deposition experiments were conducted at a temperature of 350°C;

FIG. 18 illustrates a change in n-octane conversion as a function of SiO_2 deposition time on the $\text{Ni}/\text{Al}_2\text{O}_3$ core during hydrocracking of n-octane at 400 °C and atmospheric pressure;

FIG. 19 illustrates N_2 uptake with varying deposition times of the SiO_2 permselective inner shell on the $\text{Mo}_x\text{O}_y/\text{Al}_2\text{O}_3$ core after FCVD for 0.5 h to 2 h at 350°C;

FIG. 20 is Scanning Electron Microscopy images of (A) a particle of the $\text{Mo}_x\text{O}_y/\text{Al}_2\text{O}_3$ core before deposition of the SiO_2 permselective inner shell (B) and after deposition;

FIG. 21 illustrates the Energy Dispersive Spectroscopy (EDS) spectra corresponding to samples (A) and (B) respectively of FIG. 20;

FIG. 22 illustrates the percent conversion of: (A) benzene to cyclohexane, (B) toluene to methylcyclohexane, and (C) O-xylene to di-methylcyclohexane and trimethylcyclopentane at varying temperatures using the catalyst composition in accordance with various embodiments of the invention;

FIG. 23 illustrates the percent conversion to hydrogenated species using varying amounts of the outer shell with the $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ core at varying temperatures;

FIG. 24 illustrates the $D_v(d)$ [$\text{cc}/\text{\AA}/\text{g}$] vs Diameter ($\text{\AA}$) for the distribution of pore size of Ni-containing core coated with SiO_2 under varying conditions;

FIG. 25 illustrates the uptake of H_2 and CO ($\mu L/g$) of the SiO_2 coated core comprising Ni as the first catalytic material under varying deposition times;

FIG. 26 illustrates the mass of the permselective SiO_2 inner shell (g)/g deposited on the core comprising Ni as the first catalytic material under varying deposition times;

FIG. 27 illustrates the NH_3 uptake ($\mu mol/g$) of the core comprising Ni as the first catalytic material coated with the permselective SiO_2 inner shell under varying deposition times;

FIG. 28 illustrates the BET surface area (m^2/g) of the core comprising Ni as the catalytic material coated with the permselective SiO_2 inner shell under varying deposition times; and

FIG. 29 illustrates the efficacy of the catalyst composition according to various embodiments of the invention for hydroprocessing a hydrocarbon feed.

DETAILED DESCRIPTION

Reference will now be made in detail to implementations and embodiments of various aspects and variations to the invention, examples of which are illustrated in the accompanying drawings.

Referring to FIG. 1, there is shown a first embodiment of a catalyst composition 10 suitable for use in various oil sands processing and refining applications, according to one aspect of the present invention. As is shown in the embodiment in FIG. 1, the catalyst composition 10 comprises a core 12, a permselective inner shell 14 applied to the core 12, and an outer shell 16 applied to the permselective inner shell 14. As is further illustrated in FIG. 2, the core 12 comprises a high surface area porous support 18 (also referred to as support 18) and a first catalytic material 20.

The porous support **18** of the core **12**, with and without the first catalytic material **20** described below, comprises walls defining pores and channels (i.e., porous support pores), which are sufficiently large to permit chemical species **26** (e.g., hydrogen sulfide) derived directly or indirectly from a hydrocarbon feed **24** (not shown) to enter or exit the porous support pores. In various embodiments, the porous support **18** may comprise, but is not limited to, aluminum oxide also known as alumina, which may be synthetic or natural (e.g., any form of aluminum oxide formed from precursor aluminum compounds including *alpha*, *gamma*, *theta* aluminum oxide), zeolite, silicon oxide, also known as silica, clay or combinations thereof. In selected embodiments, as is illustrated in the Examples, the support **18** comprises sol-gel prepared alumina and *gamma*-alumina ($\gamma\text{-Al}_2\text{O}_3$). In various embodiments, the content of aluminum oxide in the porous support **18** may range from about 100% to 0%. In various embodiments, one or more porous supports **18** may be combined in various ratios to modulate, for example, the dispersion of the first catalytic material **20** within the porous support **18** while maintaining appropriately sized porous support pores.

In various embodiments, the porous support **18** may be physically or chemically pretreated prior to use in the preparation of the catalyst composition **10** to tailor, for example, the properties of the support **18** for optimal dispersion of the of the first catalytic material **20**. In various embodiments, the porous support pores of the support **18** allow a higher degree of dispersion of the first catalytic material **20** in the support **18**, and subsequently more efficient diffusion of reagents (e.g., hydrogen) and products (e.g., activated hydrogen) entering or exiting the core **12**, which results in improved catalytic activity of the composition **10**. In various embodiments, the first catalytic material **20** is substantially uniformly dispersed, in various concentrations, in the support **18**. In various embodiments, dispersion of the catalytic material **20** in the support **18** is such that the catalytic material **20** present in the porous support pores of the support **18** may come into contact with hydrogen from a hydrogen source for example, or with chemical species **26** derived directly or indirectly from the hydrocarbon feed **24**. Optimal dispersion of the first catalytic material **20** in the porous support **18** increases the performance of the catalyst composition **10** including increased efficiency of reactions taking place in the core **12** (e.g., conversion of hydrogen to activated hydrogen species) and subsequent reactions taking place on

the outer shell **16** (e.g., hydrogenation), long-term activity, and mechanical stability of the catalyst composition **10**.

5 Examples of physical pretreatments of the porous support **18** include processing the porous support **18** to suitable particulate size (e.g., grinding), washing, thermally treating (e.g., calcining, sintering), purifying, crystallizing, pelletising, extruding, shaping or combinations thereof. Examples of chemical pretreatment of the porous support **18** include modifications of surface chemistry, the level of various promoters, or combinations thereof. The physical and chemical pretreatments may be used to
10 produce the porous support **18** having desired pore morphology, crystallinity, size, chemistry tailored for achieving optimal dispersion of the first catalytic material **20** in the porous support **18**, and optimal catalytic activity of the core **12**. In various embodiments, the porous support **18** may comprise particulates having diameters ranging from about 1 μm to about 250 μm .

15 The first catalytic material **20** is dispersed in the porous support **18** such that it can contact hydrogen entering the porous support pores of the support **18** and activate it into reactive hydrogen species. Suitable first catalytic materials **20** comprise at least one catalytically active metal species of metals in Group 8. In selected embodiments,
20 as is shown in the Examples, the first catalytic material **20** comprises platinum, nickel, or palladium. The amount of first catalytic material **20** in the support **18** may range from about 1 to 40% wt/wt, 5 to 100% wt/wt or any ratio between 1 to 100% wt/wt.

25 The first catalytic material **20** may initially occur in the porous support **18** as a precursor of the first catalytic material **20**, which may be then transformed through subsequent treatment into the first catalytic material **20**. Examples of suitable precursors of the first catalytic material **20** include, but are not limited to, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$, $\text{Pt}(\text{CH}_3\text{NH}_2)_4\text{Cl}_2$, $\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$, and $\text{Pt}(\text{C}_4\text{H}_9\text{NH}_2)_4\text{Cl}_2$, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and PdCl_2 .

30 The core **12** may be prepared using various methods, including sol-gel techniques for example, that achieve dispersion of the first catalytic material **20** or the precursor of the first catalytic material **20** in the porous support **18**. Sol-gel techniques are known in

the art, and may be found, for example, in Romero-Pascual *et al.*, *Journal of Solid State Chemistry*, vol. 168, pp. 343-353 (2002) and Shubert *et al.*, *New J. Chem.*, pp. 721-724 (1998). Sol gel synthesis generally comprises four main steps: 1) Hydrolysis, 2) "Sol" formation, 3) "Gel" formation and 4) Calcination. Sol-gel techniques may be used to produce the core **12** having substantially uniform and stable distribution of the first catalytic material **20** or the precursor of the first catalytic material **20** in the porous support **18**, tunable particle and pore sizes, and high surface area. The Examples describe particular embodiments in which sol-gel synthesis was used for the preparation of the core **12**.

In other embodiments, as is illustrated in the Examples, the core **12** may be prepared by other techniques such as incipient wetness impregnation or ion exchange. For example, in incipient wetness impregnation, the porous support **18** is dried and then wetted with a solution containing the first catalytic material **20** or the precursor of the first catalytic material **20**. In ion exchange, the first catalytic material **20** or the precursor of the first catalytic material **20** is dissolved to form a solution, and the solution is then mixed with the porous support **18**. The ions of the first catalytic material **20** or the precursor of the first catalytic material **20** in the solution will exchange with ions in the porous support **18**.

Once prepared, the core **12** may be further treated using, for example, heat treatment in various atmospheres (e.g., oxygen, helium), calcination, reduction or combinations thereof, as is illustrated in the Examples, to impart desired properties to the core **12**.

Following the preparation of the core **12** of the catalyst composition **10**, the permselective inner shell **14** is applied to the core **12**. As is illustrated in the embodiment in FIG. 1 and in more detail in FIG. 3, the permselective inner shell **14** forms an interface between the core **12** and the outer shell **16**. The permselective inner shell **14** comprises permselective inner shell pores which overlay or coat, at least in part, the porous support pores of the support **18** of the core **12**. The permselective inner shell pores are sized to exclude chemical species **26** such as hydrogen sulfide from the core **12** while being permeable to hydrogen, activated hydrogen, or to chemical species **26** having sizes similar to or smaller than hydrogen

(FIG. 3). The term "feed" in the various embodiments of the invention refers to liquid, gaseous, solid or semi-solid material derived from hydrocarbon refining or oil sands processing. In various embodiments, the feed **24** may comprise chemical species **26** such as, for example, hydrogen sulfide, organosulfur and inorganic sulfur compounds or other compounds which may react during various hydroprocessing reactions to form hydrogen sulfide, saturated and unsaturated hydrocarbons, aromatic or naphtheno-aromatic hydrocarbon compounds, gaseous non-sulfur compounds (e.g., carbon monoxide) or combinations thereof.

10 As hydrogen enters the core **12** through the permselective inner shell **14**, it is temporarily trapped in the core **12** where it becomes activated to hydrogen species (e.g., hydrogen atoms $H_2 \Rightarrow 2H$ species) upon contact with the first catalytic material **20**. The activated hydrogen species may then exit the core **12** through the permselective inner shell **14** onto the outer shell **16** for participating in other reactions
15 such as hydrogenation of hydrocarbons for example. In various embodiments, the permselective inner shell pores of the permselective inner shell **14** are generally impermeable to chemical species **26** in the feed **24** (e.g., thiols) or directly or indirectly derived from the feed **24** (e.g., hydrogen sulfide) which are larger than hydrogen, such as, for example, hydrogen sulfide, carbon monoxide, nitrogen and thiols. The
20 permselective inner shell **14** provides the selectivity for hydrogen over other molecules derived directly or indirectly from the feed **24** that are larger than hydrogen. The permselective inner shell **14** may comprise silica, alumina, zeolites or combinations thereof.

25 The permselective inner shell **14** may be applied to the core **12** using various methods such as chemical vapor deposition (CVD) for example. The term "applied" in various embodiments of the invention refers to various chemical or physical methods or combinations thereof for contacting the permselective inner shell **14** with the core **12** to achieve permselective properties, and for contacting the outer shell **16** with the
30 permselective inner shell **14** to maintain the structural integrity and the permselective properties of the inner shell **14**. In the Examples, CVD was used to apply the permselective inner shell **14** to the core **12**. CVD is known in the art and is described for example in: Niwa, M., *et al.*, "A Shape-Selective Platinum-Loaded Mordenite

Catalyst For The Hydrocracking Of Paraffins By The Chemical Vapor-Deposition Of Silicon Alkoxide." *Journal Of The Chemical Society-Faraday Transactions I*, vol. 81, pp. 2757-2761, (1985); Hibino, Takashi, *et al.*, "Shape-selectivity over HZSM-5 modified by chemical vapor deposition of silicon alkoxide." *Journal of Catalysis*, vol. 128, pp. 551-558, (1991); Katada, N., *et al.*, "A continuous-flow method for chemical vapor deposition of tetramethoxysilane on gamma-alumina to prepare silica monolayer solid acid catalyst." *Journal of Chemical Engineering of Japan*, vol. 34, pp. 306-311, (2001). Sato, S., *et al.* "Catalytic and Acidic Properties of Silica-Alumina Prepared by Chemical Vapor-Deposition." *Applied Catalysis*, vol. 62, pp. 73-84, (1990). As is described in the Examples, in the various embodiments, CVD conditions may be adjusted to provide the desired properties of the permselective inner shell **14** which may enhance subsequent reactions of the feed **24** with the activated hydrogen species (e.g., acidity). In various embodiments, the permselective inner shell **14** may range in thickness in the range of several monolayers (e.g., from about 1 to 3 monolayers) as is further illustrated in the Examples and the Figures.

Following the application of the permselective inner shell **14** on the core **12**, the outer shell **16** of the catalyst composition **10** is applied to the permselective inner shell **14** (FIG. 1, FIG. 4). The permselective inner shell **14** maintains structural stability and permselective properties provided by the permselective inner shell pores following application of the outer shell **16** such that chemical species **26** larger than hydrogen (e.g., hydrogen sulfide) may be excluded from accessing the core **12**. In various embodiments, the application of the outer shell **16** on the permselective inner shell **14** can be achieved, for example, by various chemical deposition methods or physical deposition (e.g., mechanical mixing of the outer shell **16** with the coated core **12**). In various embodiments, the outer shell **16** may comprise various forms of amorphous, crystalline materials, or combinations thereof. In various embodiments, the outer shell **16** may have a chemical composition and physical properties similar to those of the porous support **18**. Examples of materials suitable for use as the outer shell **16** include, but are not limited to, alumina, silica, zeolite or mixtures thereof. In various embodiments, the outer shell **16** may be physically or chemically pretreated prior to its application to the permselective inner shell **14** as was described in connection with the

porous support **18**. In various embodiments, the ratio of the outer shell **16** to the core **12** may range from about 1 : 1 wt/wt, 2 : 1 wt/wt, 4 : 1 wt/wt, 10 : 1 wt/wt, or any ratio between about 1:1 and 10 : 1 wt/wt. Suitable ratios are those resulting in the catalyst composition **10** having optimal catalytic properties for achieving optimal processing efficiencies while being economically attractive.

The outer shell **16** functions as a support for the feed **24**, as an acceptor of the activated hydrogen species from the core **12** which react with the feed **24**, and may also have catalytic activity. For example, in various embodiments in which the feed **24** derived from oil sands comprises aromatic hydrocarbons, the outer shell **16** can provide sites for the hydrocarbons to adsorb on the outer shell **16** and react with the activated hydrogen species. Unlike the hydrogen and activated hydrogen, hydrocarbons (and hydrogen sulfide) cannot enter the core **12** through the permselective inner shell pores of the permselective inner shell **14**, which avoids poisoning of the first catalytic material **20** in the core **12**.

As is shown in the embodiment in FIG. 5, the outer shell **16** may further comprise a second catalytic material **22**. In addition to the outer shell **16**, the second catalytic material **22** catalyses the various reactions between the feed **24** and the activated hydrogen species taking place on the outer shell **16** of the catalyst composition **10**. Suitable second catalytic materials **22** comprise at least one metal from Group 6B mixed with at least one metal from Group 8. In particular embodiments, the second catalytic material **22** may comprise, but is not limited to, mixtures of Co and Mo, Ni and Co, Mo and W, or W and P. The second catalytic material **22** may be applied to the outer shell **16** by physical or chemical modification of the outer shell **16** as was described in connection with the application of the first catalytic material **20** to the support **18**. The concentration of the second catalytic material **22** in the outer shell **16** may range from about 0% to 60%, any ratio between 0% and 60%, or any ratio in which it is economically feasible to use the catalyst.

In various embodiments, in which the catalyst composition **10** is used, hydrogen is activated on the first catalytic material **20** within the core **12** into highly reactive hydrogen species, while species larger than hydrogen are substantially excluded from

the core **12** by the permselective inner shell pores of the permselective inner shell **14**. The activated hydrogen species then migrate through the permselective inner shell pores of the permselective inner shell **14** onto the outer shell **16** for consumption in the various reactions that may occur on the outer shell **16** such as hydroprocessing
5 reactions or feed purification reactions for example (e.g., purification of gaseous feed whereby activated hydrogen from the core **12** reacts with one of the gaseous components of the feed to convert it into another component or to consume it).

In selected embodiments as is illustrated in the Examples, the catalyst composition **10**
10 may be used in hydroprocessing reactions. The term "hydroprocessing" in the invention refers to various hydroprocessing applications, which may include, for example, hydrogenation (e.g., saturation of hydrocarbons such as olefins, aromatics), hydrocracking (e.g., reduction in molecular weight or size and in boiling point), and hydrotreating (e.g., removal of heteroatoms such as sulfur, nitrogen, metals). The term
15 "hydrocarbon" in various embodiments of the present invention refers to, but is not limited to, hydrocarbons derived from, for example, oil sands, crude oil, heavy oil, bitumen, bio-derived oils and other organic molecules and mixtures used in the production of oil and oil products.

20 Hydroprocessing reactions using the catalyst composition **10** may be performed in various processing circuits comprising, for example, a fixed bed, a slurry or ebullating bed type reactor, or combinations thereof. One or more of such reactors may be arranged in various configurations in the hydroprocessing circuit.

25 In various embodiments, the feed **24** suitable for hydroprocessing using the catalyst composition **10** may comprise hydrocarbon fractions having an initial boiling point in the range from about 532 to 1025 F (HVGO), about 227 to 685 F (Coker) or about 343 to 482 C (IGO). As appreciated by those of ordinary skill in the art, such hydrocarbon fractions are difficult to precisely define by initial boiling point since there
30 may be some degree of variability in large commercial processes. Hydrocarbon fractions which may be included in this range, however, may include middle distillates, gas oils, thermal oils, residual oils, cycle stocks, topped and whole crudes, tar sand

oils, shale oils, synthetic fuels, heavy hydrocarbon fractions derived from coking processes, tar, pitches, asphalts.

EXAMPLES

5 Example 1

Preparation of the Core 12

The First Catalytic Material 20

10

In this embodiment, the precursor of the first catalytic material **20** was prepared by dissolving PtCl_2 (Sigma–Aldrich, +99% purity) in an aqueous solution of NH_3 , CH_3NH_2 , *n*-butylamine or pyridine. The solvent and excess ligands were then removed by open dish drying in a fume hood. The resulting precursors of the first catalytic material **20** were $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$, $\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$, $\text{Pt}(\text{CH}_3\text{NH}_2)_4\text{Cl}_2$, and $\text{Pt}(\text{C}_4\text{H}_9\text{NH}_2)_4\text{Cl}_2$. The platinum (Pt) content in these precursors was determined using ICP-MS (Galbraith Laboratories, Inc.). Elemental analysis for carbon (C), hydrogen (H), and nitrogen (N) content in the precursors was performed using a Perkin-Elmer 2400 CHN Analyzer. Proton and carbon NMR (Bruker AMX300) were also performed to confirm the identities of the groups present in the precursors using a BBI5 probe with the sample dissolved in dimethyl sulfoxide (DMSO) or deuterated chloroform (CDCl_3).

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The Porous Support 18

25 Samples of porous support **18** comprising dry alumina gels with and without the precursors of the first catalytic material **20** (*i.e.*, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$, $\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$, $\text{Pt}(\text{CH}_3\text{NH}_2)_4\text{Cl}_2$, or $\text{Pt}(\text{C}_4\text{H}_9\text{NH}_2)_4\text{Cl}_2$) were prepared using a sol gel method similar to the procedure by I.H. Cho, S.B. Park, S.J. Cho, R. Ryoo, *J. Catal.* 173 (1998) 295–303. Deionized water was mixed with aluminium tri-sec-butoxide (ATB) in an $\text{H}_2\text{O}/\text{ATB}$ molar ratio of 100, and then stirred for 30 min at room temperature. Next, a 0.1 g/ml HNO_3 solution was added drop-wise to the mixture, and stirred for 10 min. During the stirring, the ATB decomposed resulting in a phase containing sec-butanol forming on top of a phase containing the sol. After

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separating sec-butanol from the mixture, additional HNO₃ solution was added to the sol until the HNO₃/Al ratio reached about 0.5. For selected samples, the precursor of the first catalytic material **20** was added to the alumina sol, which was stirred at room temperature for about 1 h, and then sonicated for about 30 min. The sol was then placed in the fume hood for about 48 h to allow the gel to form and the solvent water to evaporate. The dry gel was further dried at about 110°C for 12 h, and then at about 200°C for 2 h to produce the core **12** (i.e., the support **18** comprising the first catalytic material **20**).

10 *Treatment of the Core 12*

In this embodiment, the core **12** was subjected to heat treatment, which involved drying in air, oxygen or helium at various temperatures. Heat treatment at about 550°C is referred to as calcination. A first sample of the core **12** was calcined by a one-step process at about 550°C in one of three ways: (1) in flowing oxygen for 2 h in a U-tube flow reactor heated on the outside by an electric furnace; (2) in flowing air for 2 h in the same U-tube flow reactor or (3) in static air in a muffle furnace for 2 h. In order to investigate the influence of heating rate, two ramping rates were used: 2 or 10°C/min. A second sample of the core **12** was calcined by a two-step process: first at about 550°C (2 or 10°C/min heating rate) in flowing helium for 0.5 h, and after cooling to 50°C, the flow was switched to pure oxygen and the temperature was then ramped to 550°C at 2 or 10°C/min and held for 2 h.

For some of the calcination treatments, the exhaust gas composition was monitored during the temperature ramp using a Cirrus 200 Quadrupole Mass Spectrometer system (MKS) to determine which products were being produced during the calcination. Table 1 shows the properties of the resultant samples of the core **12** (Al-200, Al-1, Al-2, N-200, N-1, N-2, Py-200, Py-1, Py-2) as compared to the commercial untreated porous support **18** (γ -Al₂O₃). For instance, "Al-1" refers to the core **12** comprising only alumina and calcined in oxygen at 550°C, while "Py-2" refers to the core **12** comprising Pt-pyridine as the precursor of the first catalytic material **20** and

alumina as porous support **18** calcined in two steps with helium first and then oxygen (see Table 1, FIG. 6).

TABLE 1

Sample	Support 18	Catalytic Material 20	Core 12	Surface Area (m ² /g)*	Pore Volume (ml/g)*
			Heat Treatment; Time		
Al-200	Al ₂ O ₃	---	Air at 200°C; 2 h	9.4	0.012
Al-1	Al ₂ O ₃	---	O ₂ at 550°C; 2 h	281	0.35
Al-2	Al ₂ O ₃	---	He at 550°C; 0.5 h O ₂ at 550°C; 2 h	254	0.30
Commercial	γ-Al ₂ O ₃	---	---	208	0.31
N-200	Al ₂ O ₃	Pt(NH ₃) ₄ Cl ₂	Air at 200°C; 2 h	0	—
N-1	Al ₂ O ₃	Pt(NH ₃) ₄ Cl ₂	O ₂ at 550°C; 2 h	269	0.34
N-2	Al ₂ O ₃	Pt(NH ₃) ₄ Cl ₂	He at 550°C; 0.5 h O ₂ at 550°C; 2 h	262	0.33
Py-200	Al ₂ O ₃	Pt(C ₅ H ₅ N) ₄ Cl ₂	Air at 200°C; 2 h	0	—
Py-1	Al ₂ O ₃	Pt(C ₅ H ₅ N) ₄ Cl ₂	O ₂ at 550°C; 2 h	272	0.32
P y-2	Al ₂ O ₃	Pt(C ₅ H ₅ N) ₄ Cl ₂	He at 550°C; 0.5 h O ₂ at 550°C; 2 h	254	0.32

*Error ± 5%

5 Characterization of the Core 12

In various embodiments, the analytical techniques described below may be used to characterize the core **12**. The characterization techniques used were, for example, N₂ physisorption, H₂ and CO chemisorption, X-ray diffraction (XRD), differential thermal and thermogravimetric analyses (DTA/TGA), NH₃ temperature-programmed desorption (TPD), and inductively coupled plasma-mass spectroscopy (ICP-MS).

H₂ chemisorption measurements were carried out on an AUTOSORB-1C instrument (Quantachrome Instruments). For H₂ chemisorption measurements, approximately 1.0 g of the core **12** sample was placed in a quartz U-tube (i.d. = 10 mm), and reduced in a H₂ flow of 15 ml/min at about 300°C for 2 h. After reduction, the sample cell was evacuated at about 300°C for 2 h, and then cooled to 40°C for the H₂ chemisorption measurement. The H₂ monolayer uptake of the core **12** samples was calculated by

- extrapolating the H₂ adsorption isotherm to zero pressure. The particle diameter of the first catalytic material **20**, which in this embodiment is Pt, (d_{Pt}) in the core **12** was calculated using the formula, $d_{Pt} = 6V/S$ (Equation 1), where V is the volume of total metallic Pt, and S is the active Pt surface area, assuming the Pt²⁺ ions were reduced completely and the Pt particles were spherical in shape. An adsorption stoichiometry of one hydrogen atom adsorbed per surface Pt atom ($H/Pt_s = 1$) was assumed. The percent Pt dispersion was calculated by dividing the number of exposed surface Pt atoms (as determined by H₂ chemisorption) by the total amount of Pt in the core **12**.
- 10 In another embodiment, H₂ and CO chemisorption experiments were performed on a ChemBET 3000 (Quantachrome Instruments) to determine the H₂ and CO uptakes before and after SiO₂ coating of the Ni/Al₂O₃ core **12**. All core **12** samples studied (with and without SiO₂ deposition) were pretreated by reduction in flowing H₂ at 550°C for 4 h before chemisorption measurements. In selected embodiments, the coated samples have been reduced twice while the uncoated samples have only been reduced once for chemisorption measurements. To test whether CO can penetrate the SiO₂ coating, each of the samples coated for 2 and 2.5 h was exposed to 60 mL/min of pure CO for 30 min at 40°C. Following the CO exposure, each of the samples was purged with flowing N₂ for 1 h to remove any physically adsorbed CO.
- 15 20 Each of the samples was tested for H₂ uptake following the exposure to CO. An uncoated Ni/Al₂O₃ core **12** was also tested for H₂ uptake after CO exposure to obtain a baseline for comparison.
- N₂ physisorption was performed using the Autosorb-1C adsorption apparatus (Quantachrome Instruments) to determine surface area, pore volume, and pore size distribution. All samples were evacuated at 120°C until the outgas rate was below 15 µmHg/min (or 2 Pa/min) prior to analysis. The surface area was calculated using the Brunauer, Emmett, and Teller (BET) method, while the pore volume and pore size distribution were calculated by the Barrett-Joyner-Halenda (BJH) (Barrett, E. P.; Joyner, L. G.; Halenda, P. P., The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *J. Am. Chem. Soc.* 1951, 73, (1), 373) using the desorption leg of the isotherm. The total pore volume was determined at a relative pressure P/P_0 .
- 25 30

= 0.99. Pore size distributions were calculated from the desorption isotherms using the BJH method. The desorption leg of the isotherm is preferred for pore analysis because it is thermodynamically more stable than the adsorption leg because of the lower Gibb's free-energy change. In these embodiments, the error in the surface area
5 measurements is about 2% on the basis of repeat analysis of the samples.

XRD spectra for the core **12** were recorded on a Multiflex X-ray diffractometer (Rigaku) using CuK α 1 radiation ($\lambda = 1.54056 \text{ \AA}$) at 40 kV tube voltage and 40 mA tube current with a scanning speed of either 0.2 or 2°/min. The generated XRD patterns
10 were referenced to the powder diffraction files (ICDD-FDP database) for identification. If possible, the average crystallite diameter of metallic Pt was calculated using Scherer's method, $D_{\text{Pt}} = K\lambda/\beta\cos\theta$ (Equation 2), where the constant K was taken as 0.9 and β was the full width at half maximum (FWHM) of the Pt(3 1 1) peak at $2\theta = 81.3^\circ$. XRD was performed to monitor changes in the oxidation state of the first catalytic
15 material **20** (e.g., Ni or Pt phase) during the coating procedure with the permselective inner shell **14**.

TEM images of the core **12** were recorded on an H-7000 transmission electron microscope (Hitachi) at 75 kV. The samples were ground to a fine powder, and mixed
20 with acetone to make a suspension. A drop of the suspension was placed on a lacey carbon nickel grid, which was subsequently dried at room temperature before the measurement.

DTA/TGA analyses were performed on three core **12** samples (i.e., A1-200, N-200,
25 and Py-200 in Table 1) to examine the thermal and gravimetric changes that occur in those samples during calcination. A DSC/TGA Q600 instrument (TA Instruments) was used for this analysis. The analysis conditions were selected so as to mimic the calcination procedure. Three different types of tests were performed as follows: (1) the samples were heated under air flow from room temperature to 550°C at 2°C/min
30 and held at 550°C for 30 min; (2) the N-200 sample was heated under air flow from room temperature to 550°C at 10°C/min and held at 550°C for 30 min and (3) the N-200 sample was heated under He flow from room temperature to 550°C at 10°C/min

and held at 550°C for 30 min. Heat flow, mass loss, and differential temperatures were recorded during the analyses.

NH₃ TPD was performed using the ChemBET 3000 instrument with 10% NH₃ diluted in He, before and after SiO₂ deposition, to determine the effect of the deposition on the acidity of the Al₂O₃ support. The NH₃ was adsorbed at 40°C and desorption was performed in the temperature range of about 40-550°C with a heating rate of 10°C/min.

10 Physical Properties of the Core 12

Surface Area and Pore Volume

Table 1 shows the surface areas and pore volumes for samples of the core 12 prepared using various precursors of the first catalytic material 20 comprising Pt, and various treatment parameters. The Al-200 porous support 18, and N-200, and Py-200 core 12 samples appeared to have very low surface areas (<10m²/g), which indicates that aluminum hydroxide and nitrate were probably not decomposed to refractory oxide Al₂O₃ after being dried in air at 200°C for 2 h. The remaining samples shown in Table 1 had surface areas between about 254 and 281 m²/g, and pore volumes between about 0.30 and 0.35 ml/g. The pore size distributions were similar for all of the calcined samples, with mean pore diameters of about 3.8 nm.

As is also shown in Table 1, the surface area of the commercial γ -Al₂O₃ alumina support 18 appears to be slightly lower (about 208 m²/g) than the surface areas of the core 12 samples comprising prepared alumina supports 18, while the pore volume is similar. FIG. 6 compares the pore size distributions and adsorption isotherms of the core 12 comprising commercial γ -Al₂O₃ and sample Al-1 support 18 (Table 1). The in-house prepared alumina appears to have pore volume similar to the pore volume of the commercial γ -Al₂O₃.

Based on the elemental analysis performed by ICP-MS (Galbraith Laboratories, Inc.), the content of the first catalytic material **20** as is shown in another embodiment in Table **2** (i.e., Pt) within the core **12** samples was about 1.58% for N-batch, 1.43% for Py-batch, 1.54% for MA-1, and 1.19% for BA-1.

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The active surface areas of the first catalytic material **20** and its degree of dispersion in the core **12**, as determined by H₂ chemisorption, are also shown in Table **2**. The dispersions range between about 11% and 106 % for the embodiments in Table **2**. Dispersions above 100% may be attributed to potential errors in the Pt metal content, errors, for example, in the adsorbed H₂ determination, or hydrogen spillover from the Pt.

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Dispersion of the First Catalytic Material 20

Pt dispersions ranging between about 11% and 106% were obtained for 1.5 wt% Pt/Al₂O₃ core **12** prepared by sol gel synthesis. The Pt dispersion was found to be strongly dependent on the platinum precursor, and a larger precursor molecule did not result in better dispersion. Specifically, in terms of highest Pt dispersion, Pt(NH₃)₄Cl₂ was the best precursor followed by Pt(CH₃NH₂)₄Cl₂, Pt(C₅H₅N)₄Cl₂, and finally Pt(C₄H₉NH₂)₄Cl₂.

20

In the embodiments shown in Table **1** and **2**, the first catalytic material **20** used to prepare the core **12** comprised various platinum species including Pt(NH₃)₄Cl₂, Pt(CH₃NH₂)₄Cl₂, Pt(C₅H₅N)₄Cl₂, and Pt(C₄H₉NH₂)₄Cl₂. The identity of these species was confirmed through a CHN analysis to obtain the C, H, and N ratios. The molecular diameters of the precursors were estimated by bond lengths and are approximately 5, 7, 12, and 13Å for Pt(NH₃)₄Cl₂, Pt(CH₃NH₂)₄Cl₂, Pt(C₅H₅N)₄Cl₂, and Pt(C₄H₉NH₂)₄Cl₂, respectively.

25

The results shown in FIG. **8** were generated from Table **2** for samples N-5, Py-5, MA-1, and BA-1. The results in FIG. **8** indicate that the dispersion of the first catalytic material **20** within the support **18** (i.e. Pt dispersion in this embodiment) appears to be

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dependent on the type of the first catalytic material **20**. In this embodiment, the dispersion appears to increase from about 11% for BA-1 (largest first catalytic material **20**) to about 87% for N-5 (smallest first catalytic material **20**).

- 5 The comparatively low dispersion of BA-1, obtained using $\text{Pt}(\text{C}_4\text{H}_9\text{NH}_2)_4\text{Cl}_2$ as precursor, may be potentially due to the relatively poor solubility of the precursor in water. During the preparation of BA-1, the water solution comprising 15 ml water with 0.1 g of Pt species in Table **2** had to be heated to 60°C in order to dissolve the precursor.

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TABLE 2

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Sample	Catalytic Material 20 *	Core 12	Heating Rate (°C/min)	Metal Content in Catalytic Material 20 (%)	Active Surface Area of Catalytic Material 20 (m ² /g)	Dispersion of Catalytic Material 20 (%)**	Particle Size of Catalytic Material 20 (nm)
Heat Treatment; Time							
N-1	$\text{Pt}(\text{NH}_3)_4\text{Cl}_2$	O ₂ at 550°C; 2 h	10	1.58	1.4	35	3.2
N-2	$\text{Pt}(\text{NH}_3)_4\text{Cl}_2$	He at 550°C; 0.5 h O ₂ at 550°C; 2 h	10	1.58	2.3	59	1.9
N-3	$\text{Pt}(\text{NH}_3)_4\text{Cl}_2$	O ₂ at 550°C; 2 h	2	1.58	4.1	105	1.1
N-4	$\text{Pt}(\text{NH}_3)_4\text{Cl}_2$	He at 550°C; 0.5 h O ₂ at 550°C; 2 h	2	1.58	4.1	104	1.1
N-5	$\text{Pt}(\text{NH}_3)_4\text{Cl}_2$	Static air in muffle furnace at 550°C; 2 h	2	1.58	3.4	87	1.3
N-6	$\text{Pt}(\text{NH}_3)_4\text{Cl}_2$	Flowing air at 550°C; 2 h	2	1.58	4.1	106	1.1
Py-1	$\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$	O ₂ at 550°C; 2 h	10	1.43	2.2	63	1.8
Py-2	$\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$	He at 550°C; 0.5 h O ₂ at 550°C; 2 h	10	1.43	2.0	56	2.0
Py-3	$\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$	O ₂ at 550°C; 2 h	2	1.43	3.1	88	1.3
Py-4	$\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$	He at 550°C; 0.5 h O ₂ at 550°C; 2 h	2	1.43	2.7	77	1.3
Py-5	$\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$	Static air in muffle furnace at 550°C; 2 h	2	1.43	2.0	58	2.0
Py-6	$\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$	Flowing air at 550°C; 2 h	2	1.43	3.1	89	1.3
MA-1	$\text{Pt}(\text{CH}_3\text{NH}_2)_4\text{Cl}_2$	Static air in muffle furnace at 550°C; 2 h	2	1.54	2.2	59	1.9
BA-1	$\text{Pt}(\text{C}_4\text{H}_9\text{NH}_2)_4\text{Cl}_2$	Static air in muffle furnace at 550°C; 2 h	2	1.19	0.34	11	9.9

*On Al₂O₃ support; ** Error is ± 5%;

H₂ chemisorption was performed after reducing the catalyst on line at 300°C for 2 h in flowing H₂.

The precursor did not precipitate in the sol or wet gel likely because of the presence of sufficient water (about 50 ml). However, the precursor probably subsequently precipitated during water removal by heat treatment. If the precipitate separated from the alumina gel during subsequent heat treatments, large Pt particles may have
5 formed.

A TEM analysis of the reduced BA-1 (FIG. 9) indicated that large Pt particles have formed. The darker particles in FIG. 9(a) are on the order of 200 nm in size and are likely Pt particles or agglomerates. The lighter particles are the alumina support 18.
10 In FIG. 9(b), Pt particles are visible at the edges of the alumina particles with sizes of 10–50 nm. A homogenous Pt distribution was not obtained from this Pt precursor as the majority of the alumina particles did not appear to contain any visible Pt particles. On all other samples, no Pt particles were visible, consistent with the hydrogen chemisorption and XRD results.

15 The chemical nature of the Pt precursors (i.e., the precursors of the first catalytic material 20) and their interaction with the support 18 (e.g., silane as precursor of silica support 18) may also be a factor in the resulting metal dispersion. Pt (II) may interact more strongly with the support 18 than Pt(IV).

20 In the presence of organic ligands in the precursor of the first catalytic material 20, the degree of dispersion appears to have varied with the calcination conditions. For example, using $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]\text{Cl}_2$ as a precursor, the Pt dispersion decreased from about 41% to 28% when treatment in flowing He before calcination in air was
25 removed. In contrast, the dispersions were relatively constant regardless of calcination procedure if a non-organic precursor such as $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ was used. It is possible that localized heating occurred when the organic ligands of the precursor were oxidized in air, and this temperature increase resulted in sintering of the Pt particles.

30 The results in Table 2 appear to indicate that a lower heating rate ($2^\circ\text{C}/\text{min}$ versus $10^\circ\text{C}/\text{min}$) results in an increased dispersion of the first catalytic material 20 within the support 18 of the core 12.

The effect of the Pt precursor on dispersion may be related to the composition of the precursor. In this example, the Pt precursors with organic ligands yielded lower Pt dispersions than the precursor containing ammonia. The dry gel containing a pyridine Pt(II) ligand (Py-200) produces approximately **20** times the amount of CO₂ during calcination than the dry gel containing an ammonia Pt(II) ligand (N-200). The localized heating from the oxidation of the organic ligands may have been sufficient to result in sintering of the Pt particles. In contrast to the work on Pt/SiO₂, with Pt/Al₂O₃ He treatments before calcination in oxygen only improved the dispersion for the ammonia precursor with a heating rate of 10°C/min. The mass spectrometer results indicated that the pyridine and ammonia precursors were completely oxidized in He and a second treatment in O₂ was not required. The decomposition of NO₃-groups produced significant amounts of O₂ and NO_x which can act as oxidants. Likely these species were sufficient to completely decompose the precursors.

15 *Effect of Heat Treatment*

Heat treatment parameters also appear to have a potential effect on the properties of the core **12**. As is shown in the embodiments in Table **1** and **2**, a heating rate of 2°C/min under all calcination conditions used in this embodiment resulted in higher dispersions of the first catalytic material **20** within the support **18** than a heating rate of 10°C/min. FIG. **10** presents the results for the core **12** derived from Pt(NH₃)₄Cl₂ precursor of the first catalytic material **20**. As is shown in Table **2**, samples N-1 (about 35% dispersion) and N-3 (about 105% dispersion) were both calcined in O₂ at about 550°C for 2 h, while samples N-2 (about 59% dispersion) and N-4 (about 104% dispersion) were calcined in a two-step process involving He and then O₂. The results appear to indicate that a slower heating rate results in higher dispersions. Similar trend was observed for the core **12** prepared with Pt(C₅H₅N)₄Cl₂ as the precursor of the first catalytic material **20**. For example, the Pt dispersion for Py-3, heated at 2°C/min, was about 88%, compared to a Pt dispersion of about 63% for Py-1, which was heated at 10°C/min.

Heating in a muffle furnace (i.e. treatment in static air) is a simpler method than heating in a flow apparatus, and may be used in selected embodiments. Such treatment, however, appears to have resulted in lower dispersions of the first catalytic material **20** than treatment in a flow apparatus. For example, as shown in FIG. **11** and
5 Table **2**, sample N-5 was calcined in the muffle furnace and had a dispersion of the first catalytic material **20** of about 87% compared to a dispersion of about 106% for sample N-6, calcined in flowing air. Similar results were obtained for samples Py-5 and Py-6. For the samples treated in the muffle furnace, it may be possible that the water produced during the calcination was not removed quickly enough without
10 flowing gases. The presence of water may have promoted the sintering of the first catalytic material **20** (i.e., Pt).

The atmosphere during calcination also appears to have affected dispersion of the first catalytic material **20**, but the magnitude of the effect appears to have depended on the
15 heating rate and the form of the first catalytic material **20**. For example, samples N-1 and N-2 in Table **2**, were both prepared from the same precursor of the first catalytic material **20** and heated at the same rate (10°C/min) during calcination, but had different dispersions (about 35% vs. 59%). A higher dispersion was obtained by heating in He before heating in O₂. Conversely, for N-3 and N-4 (Table **2**), heated at
20 2°C/min, the dispersion was generally similar irrespective of the calcination procedure. A comparison of Py-1 with Py-2, and Py-3 with Py-4 in Table **2** appears to indicate that He pretreatment before calcination in O₂ resulted in a lower dispersion compared to no He pretreatment.

25 Mass spectrometry (MS) was used to determine what species were being formed during the calcination of the core **12**. This analysis was used in conjunction with the XRD analysis. The support **18** comprising prepared alumina was analyzed first, and then several samples containing dispersed first catalytic material **20** (Pt) were analyzed. The alumina gel is soluble in water after drying at 200°C for 2 h, indicating
30 the dry gel has a similar composition the sol or to wet gel except for solvent (H₂O) content. In order to investigate the structure of the dry gel (e.g., Al-200 in Table **1**), the XRD patterns were recorded before and after calcinations (spectra not shown). The XRD pattern of the dry gel was different from that of the sol-gel Al₂O₃ (e.g., Al-1 and

Al-2 in Table 1). Referencing the ICDD database, the dry gel had a similar structure to $\text{Al}(\text{OH})_3$, indicating the dry gel did not decompose after drying for 2 h at 200°C in air. The calcined alumina samples (Al-1 and Al-2) appear to have structures similar to a commercial $\gamma\text{-Al}_2\text{O}_3$.

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The evolution of CO_2 (mass 44) and NO_2 (mass 46) during the calcination of the dry gel in O_2 or in He was studied. Masses 18 (H_2O) and 30 were also monitored during the experiment. During calcination water was produced from the decomposition of $\text{Al}(\text{OH})_3$. In both, O_2 or in He, CO_2 was detected at temperatures between 240 and 10 470°C, while NO_2 was detected at temperatures above 250°C. The CO_2 likely originated from the oxidation of an organic compound in the gel produced during the hydrolysis of ATB. However, 2-butanol was not detected in the emissions. The organics were oxidized by oxygen or the produced NO_x in the absence of oxygen (i.e., helium atmosphere). Following the treatment in flowing He, the same sample was 15 monitored during treatment in flowing O_2 and no NO_2 or CO_2 was detected. These results suggest that complete decomposition occurred during the pre-treatment in helium and that treatment with oxygen may not be necessary in some embodiments.

The thermogravimetric and differential thermal analysis of samples Al-200, N-200, and 20 Py-200 (Table 1) was performed. In agreement with the mass spectrometry results, the mass loss in an air atmosphere corresponded to decomposition within the temperature range of 200–450°C. The differential thermal analysis was performed for two heating rates (2 and 10°C/min) as well as two atmospheres (helium and air) for sample N-200. More heat was evolved during the calcination of Py-200 (comparable 25 to Py-3 with a dispersion of 88%) than for the calcination of N-200 (comparable to N-3 with a dispersion of 105%). The largest change in heat flow occurred on sample N-200 heated in air at 10°C/min, which appears to be consistent with the lower dispersions obtained for samples heated at 10°C/min than 2°C/min (Table 2). These results appear to support the theory that localized heating during calcination may 30 contribute to sintering of the Pt resulting in lower dispersions.

Particle Size of the First Catalytic Material 20

In the embodiments in Table 2, the diameter of the particles of the first catalytic material 20 (e.g., Pt particles) in the core 12, except BA-1 appears to be less than 3.2 nm. FIG. 7 shows the XRD spectra of the samples of core 12 comprising prepared Al_2O_3 and commercial $\gamma\text{-Al}_2\text{O}_3$ as the support 18. The XRD pattern of aluminium oxide can vary depending on the preparation method and crystalline phase according to the ICDD-FDP database. The spectra in FIG. 7 indicate that the commercial $\gamma\text{-Al}_2\text{O}_3$ sample and the in-house prepared Al_2O_3 appear to have similar structures although the latter alumina has smaller crystalline size as indicated by the broader peaks at $2\theta = 67.3^\circ$. In the embodiments shown in Table 2, the XRD patterns of the two types of alumina appear to be similar despite different chemistry and particulate sizes of the first catalytic material 20 and different calcination procedures. The peaks for the first catalytic material 20 (i.e., Pt in these embodiments) overlap, at least partially, with alumina at most diffraction angles, except for the Pt(3 1 1) peak at $2\theta = 81.3^\circ$. In order to obtain accurate Pt particle size information, slow scans ($0.2^\circ/\text{min}$) were performed in the range of $78\text{--}90^\circ 2\theta$. The results were consistent with the average particle size of Pt calculated from the chemisorption results. Pt is undetectable for samples N-5 and N-6, while Py-5 and MA-1 (Table 2) both have a peak at $2\theta = 81.3^\circ$ that is too small for estimation of particle size. The calculated average particle size of Pt in core 12 of BA-1 is 23 nm, which is larger than that estimated by hydrogen chemisorption (10 nm).

Reactivity Testing of the Core 12

In this embodiment, four samples of the core 12, N-4, Py-4, MA-1, and BA-1, comprising the first catalytic material 20 (Table 2) were tested for reactivity in a fixed bed reactor using hydrogenation of toluene at atmospheric pressure as a model reaction. The results were subsequently compared with the reactivity of the core 12 modified with the permselective inner shell 14 to determine whether the permselective inner shell 14 limits access of the hydrocarbon material to the catalyst material 20 in the core 12.

The reactor was a quartz tube with inner diameter of 7 mm. Approximately 400 mg of the core **12** was used for each run. All the core **12** particles ranged in size from about 90 to 250 μm . Reactions were conducted at temperatures between about 60 and 270°C at 30°C intervals. A liquid hourly space velocity (LHSV) of 1 h^{-1} was used, with a H_2 to toluene volumetric ratio of 1250. The core **12** samples were reduced in flowing H_2 for 2 h at 300°C and then the temperature was reduced to the reaction temperature.

The reactor effluent was analyzed using a gas chromatograph (Agilent 6890) equipped with a GS-GasPro PLOT column and a flame ionization detector (FID). The reactor came to steady state after approximately 30 min on stream, and the steady-state compositions were used to calculate activities. After 120 min on stream at one temperature, the temperature was increased by 30°C. Once at 270°C, the reactor was cooled to 60°C and the testing and temperature cycle repeated. One complete temperature cycle between 60 and 270°C constituted one run. Three runs were done for each of the four samples.

FIG. **12** shows a comparison of the production of methylcyclohexane (MCH) over the core **12** samples produced from the different precursors (N-4, Py-4, MA-1, and BA-1) at 240°C and atmospheric pressure. Three runs were performed for each core **12** sample, and in each case, the only product was methylcyclohexane. Sample BA-1 had the lowest Pt dispersion (11%) and the lowest production of MCH. In contrast, sample N-4 had the highest Pt dispersion (104%) and the highest production rate. Samples Py-4 and MA-1 had intermediate Pt dispersions (77% and 59%) and intermediate activities. The activity of N-4 stayed within 2.5% of the mean activity of this sample. The other samples, however, had larger decreases in activity over time. Thus, without the permselective inner shell **14** applied to the core **12**, the first catalytic material **20** in the core **12** appears to be accessible to the toluene molecules.

Example 2

Application of the Permselective Inner Shell 14 to the Core 12

This example demonstrates the use of CVD for application of the permselective inner shell **14** to modulate the size of the porous support pores of the core **12** comprising nickel as the first catalytic material **20** and commercial alumina as the porous support **18** (i.e., a Ni/ γ -Al₂O₃ core **12**) for the selective chemisorption of H₂ (2.9 Å) and exclusion of larger molecules (N₂, 3.6 Å; CO, 3.8 Å).

10 A 25-g batch of Ni/ γ -Al₂O₃ was prepared by the wetness impregnation method. The γ -Al₂O₃ (60 mesh, Alfa Aesar) was impregnated with an aqueous solution of Ni(NO₃)₂·6H₂O. The mixture was dried at room temperature for about 16 h in a fume hood and then was transferred to a muffle furnace, where it was treated at 80 °C for 2 h followed by drying at 110°C for 10 h. The Ni-impregnated γ -Al₂O₃ was then calcined
15 in the muffle furnace at 550°C for 8 h. On the basis of temperature-programmed reduction, a reduction temperature of 550°C was chosen. The Ni/ γ -Al₂O₃ core **12** was reduced in flowing H₂ by heating to 550 °C at 10°C/min and held at 550°C for 4 h. The resulting Ni/ γ -Al₂O₃ core **12** appeared to have Ni loadings of about 17% (Galbraith Laboratories Inc.) and a surface area of about 129 m²/g ($\pm$ 2 m²/g). The surface area
20 of the purchased γ -Al₂O₃ was about 208 m²/g as measured by N₂ physisorption described earlier.

In this embodiment, the deposition of the permselective inner shell **14** (i.e. SiO₂ deposition) on the core **12** was performed using a CVD apparatus (FIG. 13, FIG. 26).
25 As is shown in FIG. 13, a fluidized bed reactor was used with steam injection through an annulus of the reactor, and silicon alkoxide introduction through the bottom of the reactor was carried by an inert gas. The fluidized bed reactor consisted of a quartz tube mounted vertically inside an electric furnace. The reactor tube had an inside diameter of 1 cm and overall length of about 41 cm. One feature of the reactor was
30 the attachment of an annular tube made of 1/8-in. stainless steel tubing for steam injection into the reaction zone inside the bed. A 1/32-in. thermocouple was also

extended through the annulus to measure the temperature of the bed. Quartz frits with openings of 15-40 micrometers were used as the distributor plate. The reactor operated at atmospheric pressure. A piston pump (Alltech 426 HPLC pump) pumped water through an evaporator into the fluidized bed with flowing N₂ (20 sccm) as the carrier. The TMOS was pumped by a syringe infusion pump (Cole Parmer), was evaporated, and was carried to the reactor by N₂ flowing at 60 sccm. The flow of N₂ was controlled by a mass flow controller (Type 1179A by MKS Instruments). FieldPoint and LabView (National Instruments) were used for data acquisition and readout.

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One gram of Ni/ γ -Al₂O₃ core **12** was placed in the fluidized bed reactor and was fluidized with N₂ (60 sccm). TMOS (1.75 mol %) was vaporized and injected into the bottom of the reactor while 14 mol % H₂O was evaporated with N₂ (20 sccm) as carrier gas and was injected into the annulus of the reactor. The purpose of steam injection was to suppress carbon formation and at the same time hydrolyze the TMOS. The deposition experiments were done with temperatures between about 150°C and 500°C. Following the deposition, the samples were calcined in flowing air at 500°C for 2 h to remove any traces of carbon and organic matter remaining in the core **12** likely caused by side reactions. The core **12** samples were coated for approximately 0.5, 1.0, 1.5, 2.0, 2.5, or 3.0 h at 350°C, and were identified according to this deposition time. For example, "Ni-0" refers to an uncoated core **12** while "Ni-2.5" refers to core **12** to which the permselective inner shell **14** has been applied in the CVD apparatus for 2.5 h.

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Silicon elemental analysis of the Ni/Al₂O₃ core **12** samples coated with the permselective SiO₂ inner shell **14** was performed using inductively coupled plasma-mass spectroscopy (ICP-MS, Galbraith Laboratories). The ICP-MS technique used to perform the silicon elemental analysis has a relative error margin of about $\pm 10\%$. Carbon elemental analysis was performed using a Perkin-Elmer 2400 CHN Analyzer to determine the carbon content before and after calcination of coated core **12** samples.

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The effect of deposition time on the subsequent adsorption of H₂, CO, and N₂ was investigated (TABLE 3 showing H₂ uptake). The samples of core **12** were characterized before and after modification with the permselective inner shell **14** using N₂ physisorption, H₂ and CO chemisorption, TPD, XRD, and ICP as was discussed earlier.

TABLE 3

Sample	Inner Shell 14 Deposition Time (h)	H ₂ Uptake (μL/g)		% Change
		Before Deposition	After Deposition	
Ni-0	0	398	96	-76
Ni-2	2	441	139	-68
Ni-2.5	2.5	430	308	-28

In addition, the samples of the core **12** with the permselective inner shell **14** have been tested with a model reaction of *n*-octane hydrocracking to demonstrate the influence of the coating on the access to the first catalytic material **20** as well as on the acidity of the core **12**. The hydrocracking of *n*-octane was carried out in a quartz fixed bed reactor with 100 mg of the core **12** sample at 400°C, a weight-hourly space velocity (WHSV) of 2.0 h⁻¹, and H₂/*n*-octane molar ratio of 20 under atmospheric pressure. Before reaction, the core **12** sample was reduced at 550°C under flowing H₂ for 4 h. The reaction products were analyzed online using a gas chromatograph (Agilent 6890 GC) with a 60-m long, 0.32-mm i.d. GS-GasPro PLOT column and a flame ionization detector (FID). Mass spectrometry (Cirrus by MKS Instruments) was also used to analyze the product stream.

In another embodiment, the core **12** comprised Mo_xO_y/Al₂O₃ (about 32% Mo loading), and was prepared by wet impregnation of γ-Al₂O₃ with (NH₄)₆Mo₇O₂₄·4H₂O. Calcination of the core **12** was performed at about 550°C for 2 hours, 2°C/min ramping rate. SiO₂ deposition of the permselective inner shell **14** on the core **12** was performed using TMOS (1-1.75%) hydrolyzed with steam (about 10%) at about 350°C and atmospheric pressure, followed by calcination at about 500 °C in air. Characterization, before and after SiO₂ deposition, was performed using the methods discussed above.

The permselective inner shell **14** comprising silica (SiO_2) was applied onto the samples of core **12** comprising either $\text{Ni}/\text{Al}_2\text{O}_3$ or $\text{Mo}_x\text{O}_y/\text{Al}_2\text{O}_3$ samples using chemical vapor deposition in a fluidized bed (FCVD). Tetramethyl oxysilane (TMOS) was used as silica precursor and was hydrolyzed with steam and nitrogen carrier gas at atmospheric pressure. The resulting permselective inner shell **14** was characterized using various techniques including N_2 physisorption, ICP, and solid state ^{29}Si nuclear magnetic resonance (NMR). Due to the ferromagnetic behavior of Ni, the $\text{Ni}/\text{Al}_2\text{O}_3$, only $\text{Mo}_x\text{O}_y/\text{Al}_2\text{O}_3$ was used for NMR experiments.

The results describing amount of deposition of the permselective inner shell **14** on the core **12** and shape-selectivity are shown in FIG. **19**, **25** and **27**. The results appear to indicate that the amount of deposition for $\text{Mo}_x\text{O}_y/\text{Al}_2\text{O}_3$ increases at the rate of 0.3 g/h of SiO_2 per g of sample for first 0.5 h, and then slows down to 0.025 g/h of SiO_2 per g of sample for more than 0.5 h of coating. The results appear to indicate that N_2 uptake of $\text{Mo}_x\text{O}_y/\text{Al}_2\text{O}_3$ decreases with increasing deposition time.

FIG. **20** illustrates the particles and spots selected for energy dispersive spectroscopy (EDS). FIG. **21** illustrates the results of the EDS for each particle shown in FIG. **20**. Table **4** illustrates spots measured by EDS on $\text{Mo}_x\text{O}_y/\text{Al}_2\text{O}_3$ particles in **20B**. The Al:Si ratio varies between about 2.1 and 3.4, while Mo:Si ratio varies between about 0 and 4.9.

TABLE 4

Element	EDS Spot						
	1	2	3	4	5	6	7
O	48.3	43.0	38.4	28.7	46.4	26.5	36.3
Al	37.1	41.4	43.8	18.6	19.5	37.7	36.9
Si	14.6	15.6	17.7	9.0	6.3	11.2	14.1
Mo	0.0	0.0	0.0	43.7	27.8	24.6	12.7
Al:Si	2.5	2.7	2.5	2.1	3.1	3.4	2.6
Mo:Si	0.0	0.0	0.0	4.9	4.4	2.2	0.9

FIG. 18 illustrates the results for n-octane cracking. In this embodiment, maximum activity for n-octane cracking was observed for 0.5 h coating. Activity for n-octane cracking appears to decrease with increasing deposition time. Cracking activity appears to be enhanced by the acid sites created at the Al-O-Si-OH interface (Katada, N.; Toyama, T.; Niwa, M., Mechanism of Growth of Silica Monolayer and Generation of Acidity by Chemical-Vapor-Deposition of Tetramethoxysilane on Alumina. *Journal of Physical Chemistry* 1994, 98, (31), 7647-7652; Sato, S.; Toita, M.; Sodesawa, T.; Nozaki, F., Catalytic and Acidic Properties of Silica-Alumina Prepared by Chemical Vapor-Deposition. *Applied Catalysis* 1990, 62, (1), 73-84; Sato, S.; Toita, M.; Yu, Y. Q.; Sodesawa, T.; Nozaki, F., Catalytic Properties of Silica-Alumina Prepared by Chemical Vapor-Deposition. *Chemistry Letters* 1987, (8), 1535-1536). In addition, as the deposition time increases, the permselective inner shell pores decrease in size relative to the size of n-octane molecules resulting in decrease in n-octane penetration into the core 12 and loss of cracking reactivity of the core 12.

Properties of the Core 12 with the Permselective Inner Shell 14

FIG. 14 illustrates the change in measured surface area with the permselective inner shell 14 deposition temperatures of 150°C, 200°C, 250°C, 300°C, 350°C, 400°C, and 500°C at a constant deposition time of 1 h. The surface area was calculated directly from the nitrogen uptake and, is therefore representative of the accessibility of the pores to nitrogen.

As is shown in FIG. 14, the measured surface areas appear to decrease until a temperature of about 400°C, at which point the surface area increased from about 80 m²/g to 100 m²/g. With a further increase in temperature to about 500°C, the surface area decreased to about 83 m²/g. This increase in nitrogen adsorption at about 400°C may potentially be due to surface coverage by methoxy species and other decomposition products, which are removed from the surfaces and pores upon calcination. At deposition temperatures of about 400°C and above, significant carbon formation was visible on the core 12 after the deposition. The carbon was removed by calcination in flowing air at about 500°C. At deposition temperatures of 350°C and

below, there was no visible carbon formation. Because of increased carbon formation at higher temperatures, a deposition temperature of about 350°C was used for the deposition of the permselective inner shell **14** on the core **12** (i.e., silica deposition on Ni/Al₂O₃).

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Nitrogen Physisorption on Ni/Al₂O₃

FIG. **28** shows the change in measured surface area as a function of SiO₂ deposition time for Al₂O₃ support **18** and the Ni/γ-Al₂O₃ core **12**. The nitrogen uptake appears to have decreased with increasing deposition time. The rate of decrease in surface area is different for the Ni/γ-Al₂O₃ core **12** than for the Al₂O₃ support **18**. After 1.5 h of deposition, the Al₂O₃ support surface area was about 3 m²/g while that of the Ni/γ-Al₂O₃ core **12** was about 35 m²/g, indicating that the deposition of SiO₂ on the support **18** alone is more rapid than the deposition on the Ni/γ-Al₂O₃ core **12**. This difference may be ascribed to the stronger affinity of SiO₂ for the alumina surface of the support **18**. In the case of the Ni/γ-Al₂O₃ core **12**, some of the surface has likely been covered by Ni.

The porous support pore volumes of the Ni/Al₂O₃ core **12** as a function of deposition time of the permselective inner shell **14** (i.e., SiO₂) at about 350°C are shown in Table 5. Consistent with the surface area measurements, the porous support pore volume appears to have decreased as the deposition time increased. After 2.5 h of deposition, the porous support pore volume had decreased to essentially zero compared to a value of about 0.193 cm³/g before deposition. FIG. **24** shows that the pore size distribution changes (pores decrease in diameter) as the amount of SiO₂ deposition increases. The reduction in pore size may potentially result from SiO₂ deposition within the porous support pores since the pores in the Ni/γ-Al₂O₃ core **12** prior to deposition of the permselective inner shell **14** (38 Å modal pore diameter) appear to be large enough for the silicon alkoxide molecule to penetrate into the core **12** (TMOS has a kinetic diameter of 8.9 Å). The degree of potential deposition of some SiO₂ into the porous support pores of the core **12** nevertheless leaves permselective inner shell pore openings of sufficient

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size for hydrogen or activated hydrogen species to pass through while excluding larger molecules, and allows for the first catalytic material **20** to remain exposed to some degree for contacting hydrogen molecules.

TABLE 5

Sample	Deposition of the Inner Shell 14 on the Core 12 (h)	Average Pore Volume (cm ³ /g)
Ni-0	0	0.193
Ni-1	1.0	0.107
Ni-1.5	1.5	0.022
Ni-2	2.0	0.005
Ni-2.5	2.5	0.0007
Ni-3	3.0	0.0005

Amount of Deposition and Carbon Formation

FIG. 15 shows the amount of the permselective SiO₂ inner shell **14**, deposited on the Ni/ γ -Al₂O₃ core **12** as a function of deposition time (as determined by ICP-MS). After 1 h of deposition, the SiO₂ fraction was about 16% relative to the core **12** without the permselective inner shell **14**. The amount of silica deposited increased to about 30% after 1.5 h and then the amount deposited remained constant up to 2.5 h of deposition. The surface may have been saturated after 1.5 h with physisorbed species that hindered the growth of Si-O-Si bonds. To verify if other species were deposited on the surface, the carbon content of the Ni/ γ -Al₂O₃ core **12** was determined by the CHN analysis after coating the core **12** with SiO₂ for 2 h at 400°C, which revealed a carbon content of 0.7%. This sample was then calcined and the carbon content was reduced to 0.2%. N₂ physisorption was also performed on the same sample before and after calcination. The surface area of the sample before calcination was about 50 m²/g compared to about 4 m²/g after calcination.

H₂ and CO Chemisorption

FIG. 25 shows H₂ and CO uptakes on the Ni/ γ -Al₂O₃ core **12** after SiO₂ deposition for various times. The H₂ uptake increased after 1 h of deposition from about 398 μ L/g to 493 μ L/g. This increase is probably due to a further reduction of the Ni/ γ -Al₂O₃ core **12** within the structure during the second reduction after the coating. After 2.5 h of deposition, the average H₂ uptake was about 430 μ L/g (Table 3 above). In contrast, the CO uptake decreased from about 405 μ L/g before coating to 5.8 μ L/g, after 2.5 h of deposition, indicating that the deposited silica had reduced the pore openings and that the technique was successful.

To further test the size-exclusion properties of the permselective inner shell **14** on the Ni/ γ -Al₂O₃ core **12**, three samples were exposed to pure flowing CO for 30 min. The H₂ uptakes, before and after this exposure, are listed in Table 5. The uncoated core **12** (Ni-0) appeared to be severely poisoned by exposure to CO, with the H₂ uptake decreasing from about 398 μ L/g before exposure to 96 μ L/g after exposure (76% change). The second and third samples, coated for 2 and 2.5 h, respectively, were less affected by the exposure to CO with decreases in H₂ uptakes of about 68% and 28%, respectively. These results indicate that the pores reduced the accessibility for CO.

The XRD spectra for the Ni/ γ -Al₂O₃ core **12** at various stages in the deposition process are shown in FIG. 19. After reduction (FIG. 16(a)), the spectrum had peaks at 44.5, 51.8, and 76.4° 2 θ corresponding to Ni and peaks at 37.3 and 67.3° 2 θ corresponding to Al₂O₃ (matched to ICDD-FDP database). After deposition (FIG. 16(b)), most of the Ni has been oxidized, as evidenced by peaks at 37.2, 43.3, and 62.9° 2 θ corresponding to NiO. The peaks around 37° 2 θ overlap; 37.2° 2 θ is associated with NiO, 37.0° 2 θ is associated with NiAl₂O₄, and 37.3° 2 θ is associated with Al₂O₃. After deposition and reduction (FIG. 16(c)), the XRD spectra appear similar to the spectra of the originally reduced Ni/ γ -Al₂O₃ core **12** (FIG. 17(a)), except that the Ni peak intensities have decreased. This decrease is likely due to the silica coating.

Temperature programmed desorption (TPD) of NH_3 on the $\text{Ni}/\text{Al}_2\text{O}_3$ core **12** was performed to monitor changes in the accessibility of the acid sites on the alumina support **18**. The TPD spectra are shown in FIG. **17** for six different samples with deposition times ranging from 0 to 3 h. The total ammonia uptake was determined by integrating the area under the TPD curves, and these areas are listed in Table **6**.

TABLE 6

Sample	Inner Shell 14 Deposition Time (h)	Total NH_3 Uptake ($\mu\text{mol/g}$)
Ni-0	0	461
Ni-0.5	0.5	448
Ni-1	1.0	246
Ni-1.5	1.5	224
Ni-2	2.0	143
Ni-2.5	2.5	113
Ni-3	3.0	4.1

Two main peaks in the TPD spectra around 160-180°C and 400-440°C likely correspond to weak and strong acid sites, respectively, and appear consistent with the literature. The ammonia uptake appears to have decreased with increasing deposition time, indicating that the acid sites were progressively blocked. SiO_2 is less acidic than Al_2O_3 . After 0-3 h of deposition, the uptake decreased from 461 $\mu\text{mol/g}$ to 4 $\mu\text{mol/g}$ (Table **6**). The NH_3 uptake decreased because of coverage of the external sites on the particles as well as narrowing of the pores preventing NH_3 from accessing internal sites. A schematic representation of the core **12** coated by the permselective inner shell **14** is given in FIGs. **3** and **4**.

25 The Effect of the Permselective Inner Shell 14 on Hydrocracking of *n*-Octane

FIG. **18** shows the conversion of *n*-octane as a function of the SiO_2 deposition time (i.e., deposition time of the permselective inner shell **14**). The conversions shown in FIG. **18** were taken after 20 min on stream. With no SiO_2 deposition, *n*-octane conversion, in this embodiment, was about 29%. The maximum conversion (about 67%) was obtained on the $\text{Ni}/\text{Al}_2\text{O}_3$ core **12** coated for 0.5 h. The conversion decreased to zero for core **12** samples coated for 1.5 h or longer. The product stream consisted of one C_4 species that is likely 1-butene. That is, the loss of activity over 3 h

on stream was about 47%, 23%, and 0% for the uncoated core **12**, the core **12** coated for 0.5 h, and the core **12** coated for 1 h, respectively.

NH₃ is an excellent probe molecule for the measurement of acidic properties of the core **12**. The temperature-programmed desorption (TPD) results (FIG. **15** and Table **6**) indicate that the silica deposition significantly reduced the acid nature of the Ni/Al₂O₃ core **12**. The acid sites were covered on the exterior of the particles and the pore openings were narrowed so that the ammonia could not penetrate into the interior of the particles.

The balance between an increase in strong acid sites and a decrease in accessibility of the SiO₂/Al₂O₃ interface is consistent with a maximum in the *n*-octane conversion (FIG. **17**). As SiO₂ is deposited on the Ni/Al₂O₃ core **12**, the number of Brønsted sites, which favor the cracking of molecules, likely increases because of the contribution of acidity from the SiO₂/Al₂O₃ interface. Further deposition of SiO₂ likely prevents access to the interface because of the large kinetic diameter (6.2 Å) of *n*-octane and, thus, the conversion decreases. Thus the permselective inner shell **14** appears to limit the access of *n*-octane to the Ni particles in the core **12**. In other embodiments, additional silica can be deposited by calcining the core **12** between deposition runs.

In various reaction systems of noble metals using H₂/CO mixture as feedstock (or H₂ with CO as contaminant), the CO tends to decrease the reactivity of the noble metal by strongly adsorbing on the surface and by inhibiting further adsorption of H₂. The present invention may be a new way for separating H₂ from CO in the reaction systems involving noble metals, thereby preserving the reactivity of noble metal against the poisoning effect of CO.

Example 3

The Catalyst Composition **10** and its Use in Hydroprocessing

In this example, hydroprocessing using the catalyst composition **10** has been demonstrated in the temperature range of about 90 to 240°C at atmospheric pressure

using toluene hydrogenation as a model reaction and the Pt/ γ -Al₂O₃ core **12** modified with the permselective SiO₂ inner shell **14**.

Preparation of the Catalyst Composition 10

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The Pt/ γ -Al₂O₃ (40 mg) core **12** modified with the permselective SiO₂ inner shell **14** was mechanically mixed with the outer shell **16** material to form the catalyst composition **10**. In this embodiment, the outer shell **16** of the catalyst composition **10** comprised zeolite 13X and gamma-Al₂O₃ in a ratio of 1:1. In another embodiment, 10 WO₃/Al₂O₃ and SiO₂ were used as the outer shell **16** also in a 1:1 weight ratio with the SiO₂-modified Pt/ γ -Al₂O₃ core **12**. The catalyst composition **10** was introduced into a differential reactor for the hydrotreating applications. In this embodiment, the reactor was operating at atmospheric pressure.

15 The reaction temperature was varied from about 90°C to 240°C to demonstrate transfer of activated hydrogen species from the SiO₂-modified Pt/ γ -Al₂O₃ core **12** onto the outer shell **16** of the catalyst composition **10**. To study the reaction kinetics the reaction temperature was varied between about 120 to 240°C. Toluene mole fraction was varied between about 0.08 and 0.19, while H₂ mole fraction was varied from 20 about 0.26 to 0.60.

The degree of conversion appears to depend on the type of the outer shell **16**. The more acidic outer shell **16**, i.e., zeolite 13X, shows a higher conversion of toluene. Neither the SiO₂-modified Pt/ γ -Al₂O₃ core **12** nor the outer shell **16** alone were active 25 towards aromatic hydrogenation, and thus, the transfer of activated hydrogen species was likely responsible for the reactivity.

The kinetics of the reaction were studied in the temperature range of about 120 to 240°C to determine whether the reactions were influenced by diffusion. The 30 theoretical model of Freeman and Doll (Freeman, D. L. and Doll, J. D., The Influence Of Diffusion On Surface-Reaction Kinetics, *Journal of Chemical Physics*, 78(10), 6002-6009) was applied to the experimental data to

obtain an estimate of the diffusion coefficients for H₂ spillover from the modified Pt/ γ -Al₂O₃ core **12**. The model of Freeman and Doll provides a relationship between diffusion-controlled rate constant k_{dc} and diffusion coefficient D , was applied to the experimental data to estimate the D as well as the activation energy for diffusion, E_{diff} .
 5 In the range of about 120 to 180°C, D values were between 7.1×10^{-3} and 1.3×10^{-2} m²/s, the average surface residence time was 2.2×10^{-15} s. E_{diff} was 15 kJ/mol, which is of the same magnitude as E_A and confirms diffusion-controlled reaction. For temperatures of about 210 to 240°C, the activation energy increased to 86 kJ/mol. The reactions were tested to see whether Eley-Rideal (ER) mechanism (Freeman, D. L.
 10 and Doll, J. D., The Influence Of Diffusion On Surface-Reaction Kinetics, *Journal of Chemical Physics*, 78(10), 6002-6009) played any role in the mechanisms. The proposed mechanism potentially involves the dissociation of H₂ into activated H species on the first catalytic material **20** (e.g., Pt), followed by the surface migration of the activated H species to attack adsorbed toluene on the outer shell **16** of the catalyst composition **10**, and the surface reaction of the activated hydrogen species with the
 15 adsorbed toluene on the outer shell **16**. It appears that only H₂ (kinetic diameter - 2.9 angstroms) could access the Pt sites within the Pt/ γ -Al₂O₃ core **12**, while toluene molecules (kinetic diameter of 6.7 angstroms) were excluded by the permselective SiO₂ inner shell **14** on the core **12**. Methylcyclohexane appeared to be the only
 20 product of the reaction of toluene using the catalyst composition **10**.

In another embodiment, the samples core **12** comprised about 17% Ni and about 10 % Mo in Ni/Al₂O₃ and MoO₃/Al₂O₃ respectively, which were prepared by wet impregnation using Ni(NO₃)₂·6H₂O and (NH₄)₆Mo₇O₂₄·4H₂O respectively as
 25 precursors. The permselective inner shell **14** comprising SiO₂ was deposited on the core **12** using the hydrolysis of tetramethoxysilane (TMOS, 1-1.75%) with steam (10-14%) in a fluidized bed reactor at atmospheric pressure using N₂ as a carrier gas. The cracking of *n*-octane was performed in a fixed bed reactor at 400°C and atmospheric pressure.

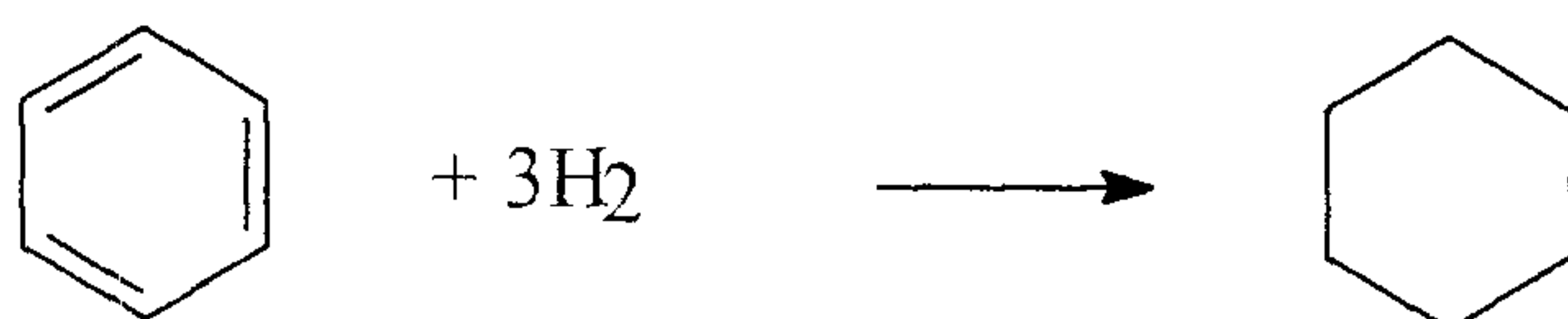
30 The BET surface areas and the pore volumes of the Ni/Al₂O₃ and MoO₃/Al₂O₃

samples of the core **12** decreased as the deposition time increased. For the Ni/Al₂O₃ sample of the core **12** coated for 2.5 hours (0.31 g SiO₂ per g of sample), CO uptake was reduced while H₂ uptake remained generally constant, as shown in FIG. **25**. This result potentially indicates that the Ni sites in the core **12** were still accessible to H₂ while CO was excluded. Similarly the NH₃ uptake (FIG. **27**) diminished to near zero for a sample of the core **12** coated for 3 hours (0.37 g SiO₂ per g of sample). The reduction in acidity may be potentially ascribed to the covering of acid sites on the external surface of the core **12** by the SiO₂ coating and reduced penetration into the pores by NH₃ because of the reduced size of the pore-openings.

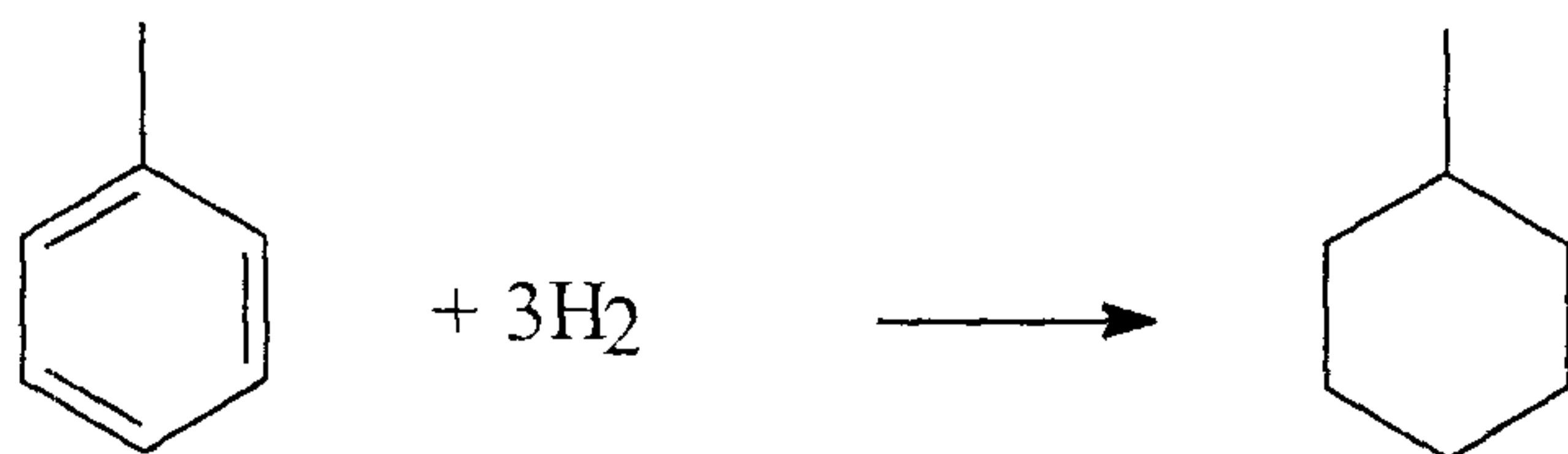
FIG. **18** shows the conversion of *n*-octane as it changes with SiO₂ deposition time during *n*-octane hydrocracking on the Ni/Al₂O₃ core **12**. The core **12** samples coated for 30 minutes showed the maximum conversion towards *n*-octane cracking, while the core **12** samples coated for 1.5 hours or longer showed no reactivity probably due to decreased acidity and narrowing of pores for *n*-octane penetration. These results appear to indicate that the permselective inner shell **14** may be used to limit access of hydrocarbon molecules to the catalyst material **20** in the core **12**.

Equations **3**, **4**, and **5** show examples of hydrogenation of various starting hydrocarbons using the catalyst composition **10** and the resulting products that may be achieved. Equation **3** shows hydrogenation of benzene, Equation **4** shows hydrogenation of toluene, and Equation **5** shows hydrogenation of *o*-xylene. The catalyst composition **10** in the various embodiments comprised a mass ratio of the outer shell **16** (Zeolite13X, γ -Al₂O₃, SiO₂ or combinations thereof) to the SiO₂-modified Pt/ γ -Al₂O₃ core **12** of about 1:1, 2:1, 4:1 (e.g., FIG. **23**). Hydrogenation reactions were conducted at about 0.6 mL/hydrocarbon, about 30 mL/min H₂ flow at 1 atm and about 90 to 240°C.

(Equation 3)



(Equation 4)



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(Equation 5)

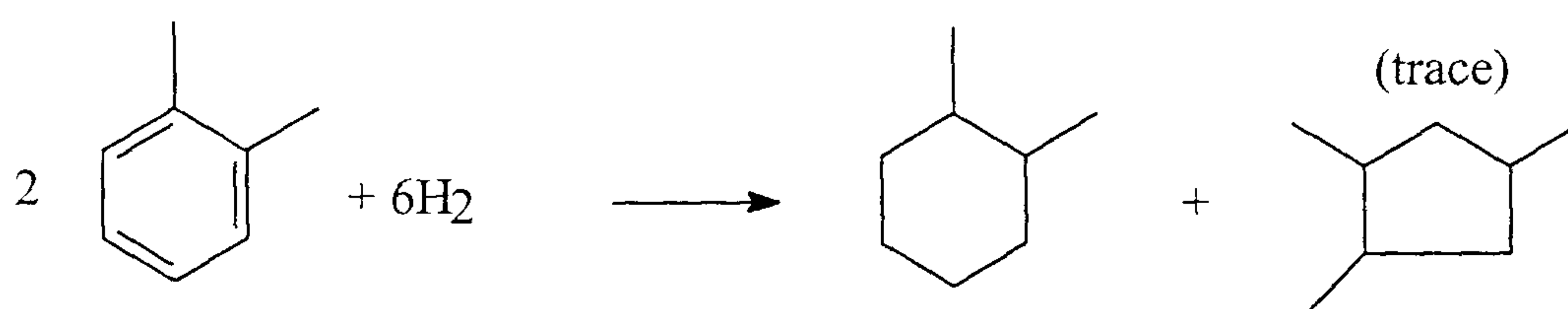


FIG. 22 illustrates the percent conversion of: (A) benzene to cyclohexane, (B) toluene to methylcyclohexane, and (C) O-xylene to di-methylcyclohexane and trimethylcyclopentane at varying temperatures using the composition 10 in accordance with various embodiments of the invention. As is illustrated in FIG. 22A for benzene hydrogenation, efficiency of the reaction appears to increase with increasing acidity of the outer shell 16 (i.e., Zeolite 13X > γ -Al₂O₃ > SiO₂). As is illustrated in FIG. 22B, the outer shell 16 appears to show no reactivity in the absence the catalyst material 20 in the core 12, which indicates that the transfer of activated hydrogen species from the core 12 to the outer shell 16 likely works. Hydrogenation results for o-xylene are illustrated in FIG. 22C. Reactivity appears to decrease in these embodiments (i.e., with increasing aromatic substituents) in the following order: benzene > toluene > o-xylene.

20

FIG. 23 shows the effect on conversion of hydrocarbon feed of the amount of the outer shell 16 relative to the core 12, and indicates that generally reactivity increases with increasing amount of the outer shell 16 in relation to the core 12. In selected embodiments, a preferred ratio of the outer shell 16 to the core 12 is about 2:1.

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FIG. 29 illustrates the results of hydroprocessing application using the composition **10** comprising the Pt/Al₂O₃ core **12**, the permselective SiO₂ inner shell **14**, and the Al₂O₃ outer shell **16** comprising CoMo as the second catalytic material **22**.

CLAIMS:

1. A catalyst comprising:
 - a core having a porous support and a first catalytic material for generating activated hydrogen dispersed in the porous support, the porous support pores being sized to permit hydrogen sulfide diffusion into the pores;
 - a permselective inner shell applied to the core, the permselective inner shell having permselective inner shell pores;
 - and
 - an outer shell applied to the permselective inner shell adapted for hydroprocessing a hydrocarbon feed

wherein the permselective inner shell pores are sized to exclude hydrogen sulfide from the core when the permselective inner shell is in contact with the outer shell while being permeable to hydrogen and activated hydrogen.
2. The catalyst of claim 1 further comprising a second catalytic material dispersed in the outer shell.
3. The catalyst of claim 2 wherein the second catalytic material comprises a mixture of at least one metal from Group 6 and at least one metal from Group 8.
4. The catalyst of claim 2 wherein the second catalytic material comprises mixtures of Co and Mo, Ni and Co, Mo and W, or W and P.
5. The catalyst of claim 2 wherein the concentration of the second catalytic material in the outer shell may range from 0% wt/wt to about 60% wt/wt.

6. The catalyst of claim 1 or claim 2 wherein the porous support comprises aluminum oxide, zeolite, silicon oxide, clay or combinations thereof.
7. The catalyst of claim 1 or claim 2 wherein the porous support comprises aluminum oxide.
8. The catalyst of claim 1 or claim 2 wherein the porous support comprises zeolite.
9. The catalyst of claim 1 or claim 2 wherein the porous support comprises a mixture of aluminum oxide and zeolite.
10. The catalyst of claim 1 or claim 2 wherein the first catalytic material may be selected from Group 8 metals.
11. The catalyst of claim 1 or claim 2 wherein the first catalytic material comprises precursors of Group 8 metals.
12. The catalyst of claim 11 wherein the precursors of Group 8 metals comprise $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$, $\text{Pt}(\text{CH}_3\text{NH}_2)_4\text{Cl}_2$, $\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$, and $\text{Pt}(\text{C}_4\text{H}_9\text{NH}_2)_4\text{Cl}_2$, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, PdCl_2 or mixtures thereof.
13. The catalyst of claim 1 or claim 2 wherein the permselective inner shell comprises silica, alumina zeolites or mixtures thereof.
14. The catalyst of claim 1 or claim 2 wherein the permselective inner shell ranges in thickness from about 1 to 3 monolayers.
15. The catalyst of claim 1 or claim 2 wherein the outer shell may be selected from silica, alumina zeolites or mixtures thereof.

16. The catalyst of claim 1 or claim 2 wherein the ratio of the outer shell to the core may range between 1:1 wt/wt, 2:1 wt/wt, 4:1 wt/wt, 10:1 wt/wt, or any ratio between 1:1 wt/wt and 10:1 wt/wt.
17. A method of forming a catalyst, the method comprising:
 - dispersing a first catalytic material for generating activated hydrogen in a porous support having porous support pores to form a core, the porous support pores being sized to permit hydrogen sulfide diffusion into the pores;
 - surrounding the core with an encapsulating permselective inner shell having permselective inner shell pores; and
 - applying an outer shell adapted for hydroprocessing a hydrocarbon feed to the permselective inner shellwherein the permselective inner shell pores are sized to exclude hydrogen sulfide from the core when the permselective inner shell is in contact with the outer shell while being permeable to hydrogen and activated hydrogen.
18. The method of claim 17 further comprising incorporating a second catalytic material into the outer shell.
19. The method of claim 17 or claim 18 wherein the core is formed by a sol-gel reaction.
20. The method of claim 17 or claim 18 wherein the core is surrounded with the encapsulating inner shell using chemical vapor deposition.
21. The method of claim 17 or claim 18 wherein the outer shell is applied using mechanical deposition.

22. Use of the catalyst composition of any one of claims 1 to 16 for hydroprocessing of a hydrocarbon feed.
23. The use of claim 22 wherein the hydrocarbon feed comprises unsaturated hydrocarbons.
24. The use of claim 23 wherein the unsaturated hydrocarbons comprise aromatic hydrocarbons.
25. The use of any one of claims 22 to 24 wherein hydroprocessing comprises hydrogenation, hydrocracking, and hydrotreating.
26. Use of the catalyst of any one of claims 1 to 16 for hydroprocessing a hydrocarbon feed comprising aromatic hydrocarbons.
27. The catalyst of any one of claims 1 to 16 for hydrotreating a hydrocarbon feed comprising aromatic hydrocarbons.
28. The catalyst of any one of claims 1 to 16 for hydrogenating a hydrocarbon feed comprising aromatic hydrocarbons.

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FIG. 1

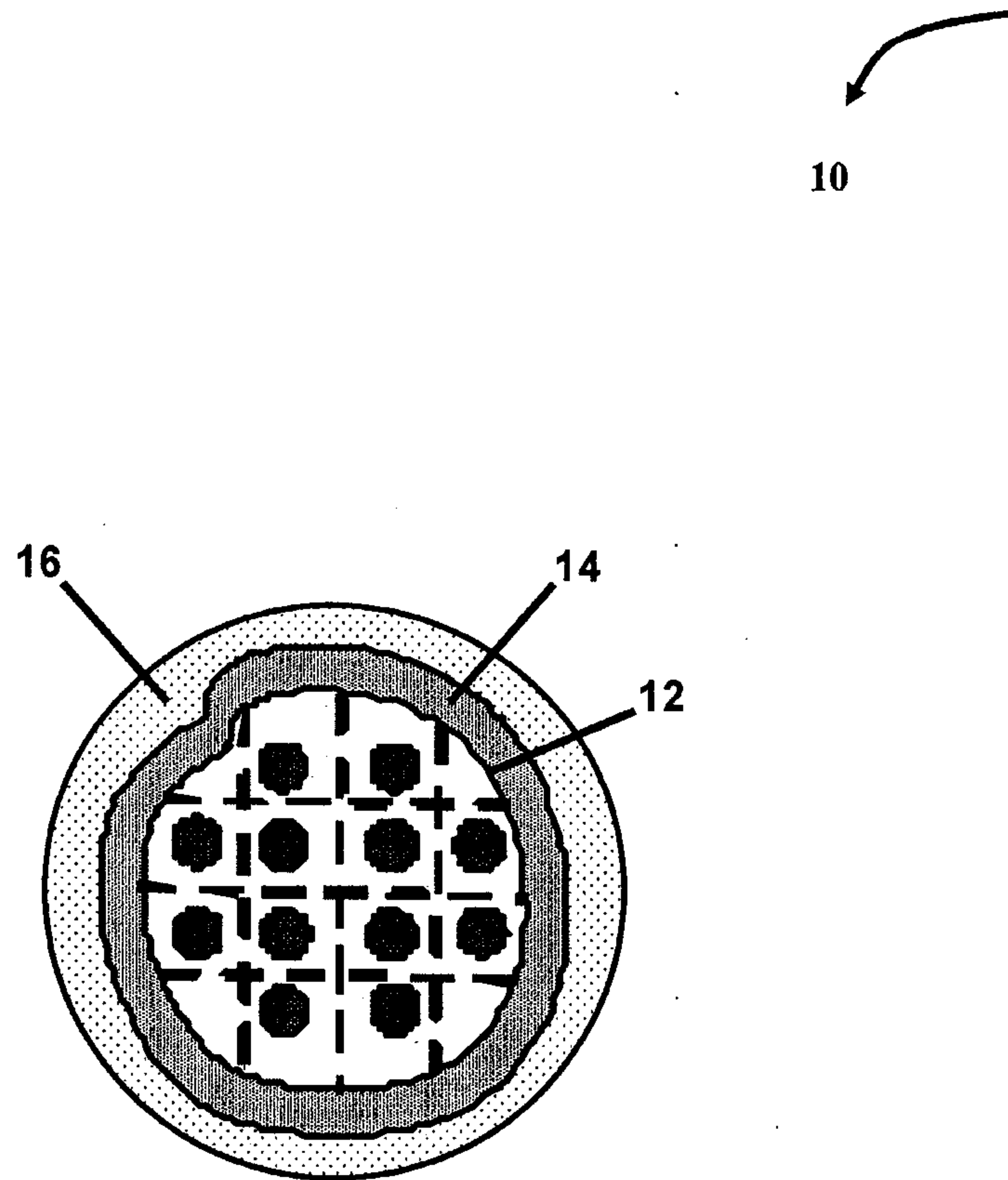


FIG. 2

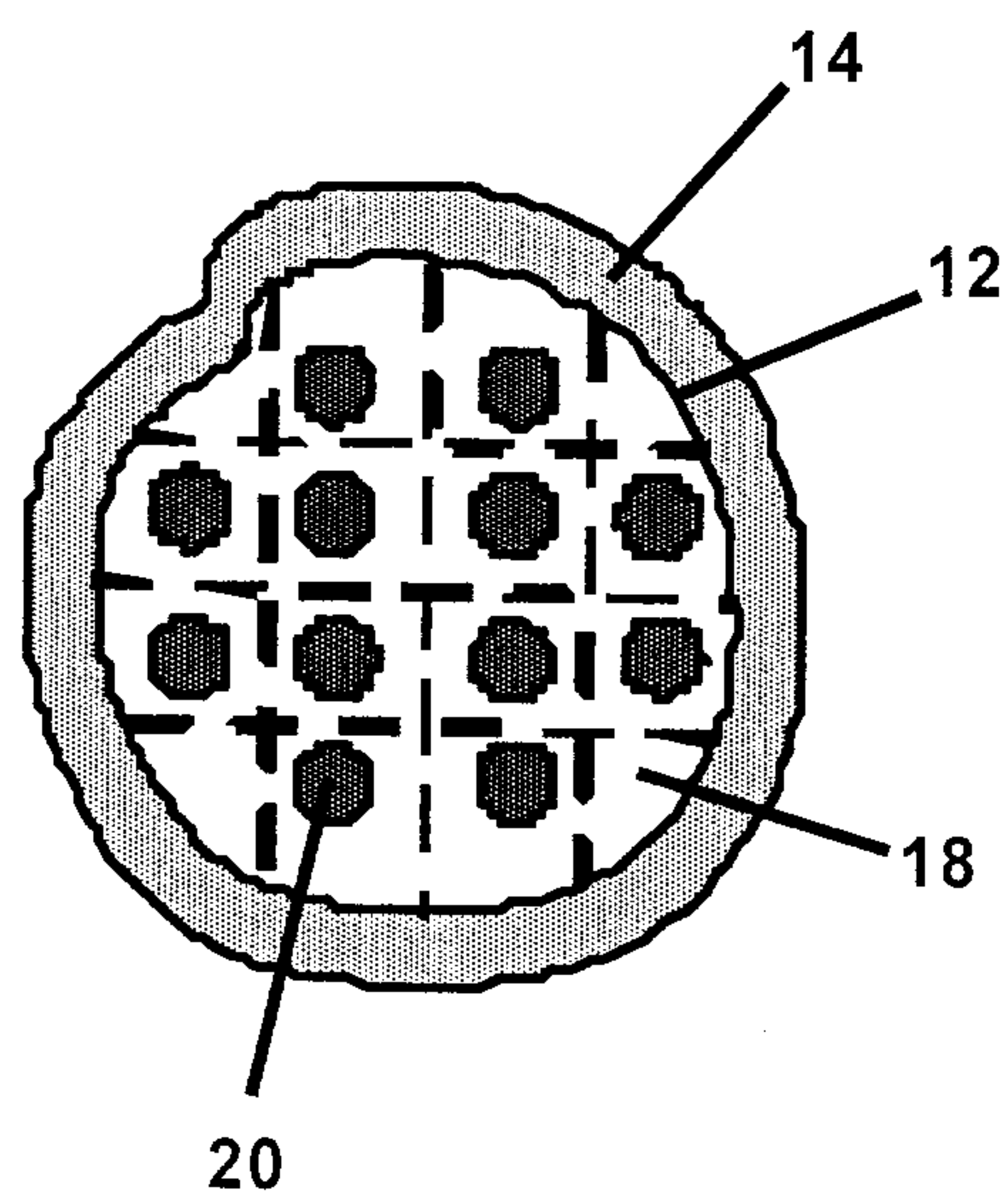
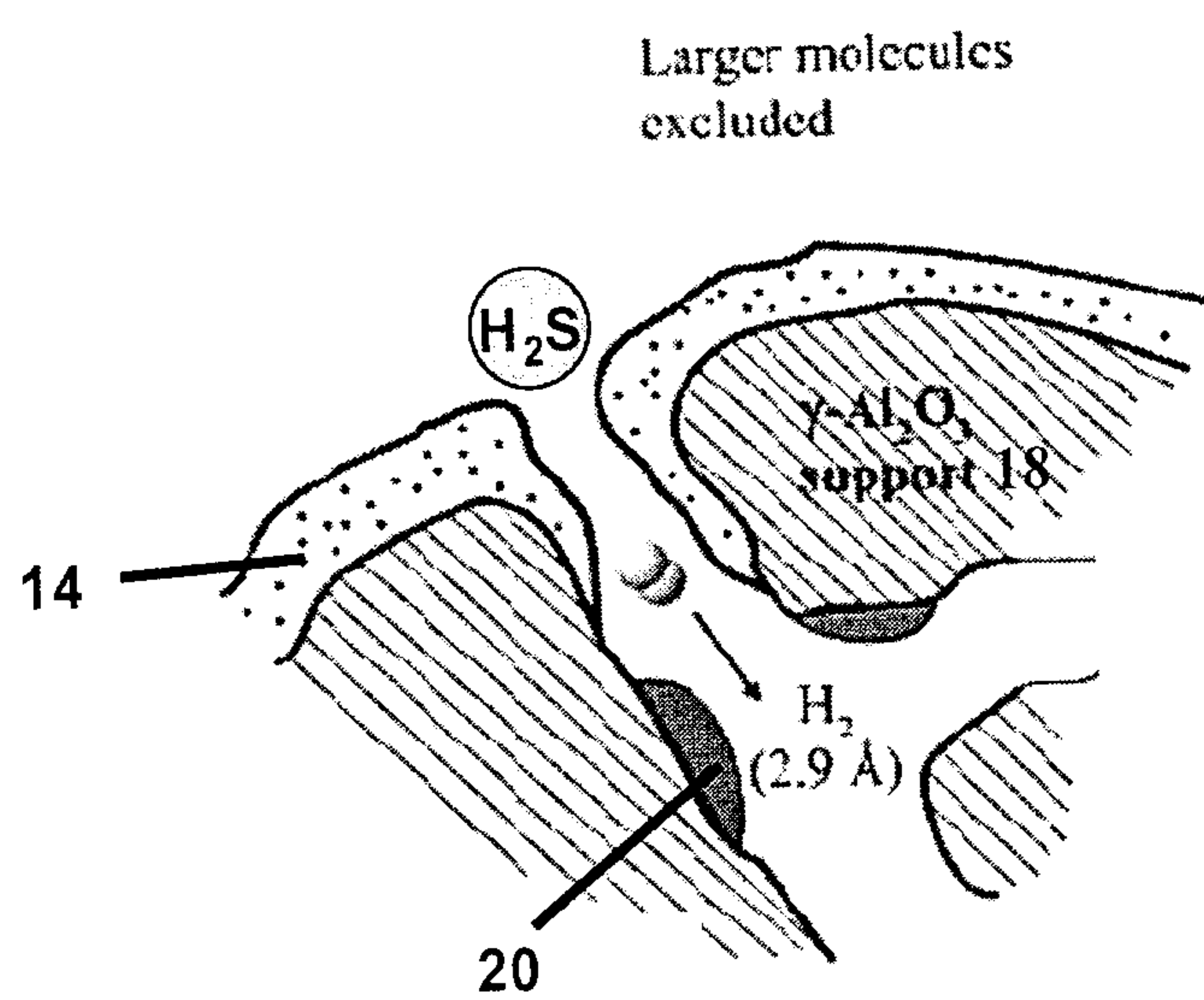
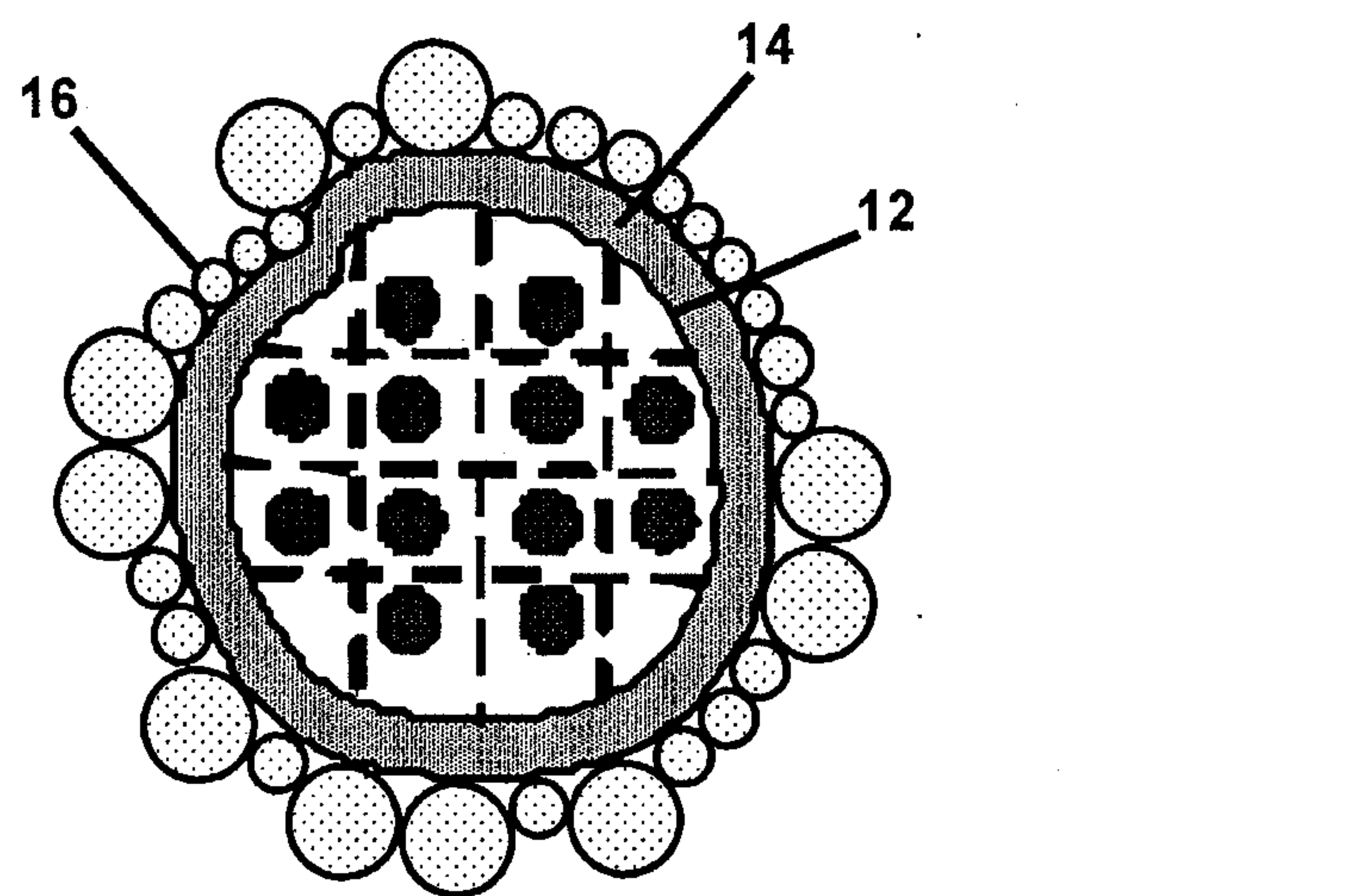


FIG. 3



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FIG. 4



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FIG. 5

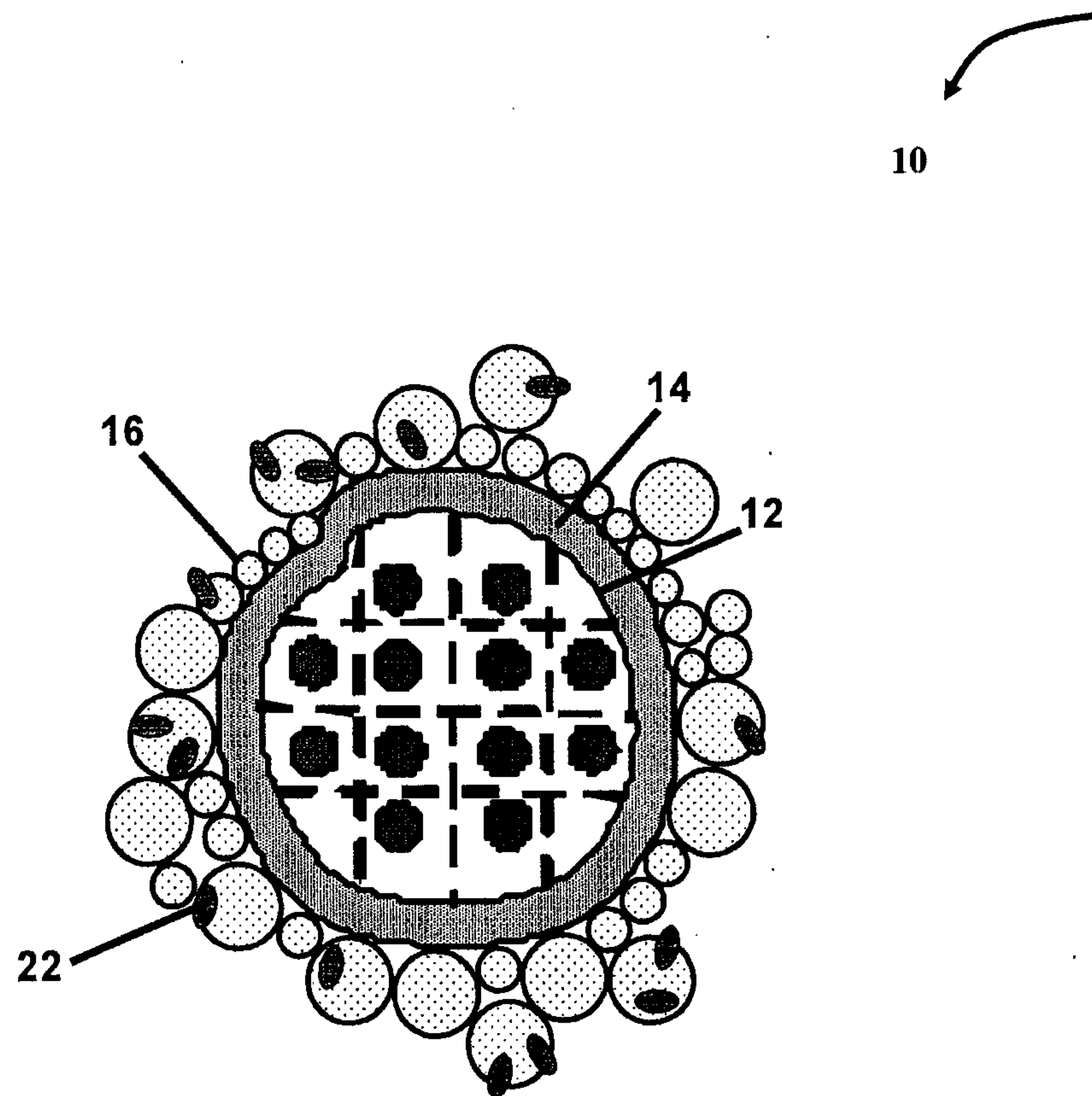


FIG. 6

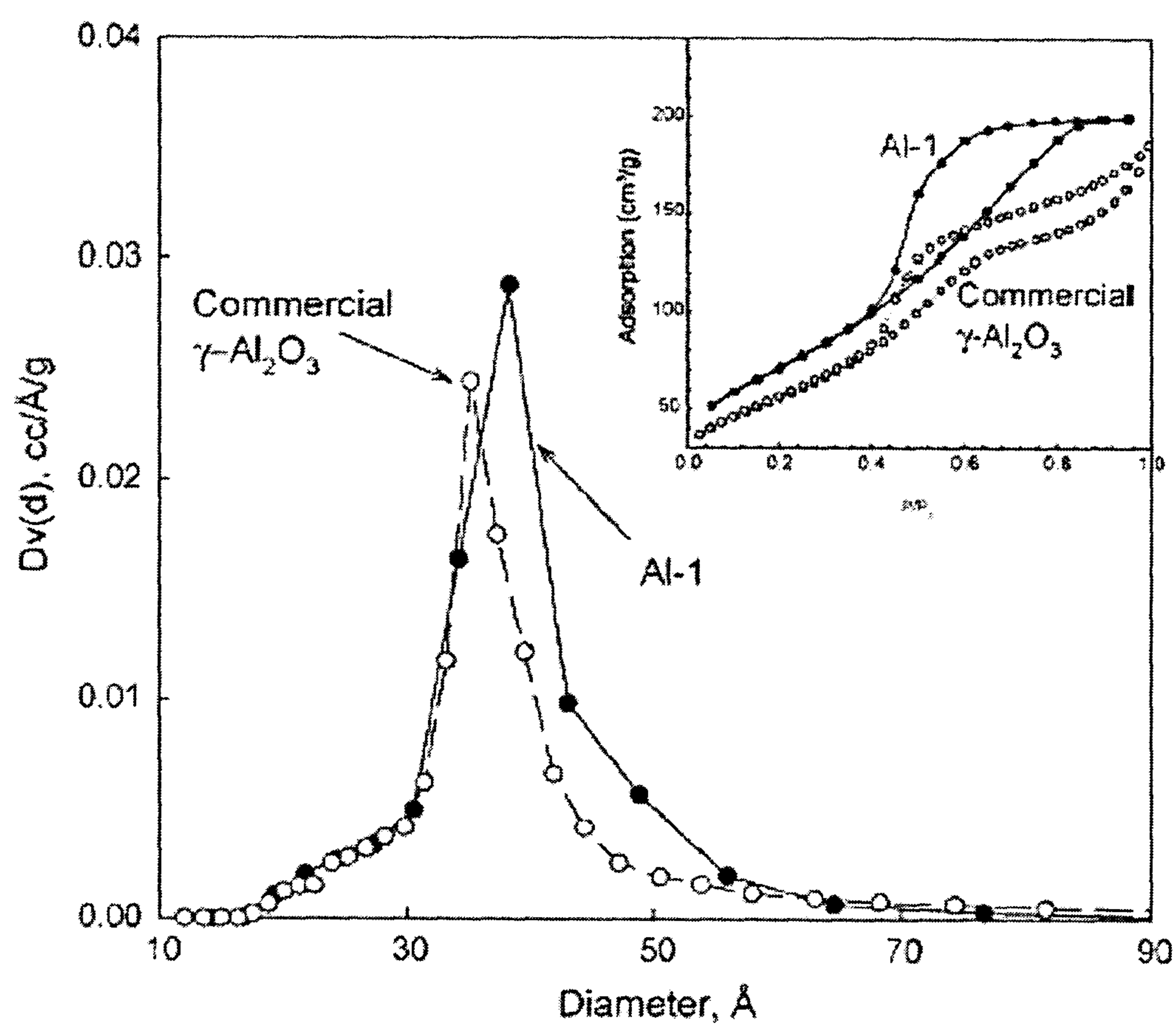


FIG. 7

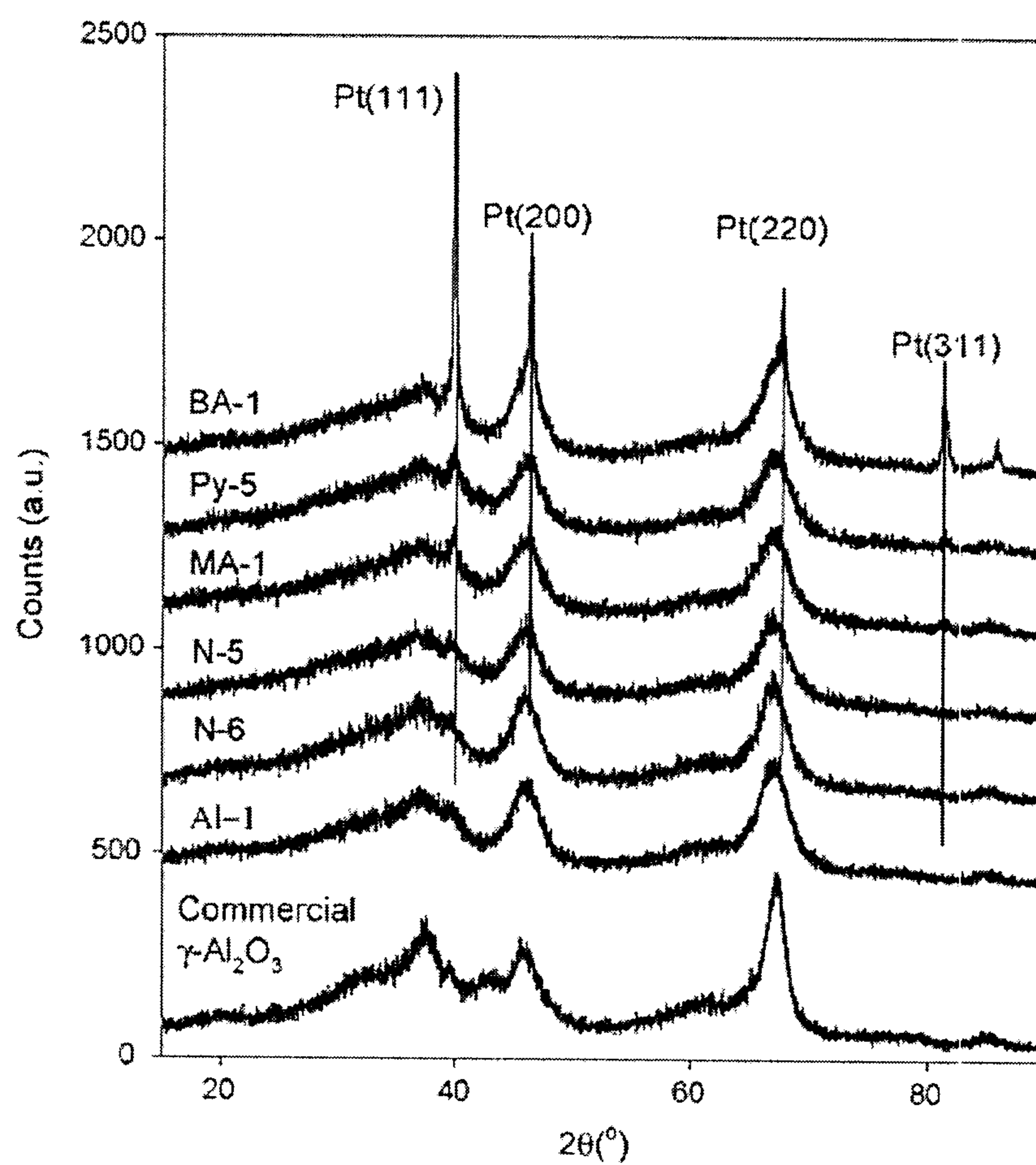


FIG. 8

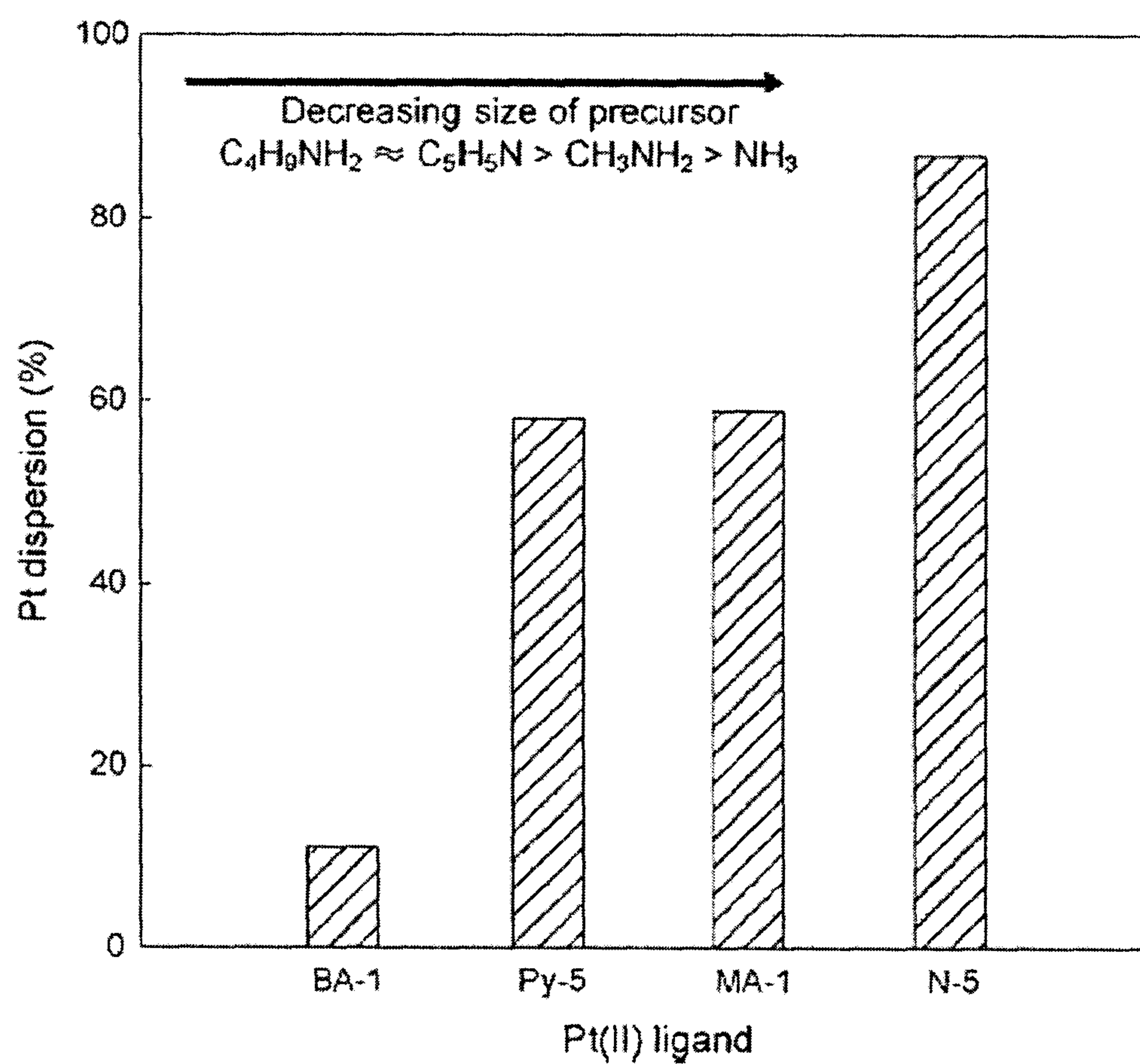


FIG. 9

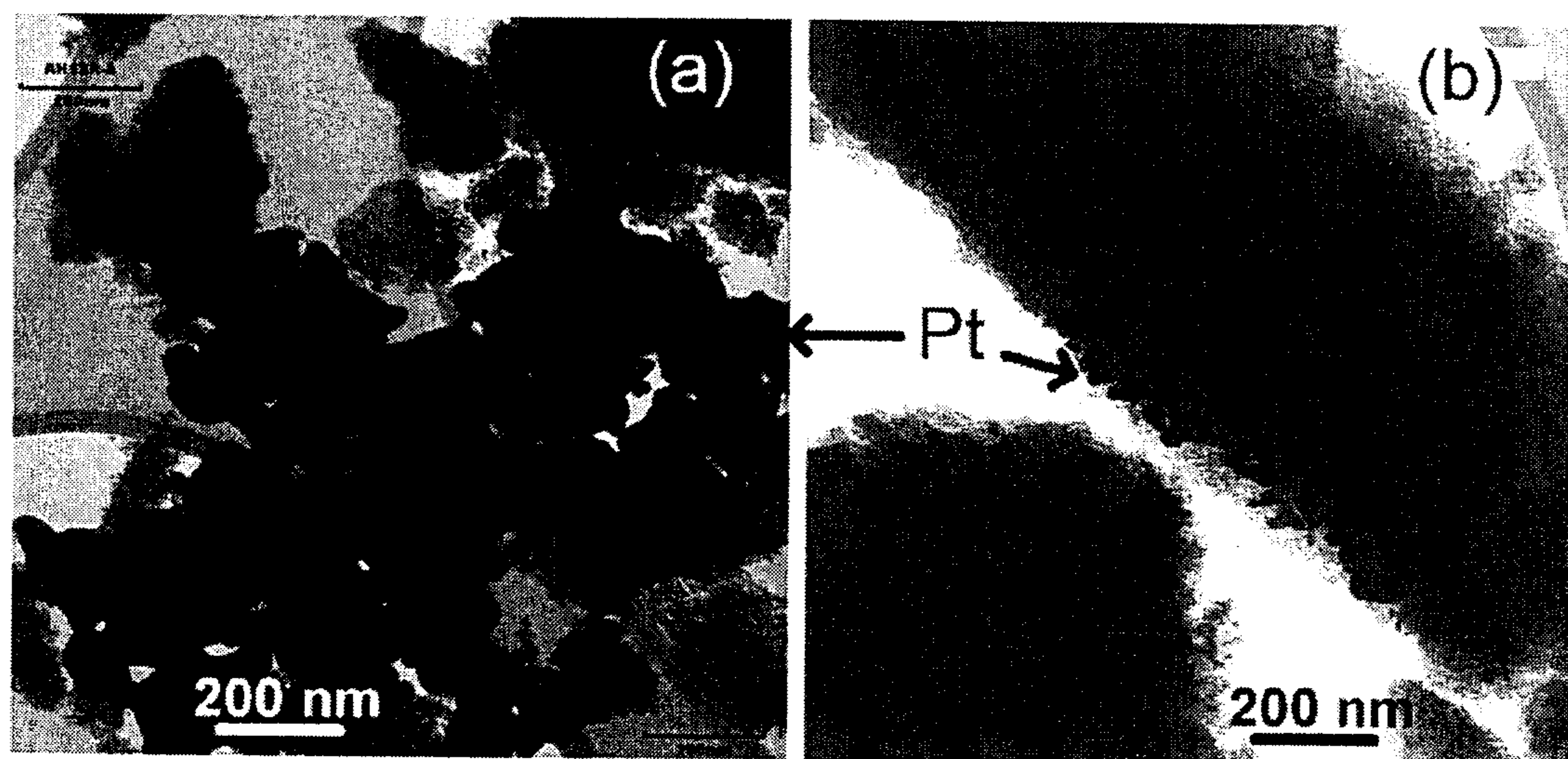


FIG. 10

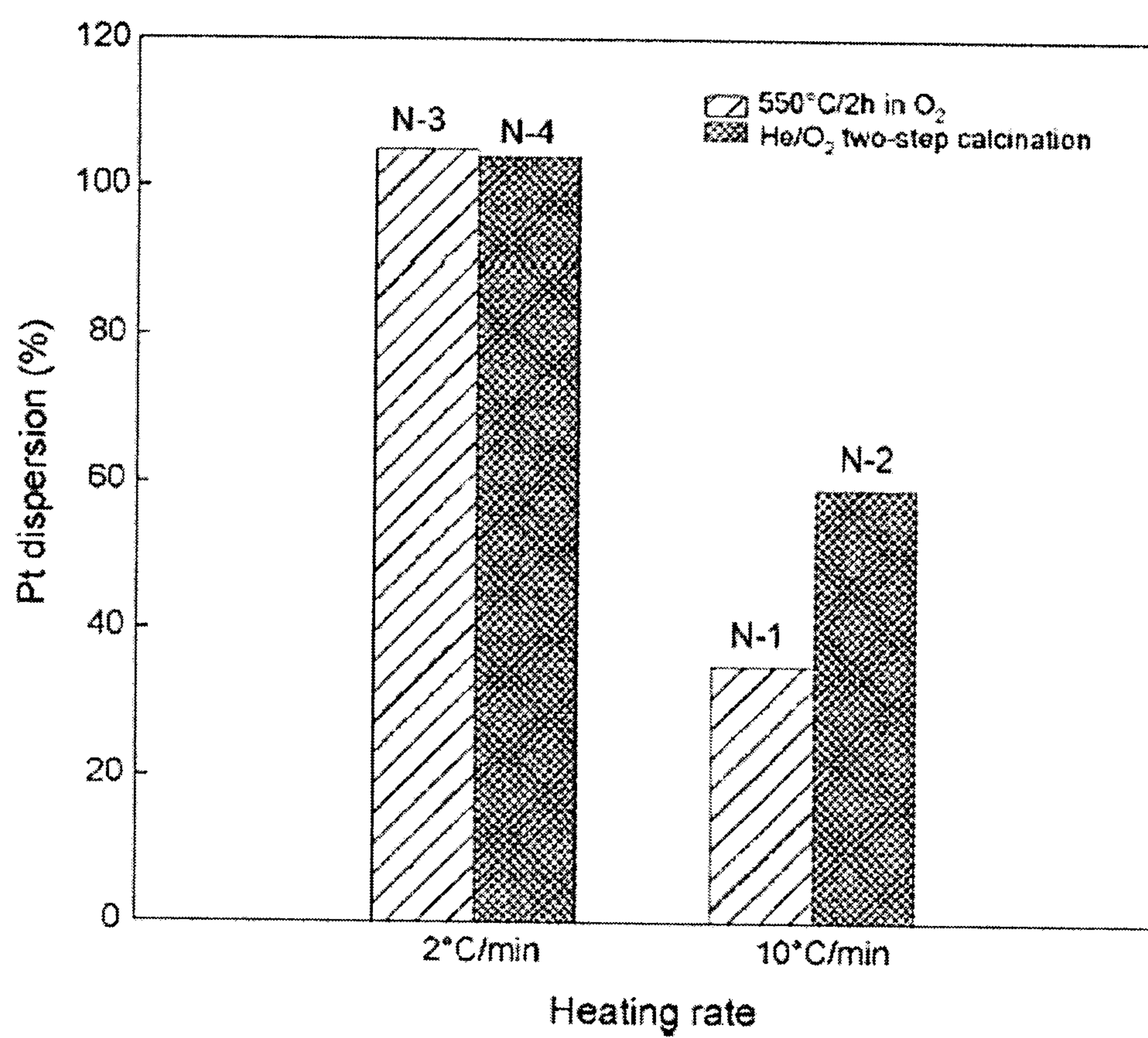
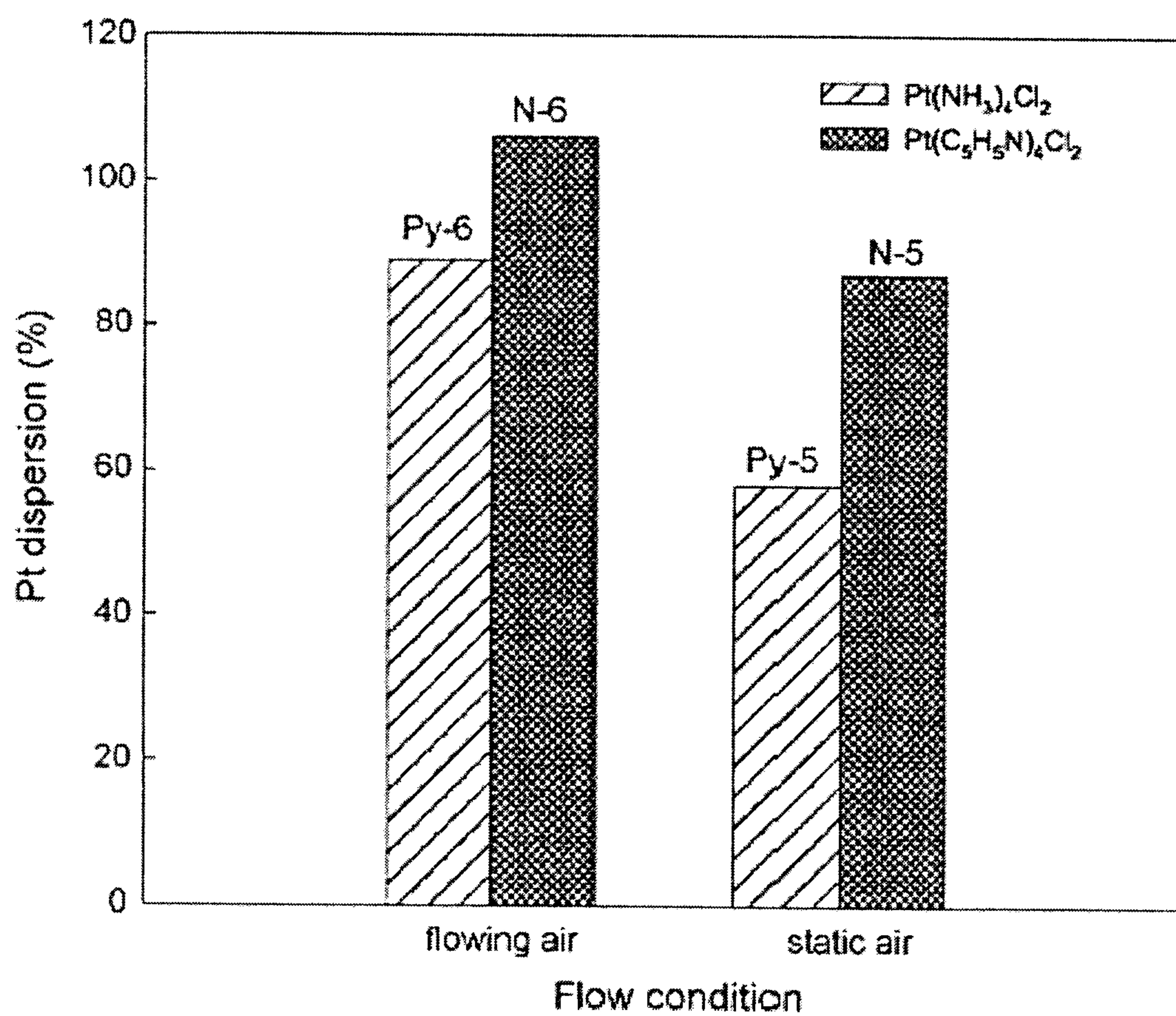


FIG. 11



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FIG. 12

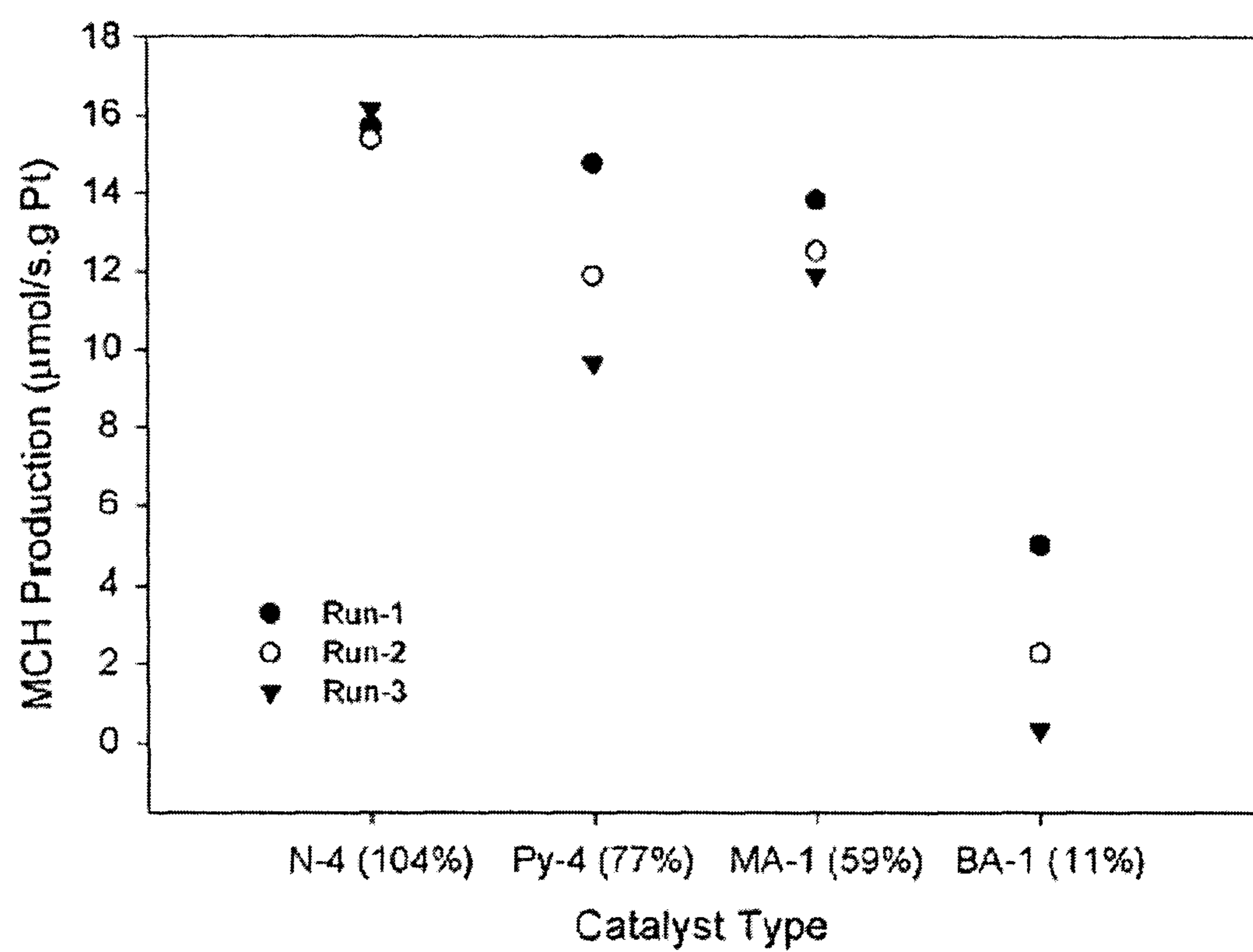


FIG. 13

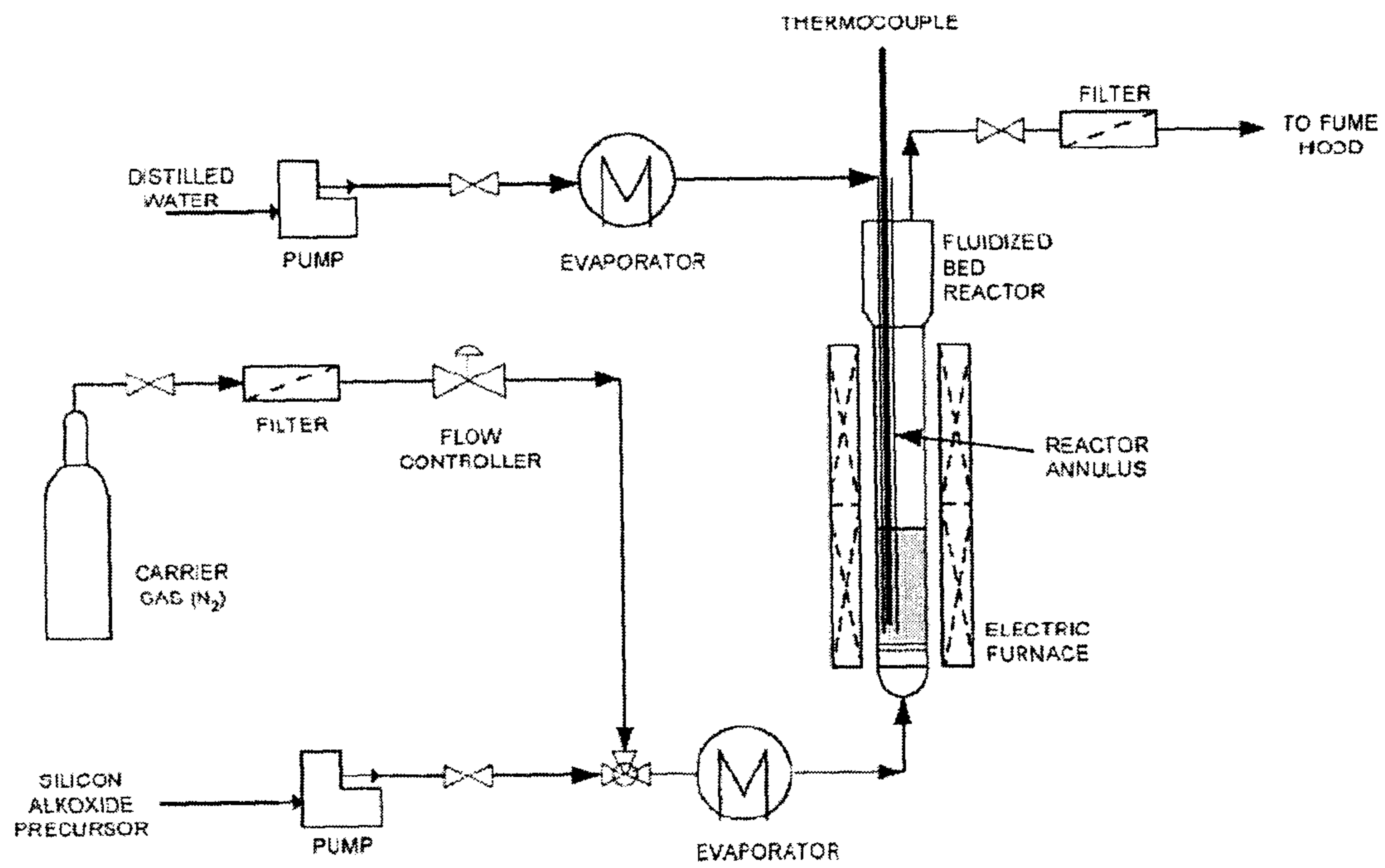


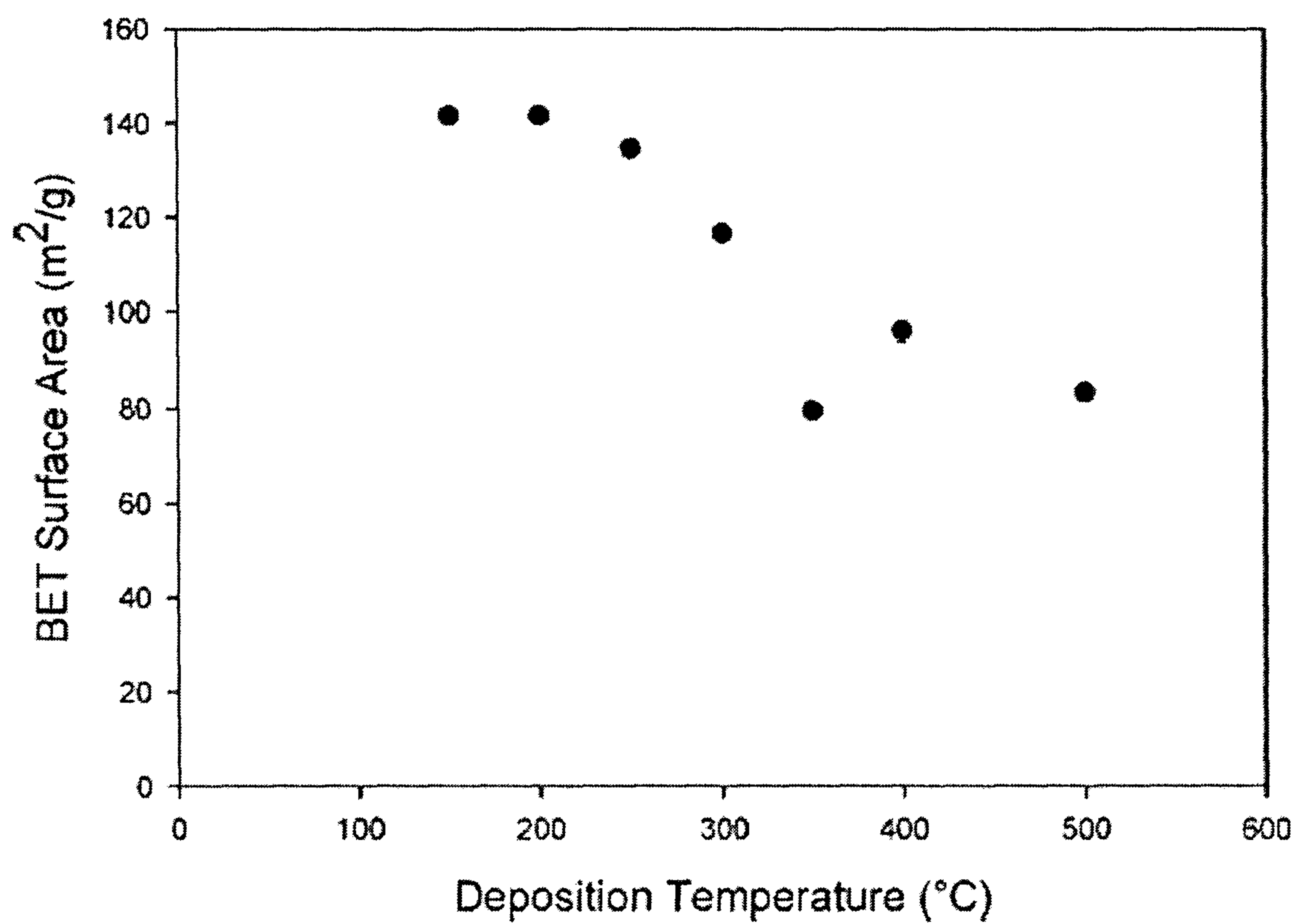
FIG. 14

FIG. 15

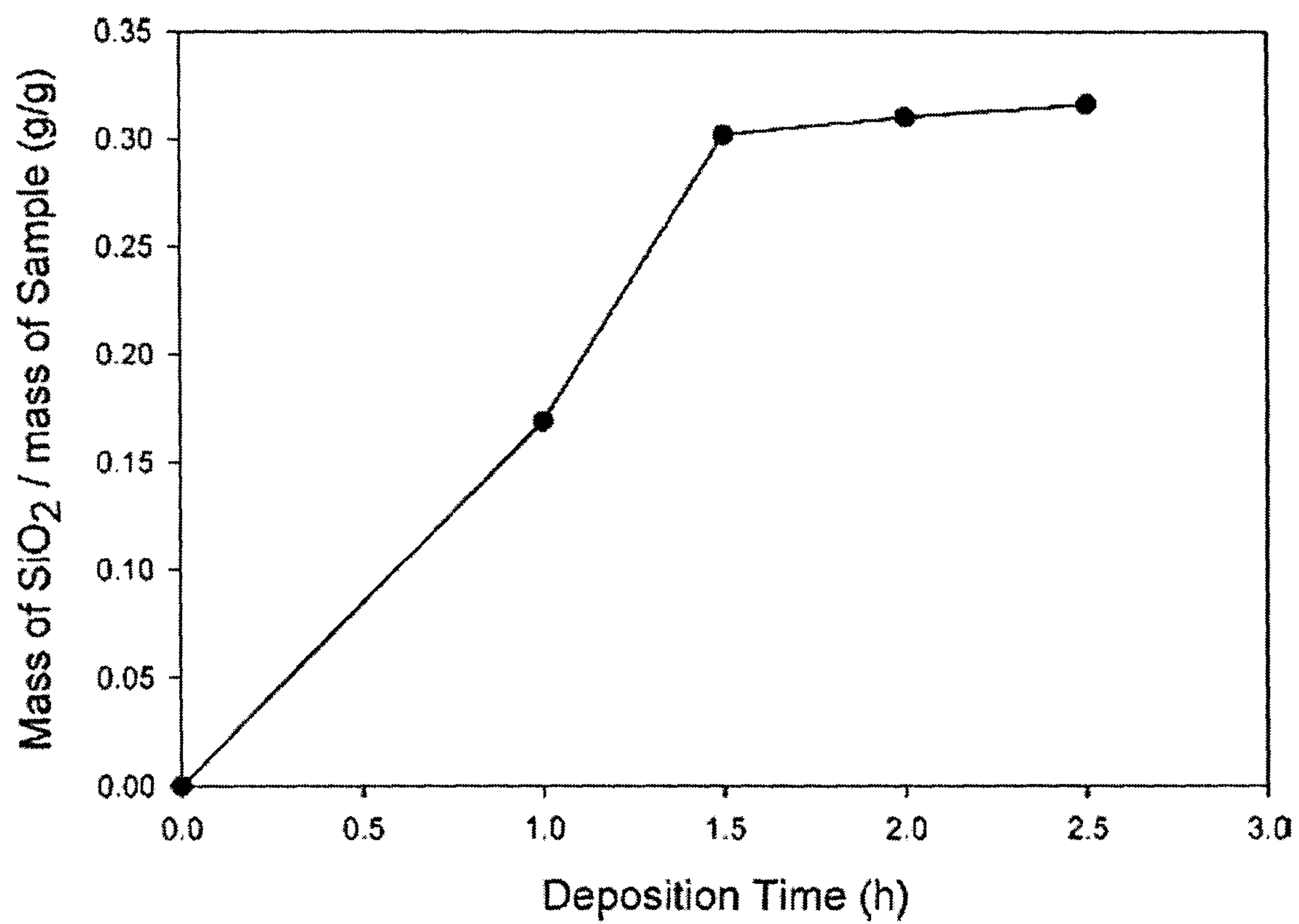


FIG. 16

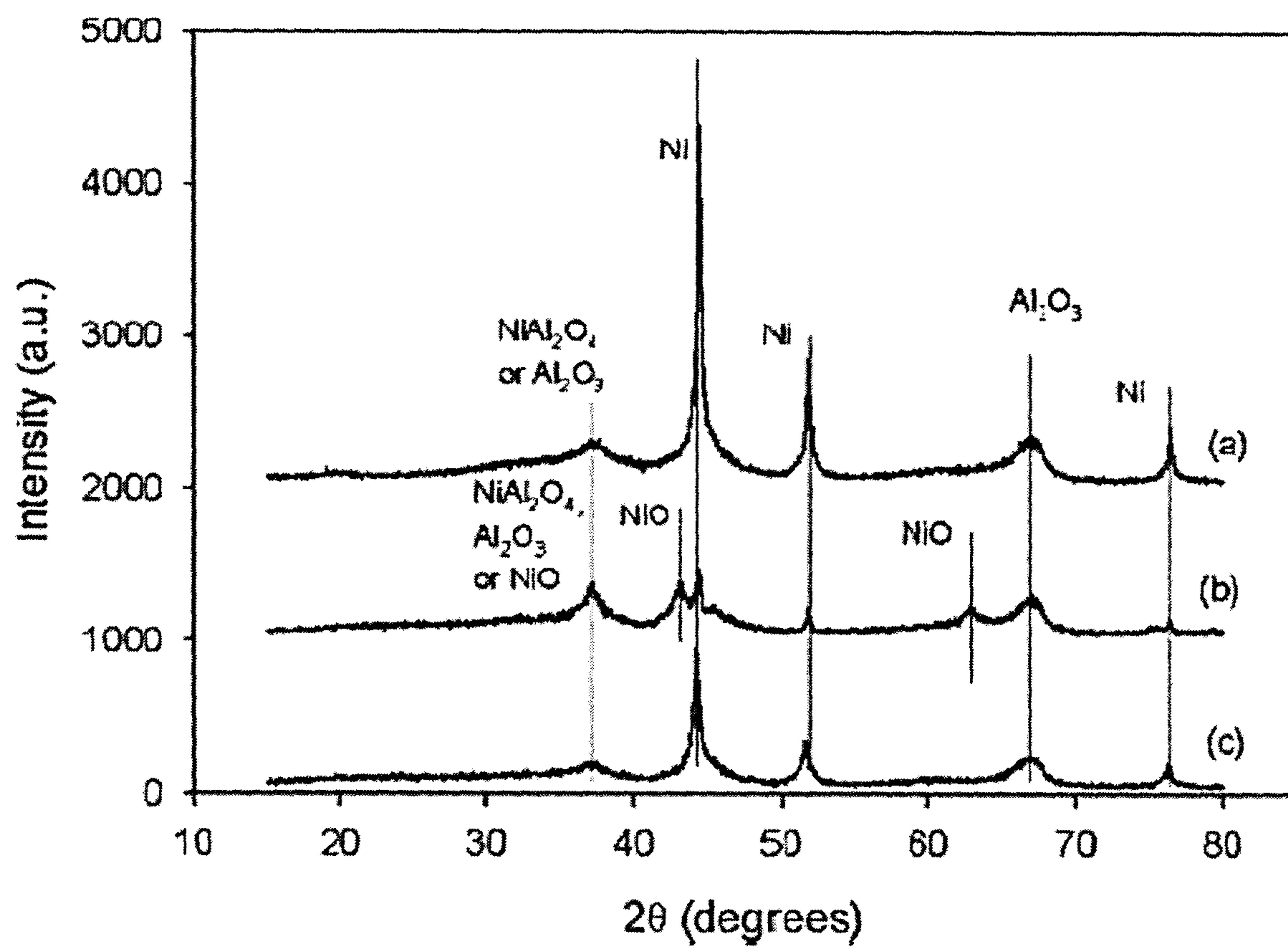


FIG. 17

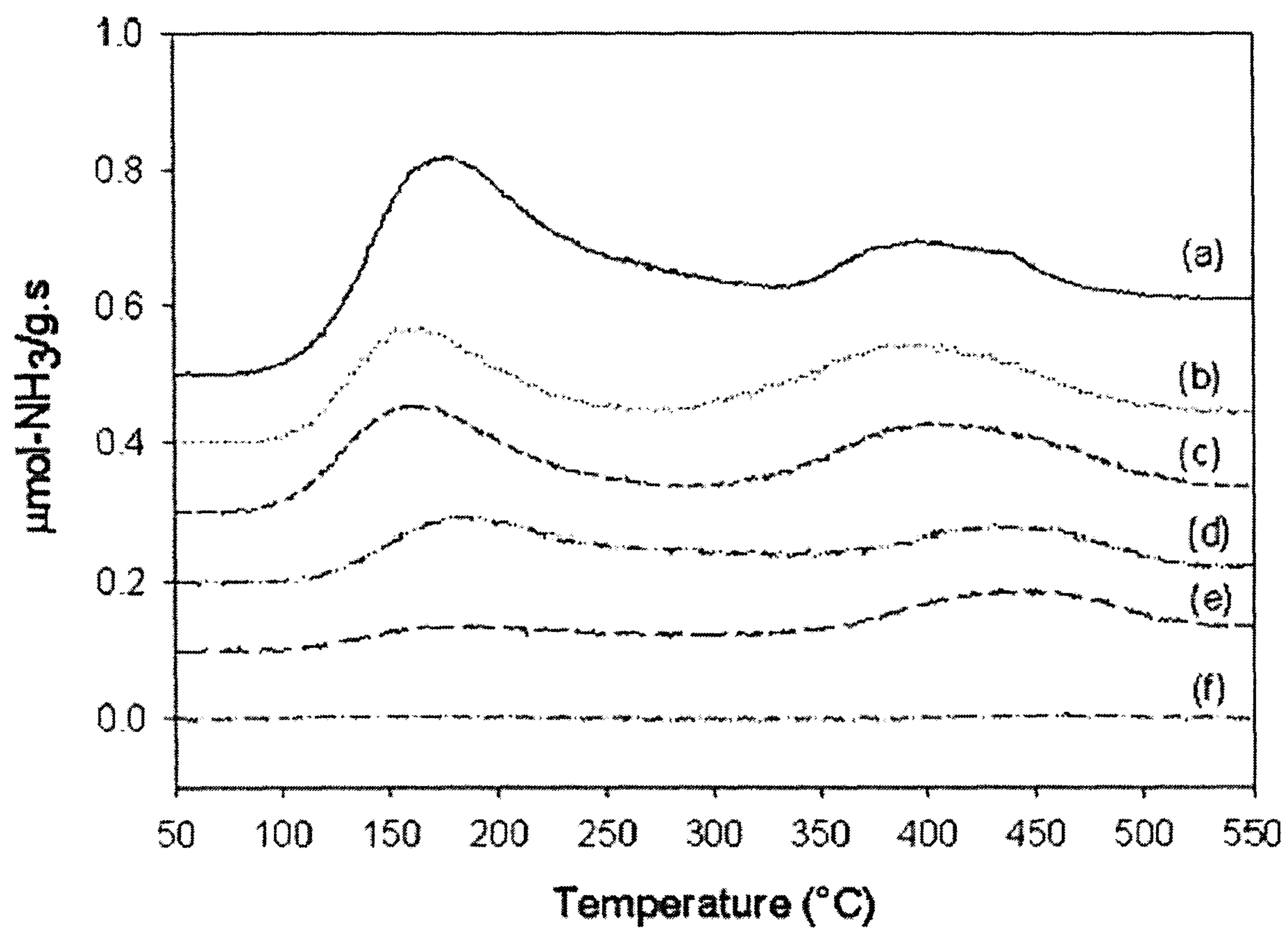


FIG. 18

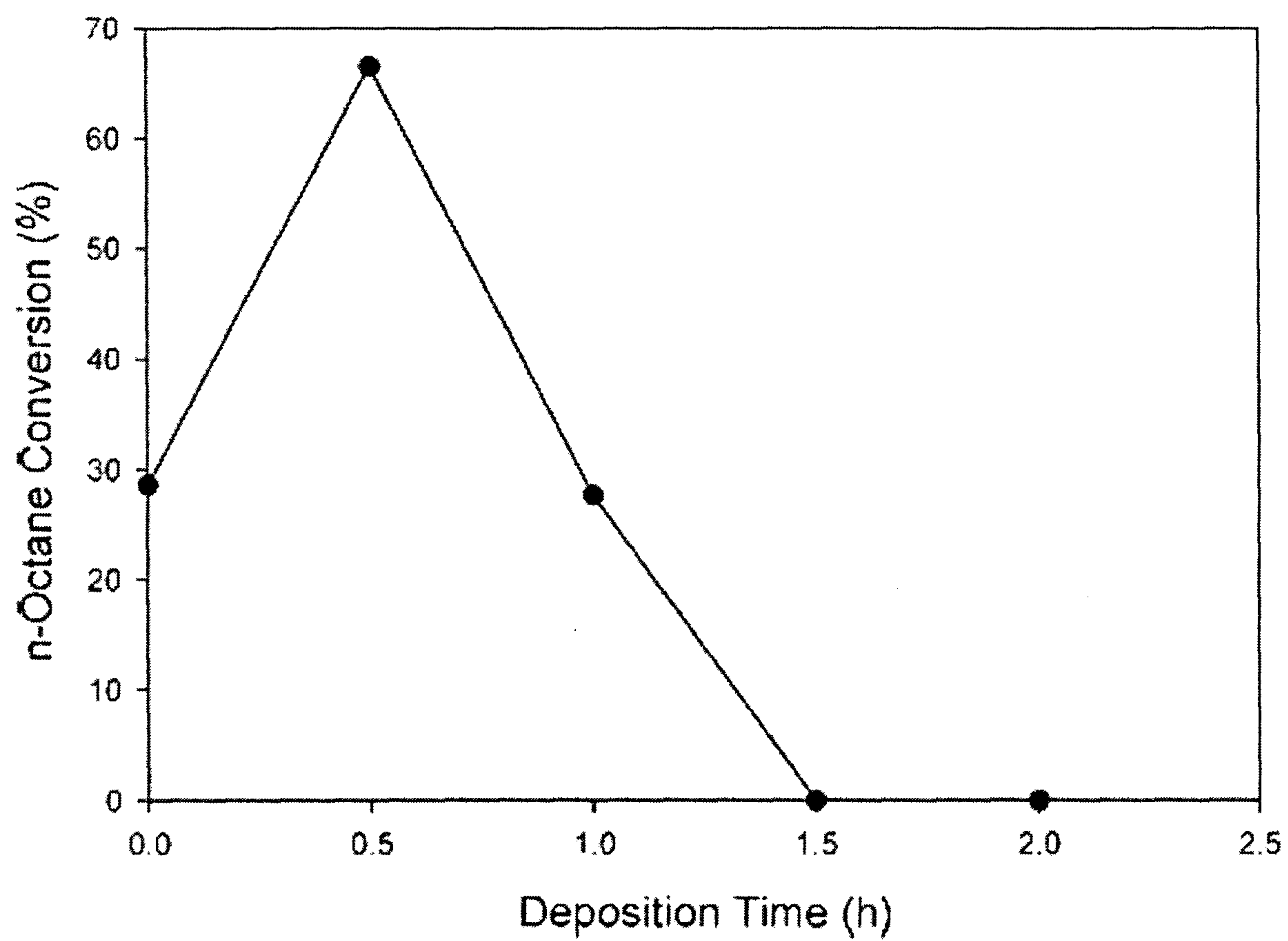


FIG. 19

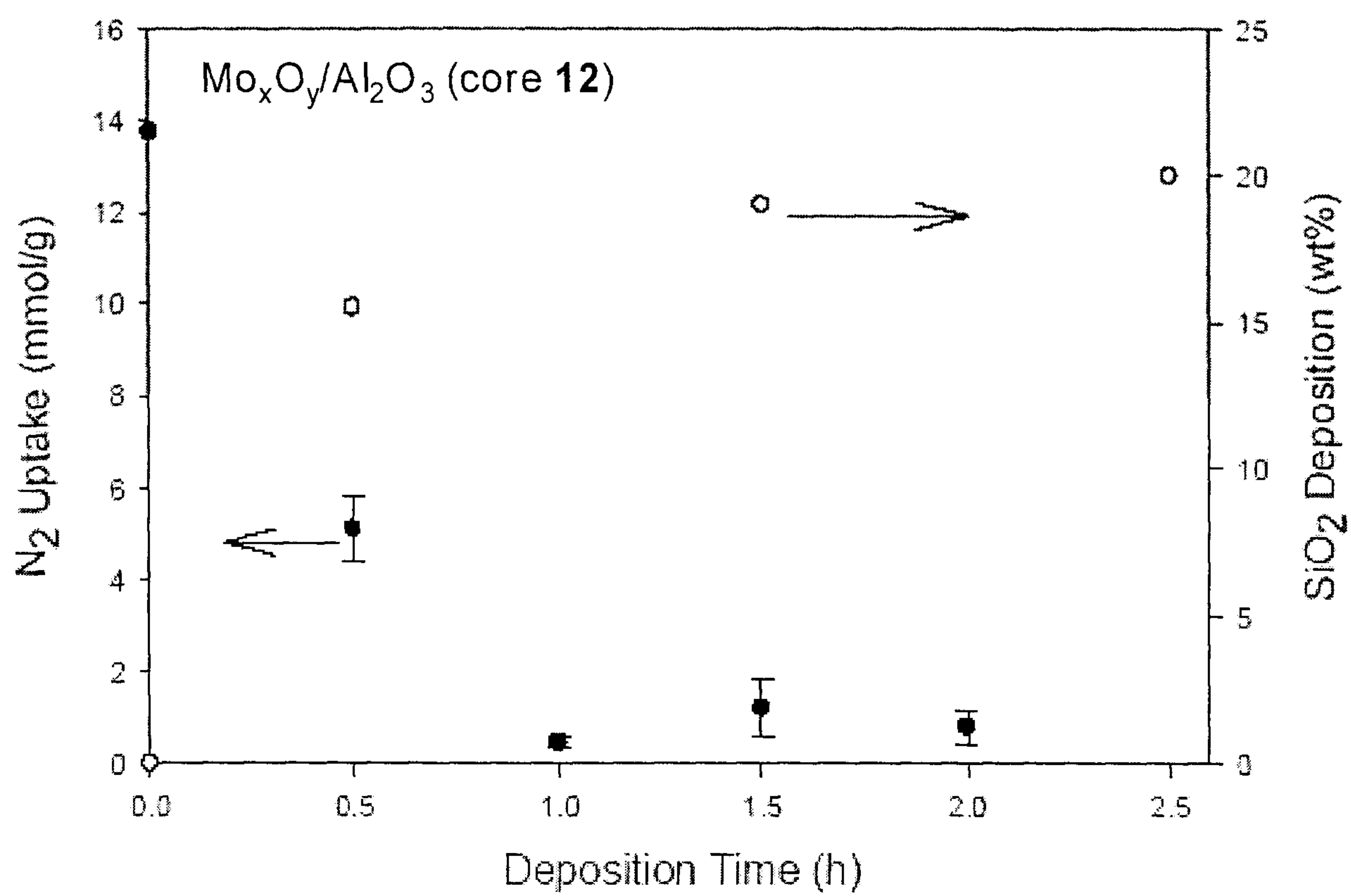


FIG. 20

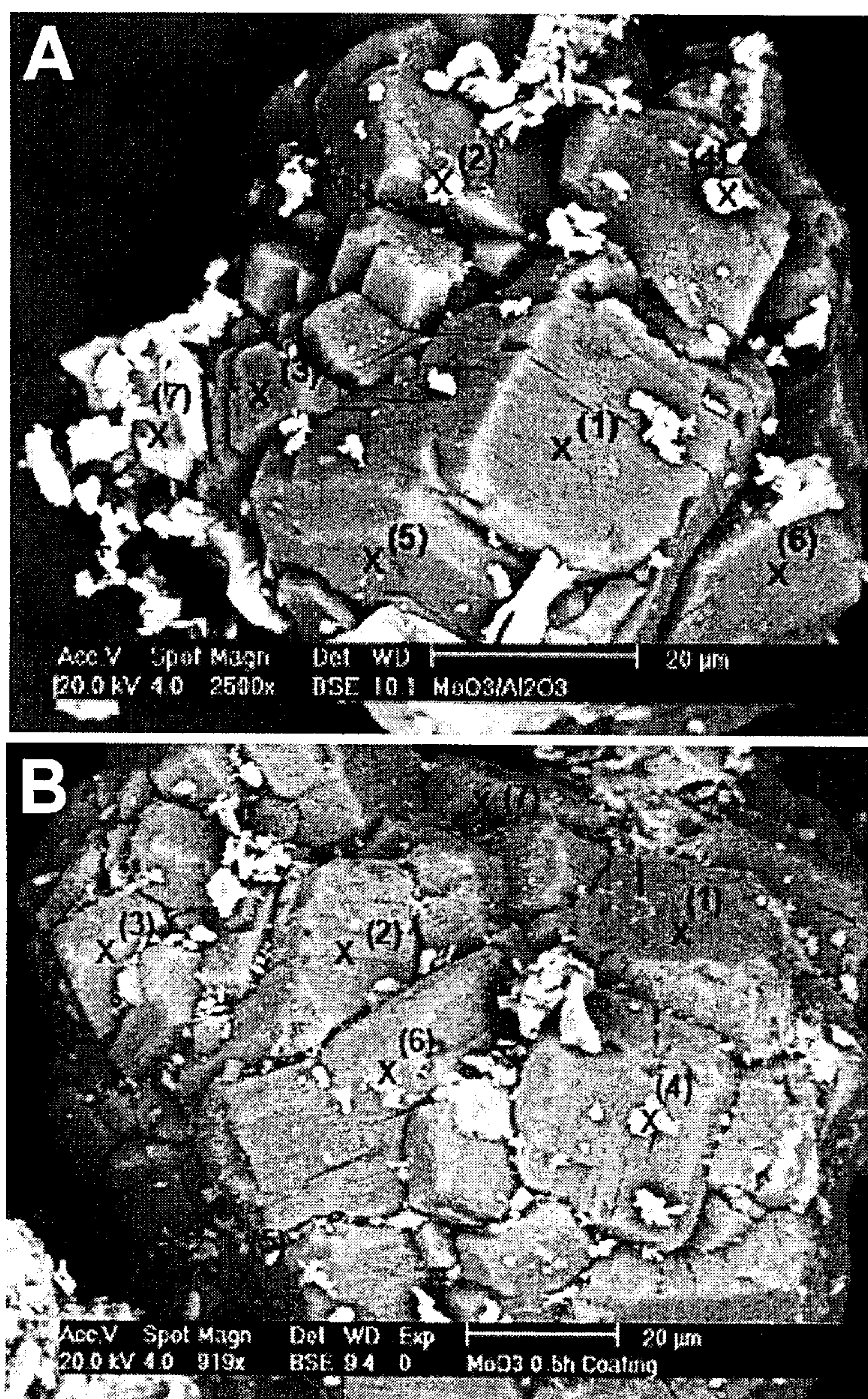


FIG. 21

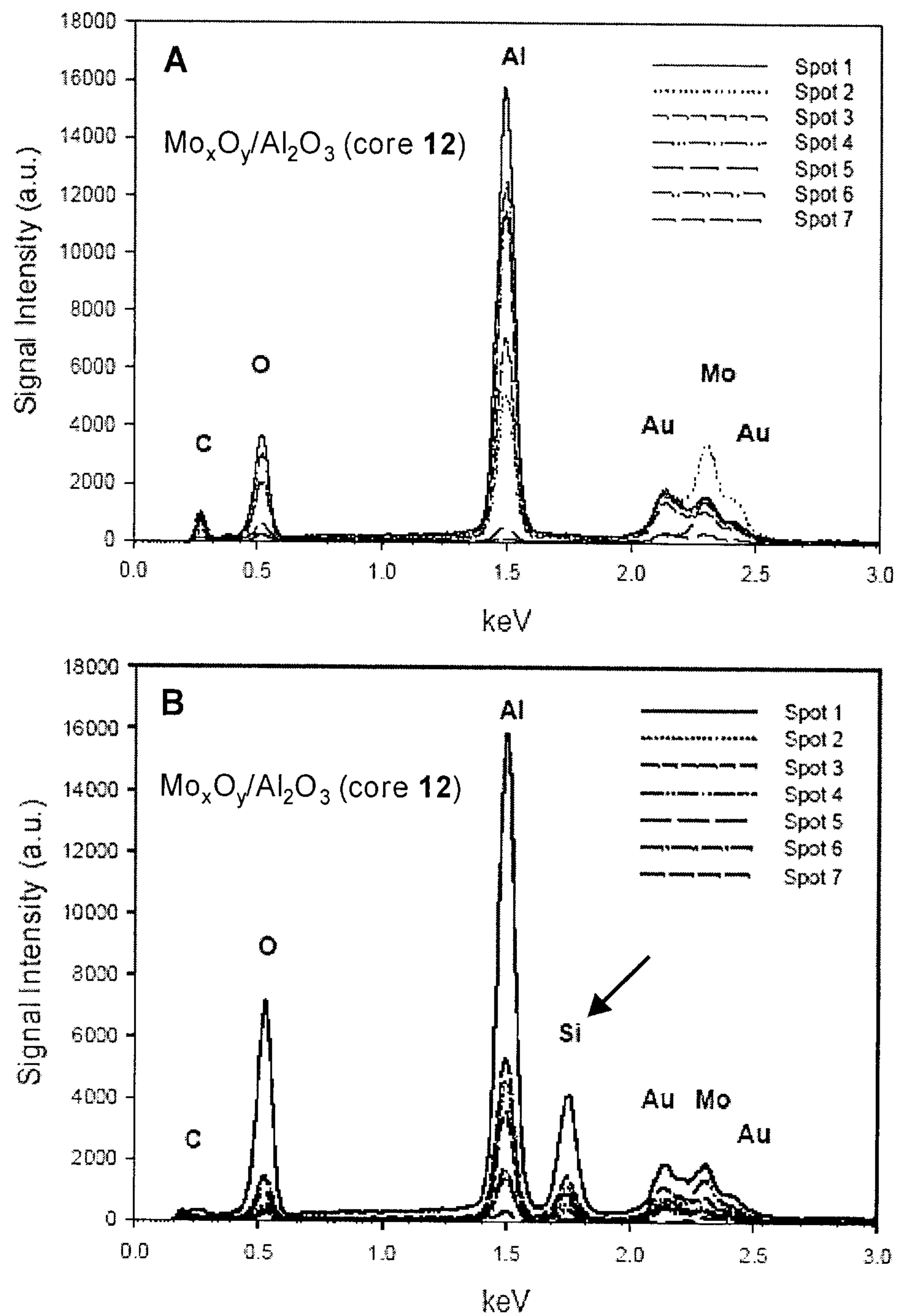


FIG. 22

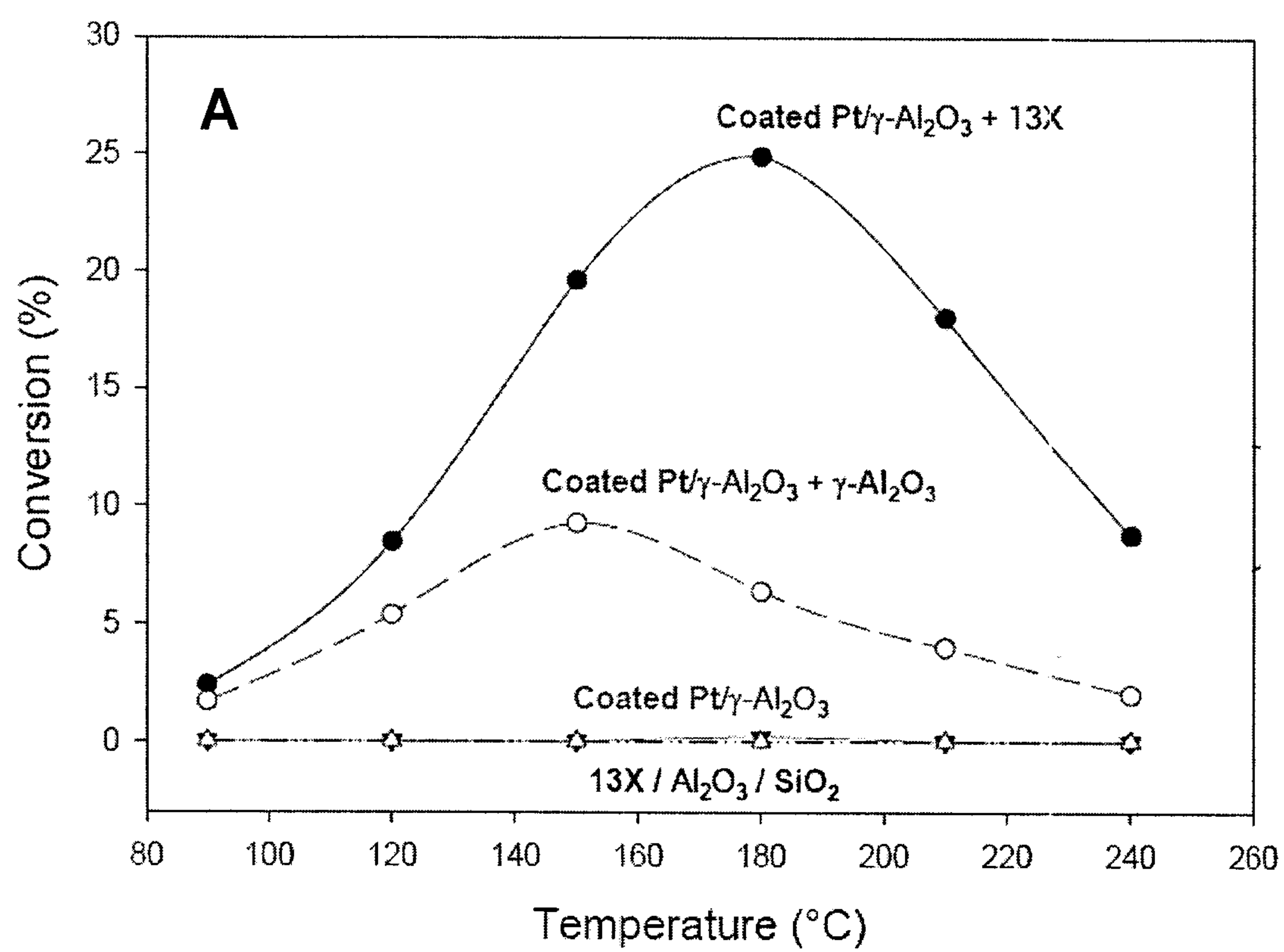


FIG. 22

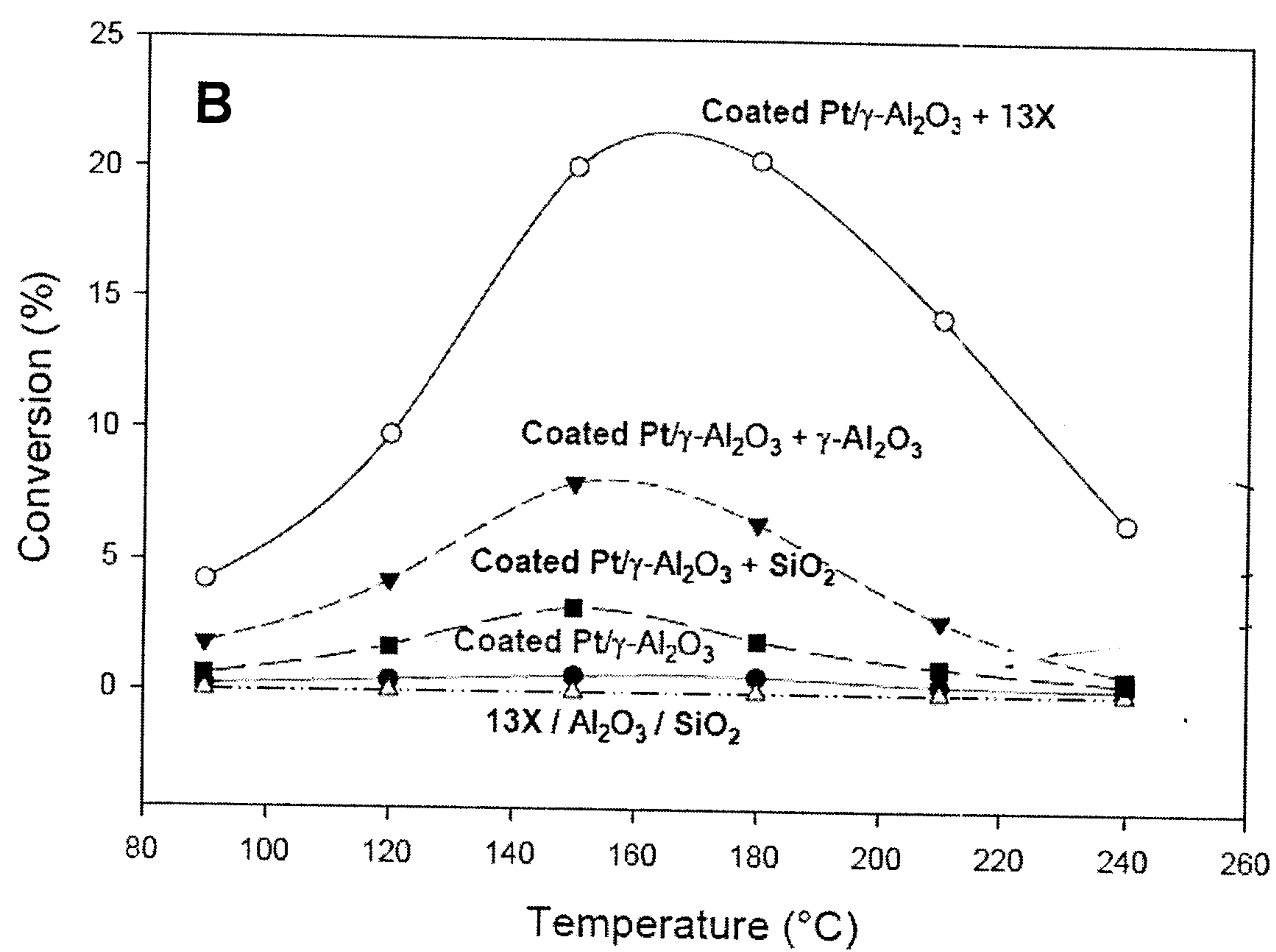


FIG. 22

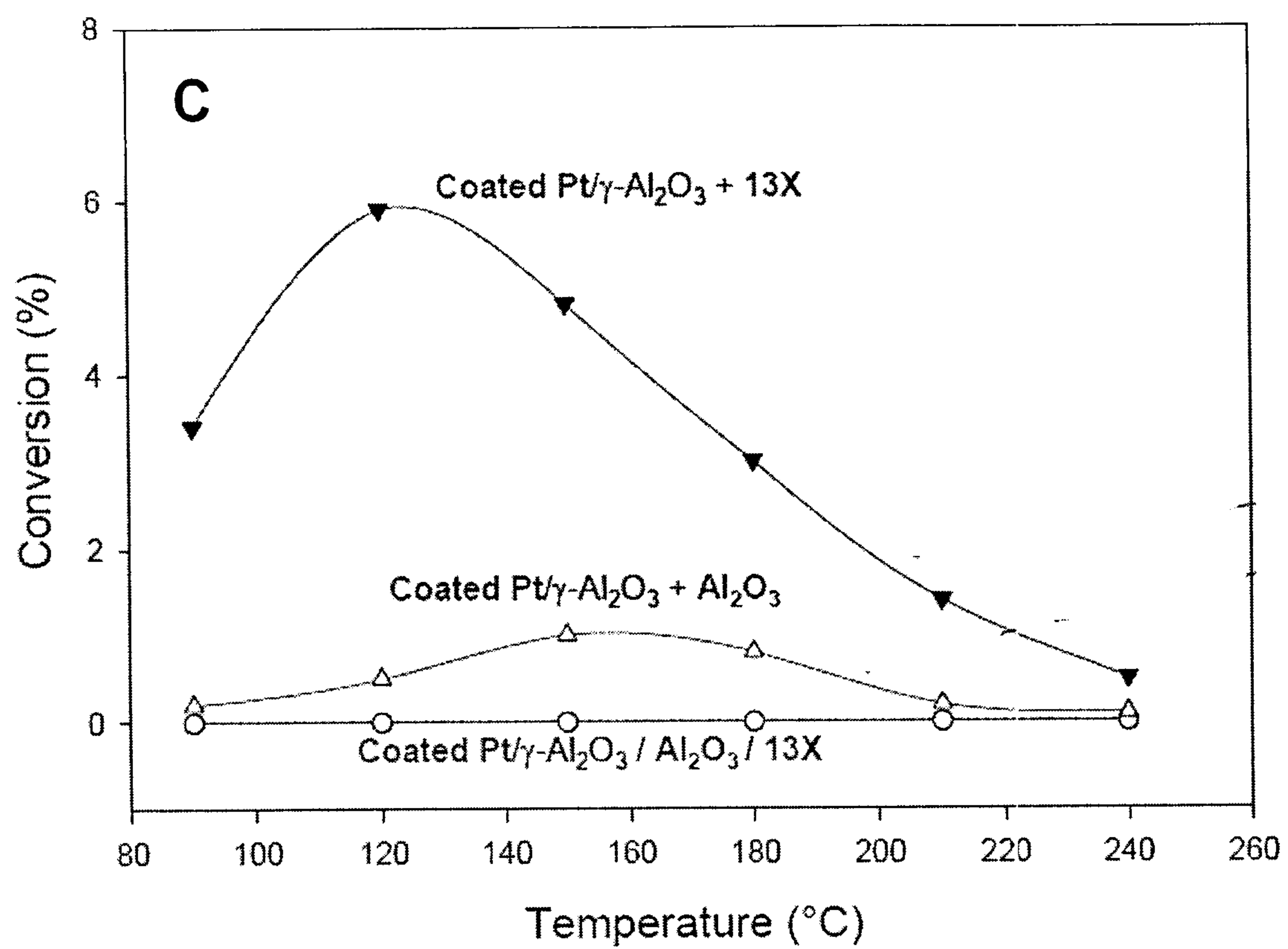


FIG. 23

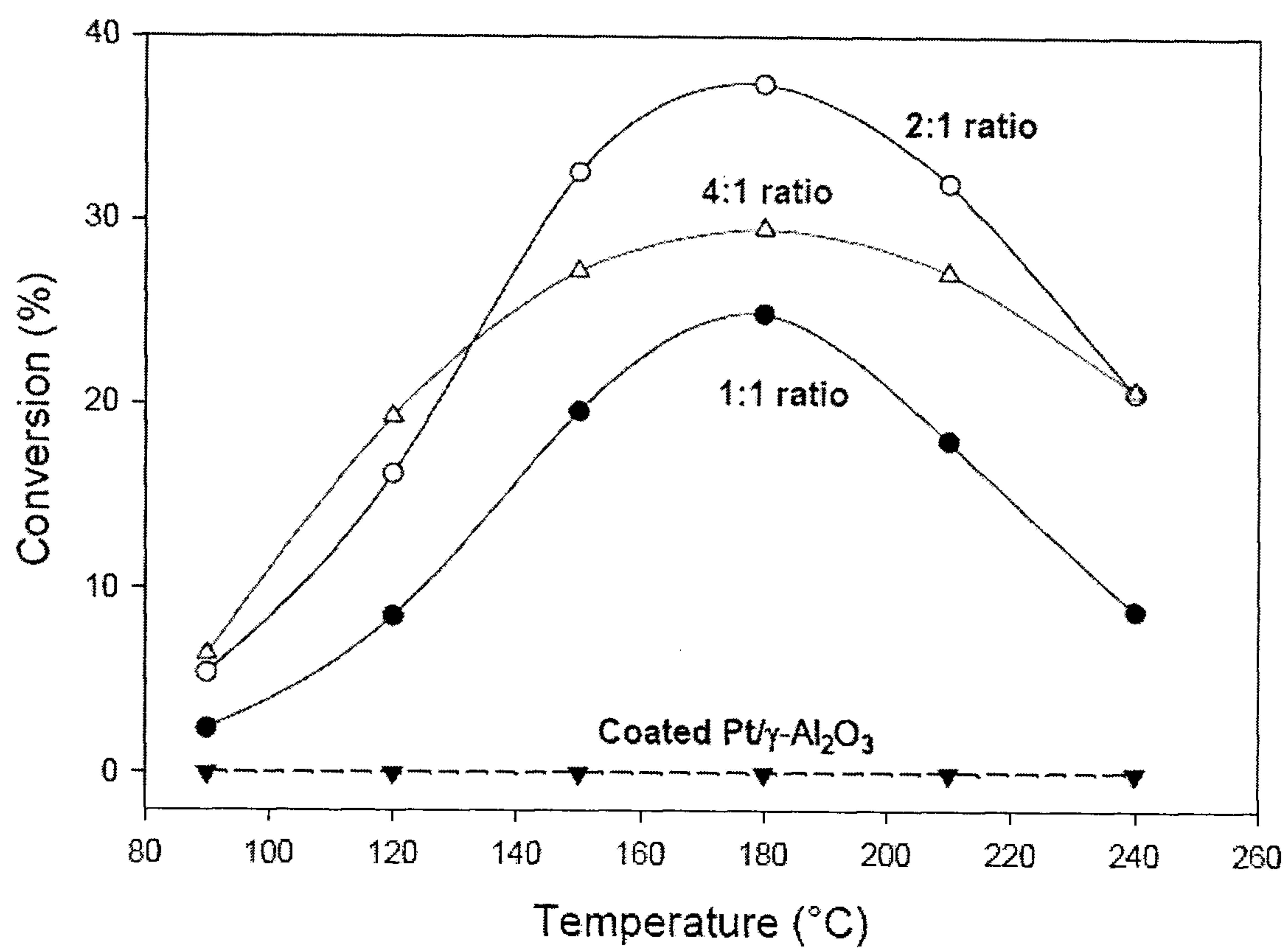


FIG. 24

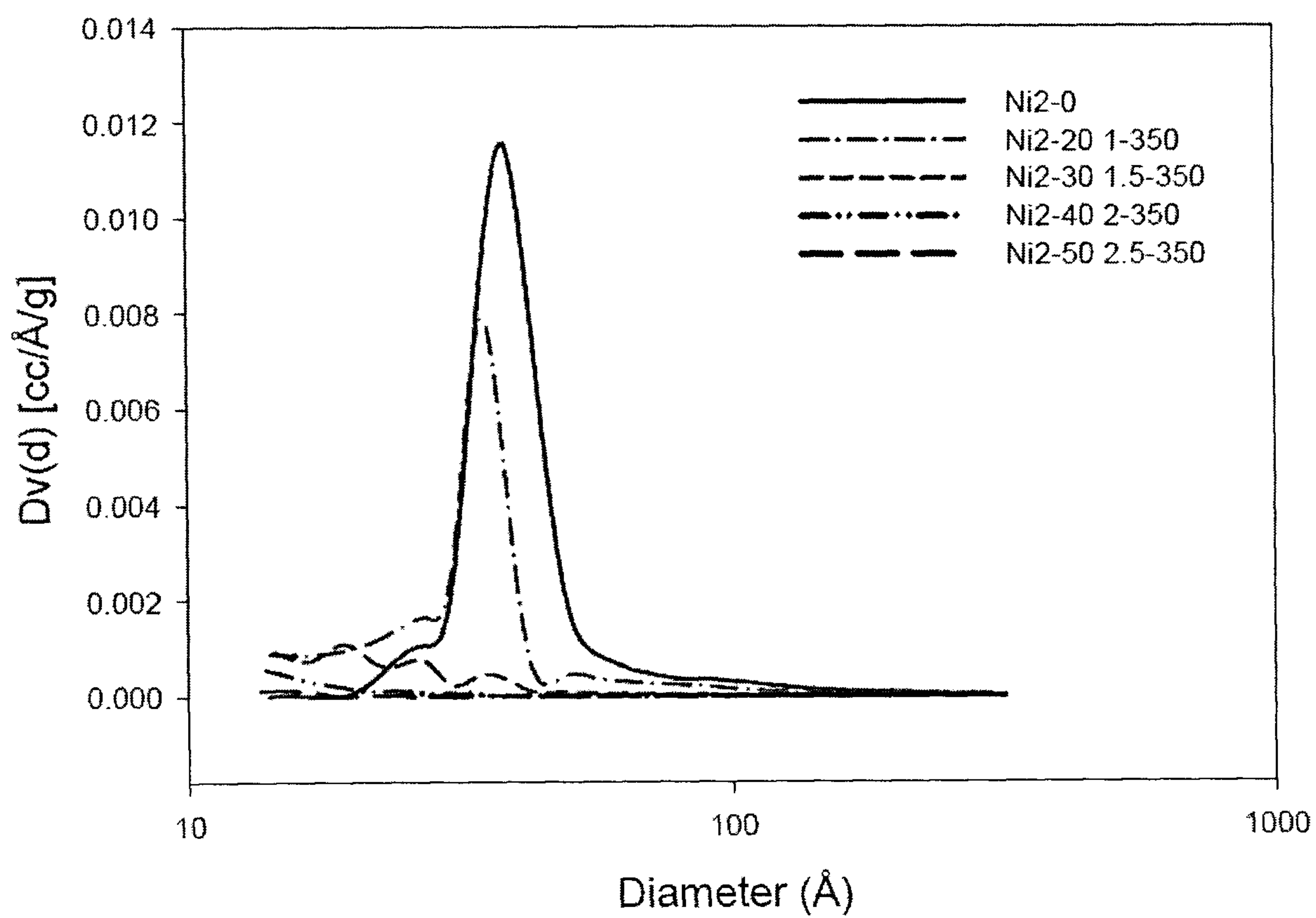


FIG. 25

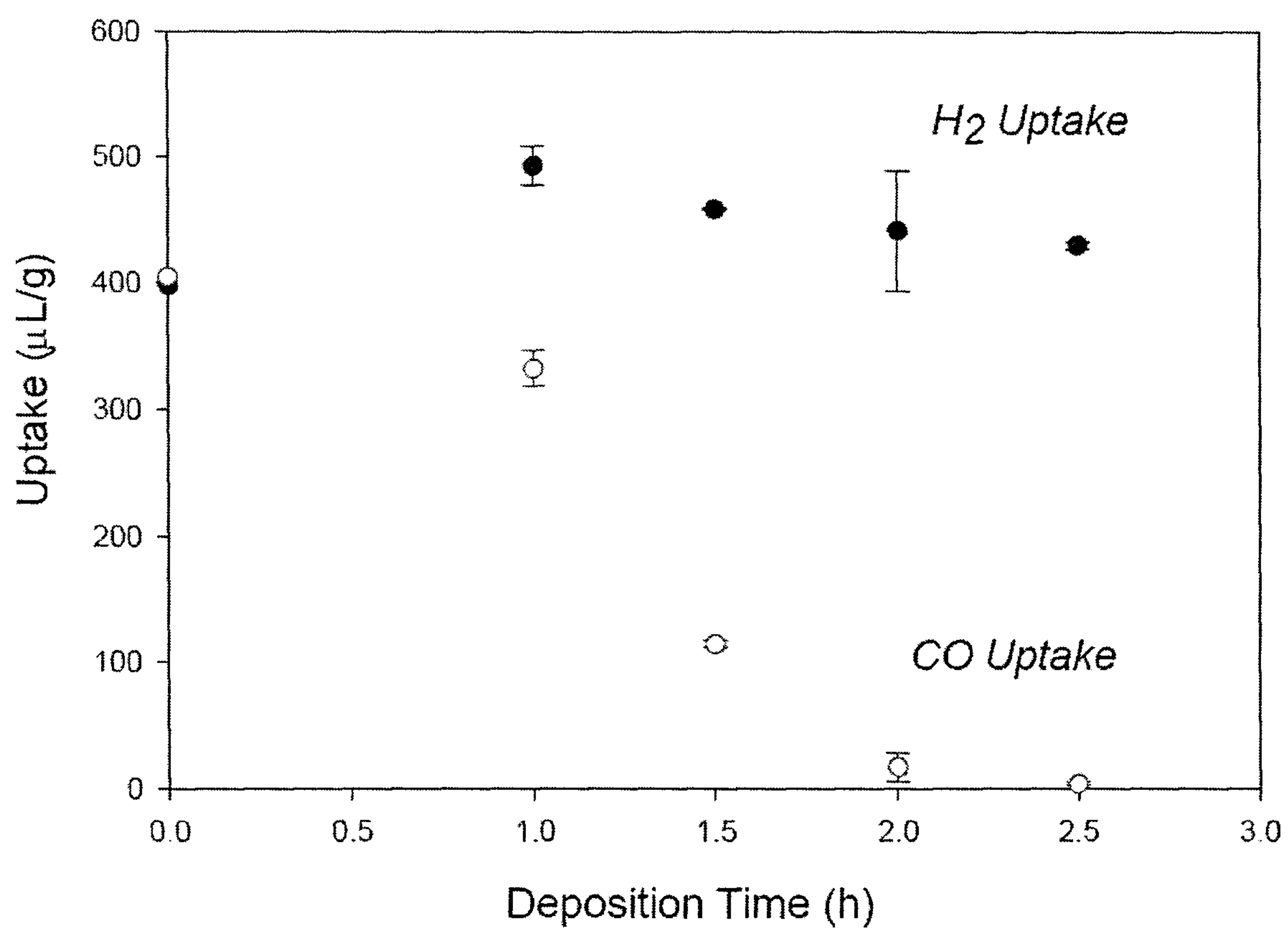


FIG. 26

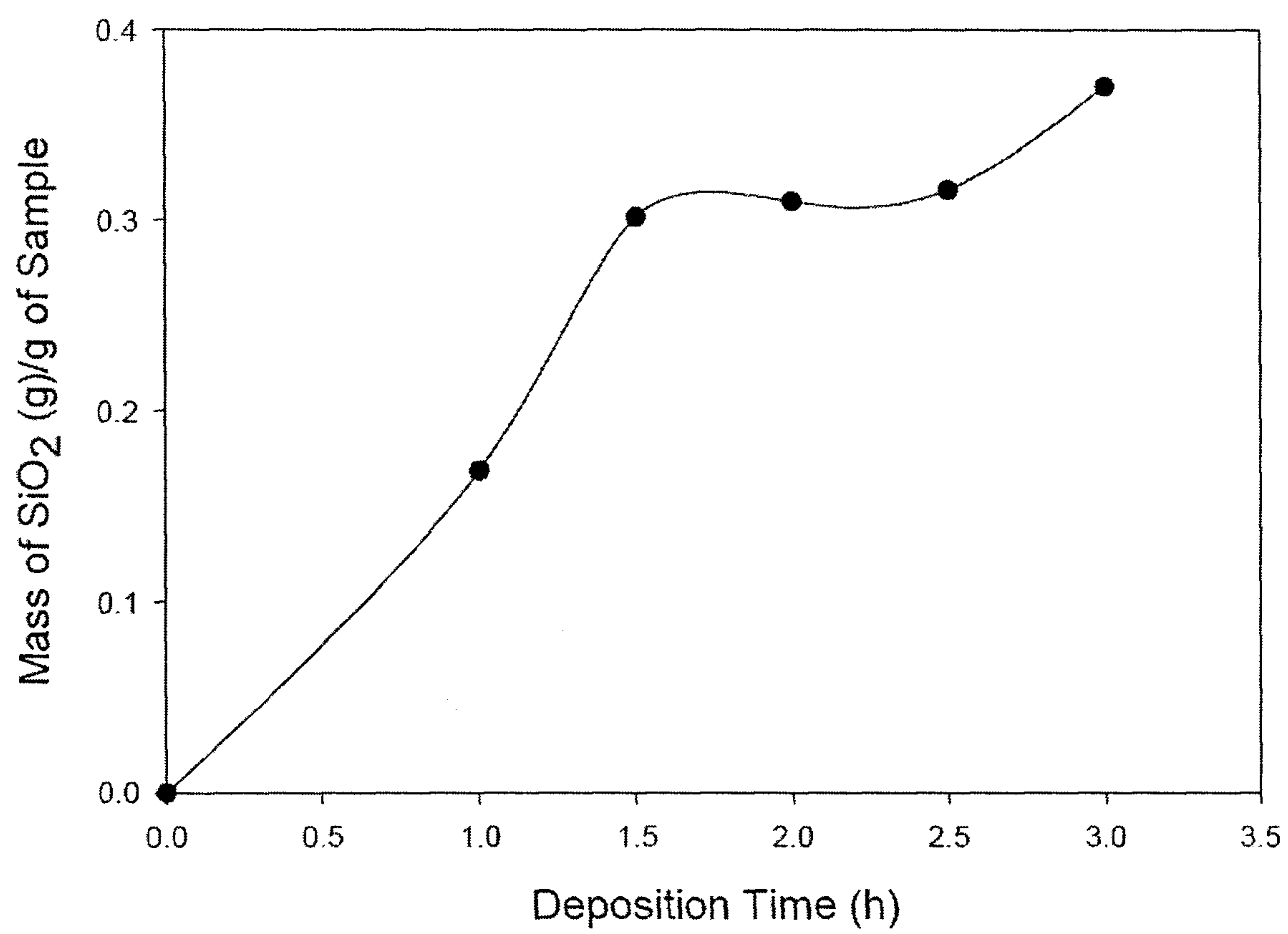


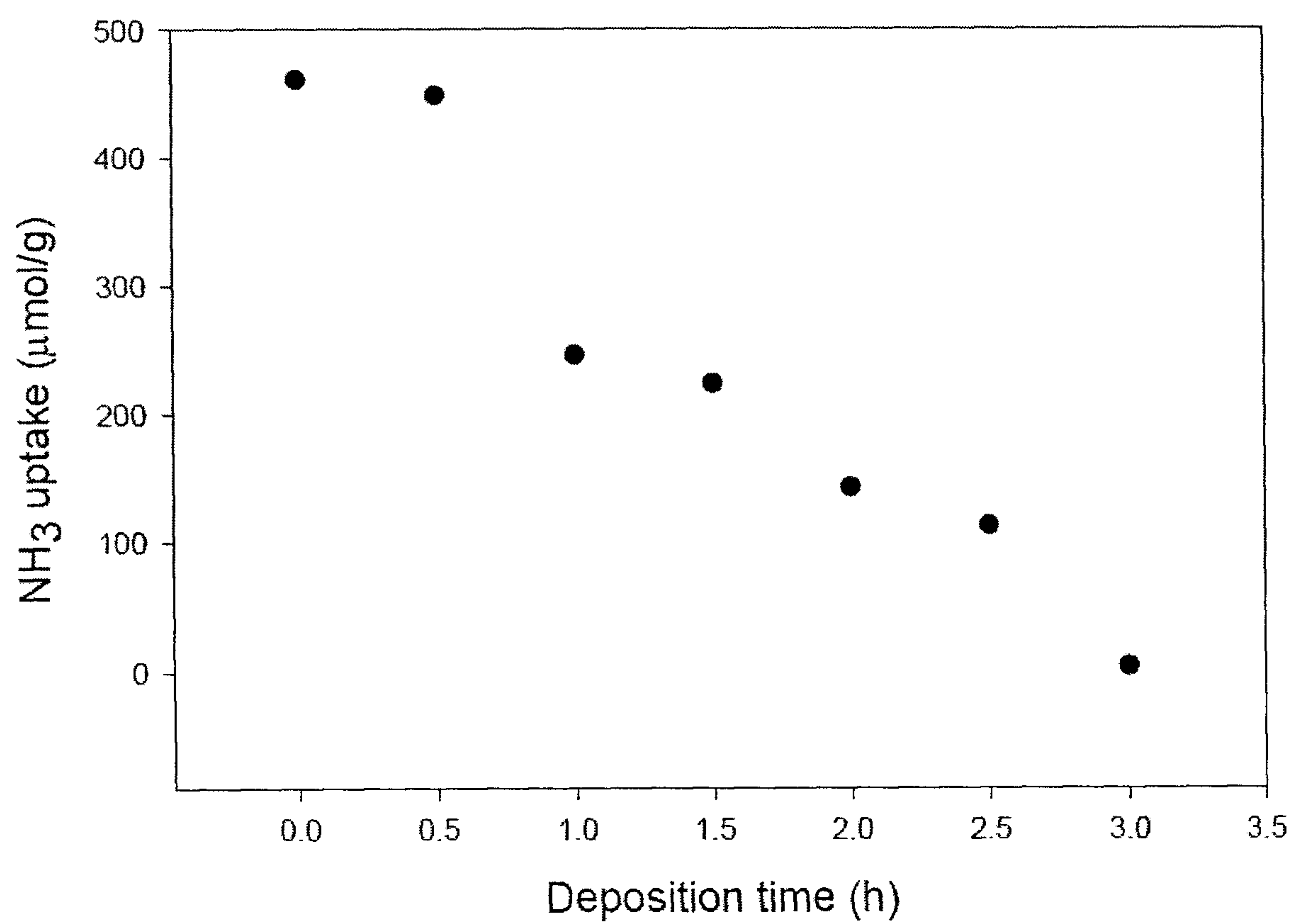
FIG. 27

FIG. 28

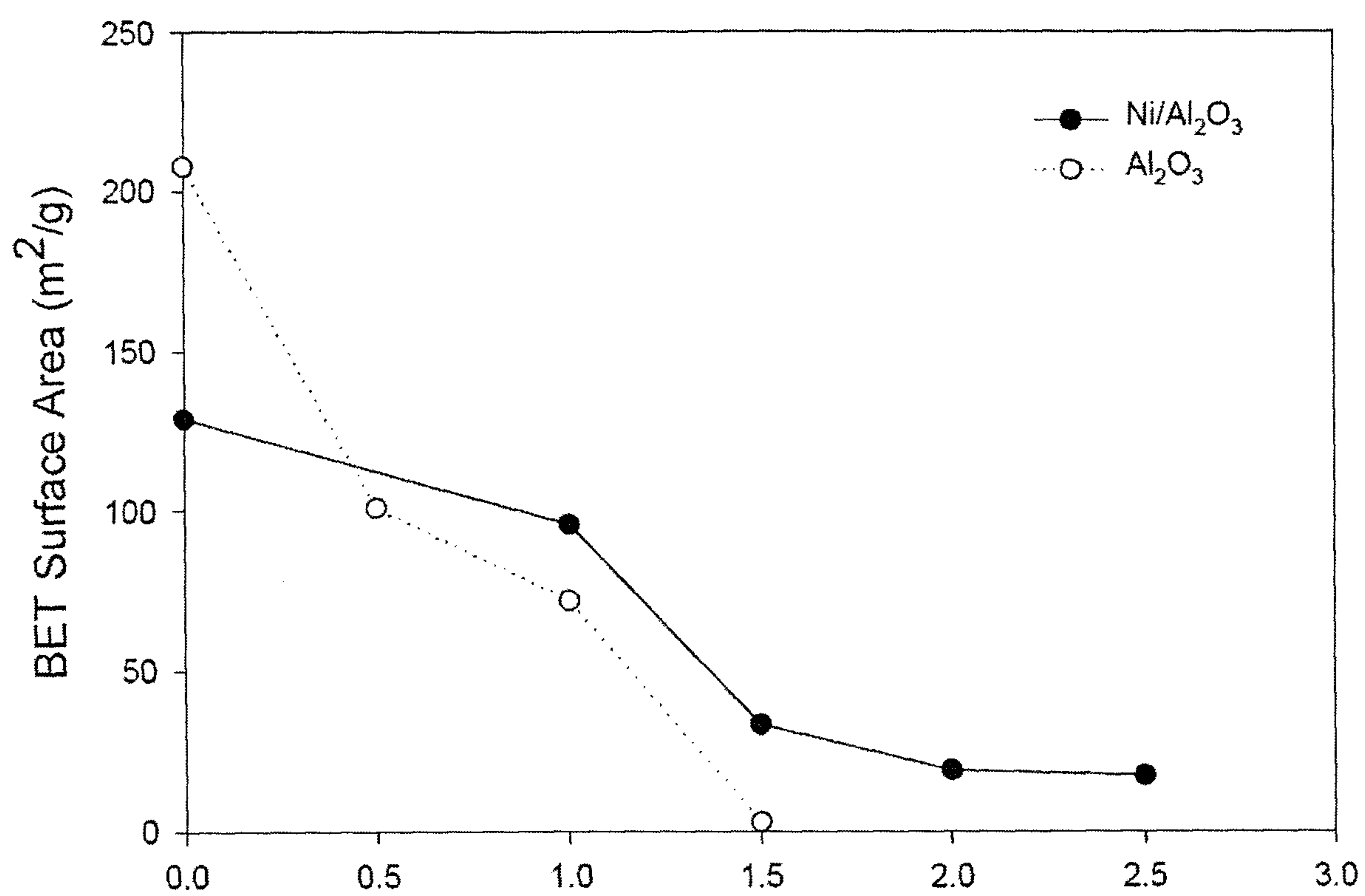
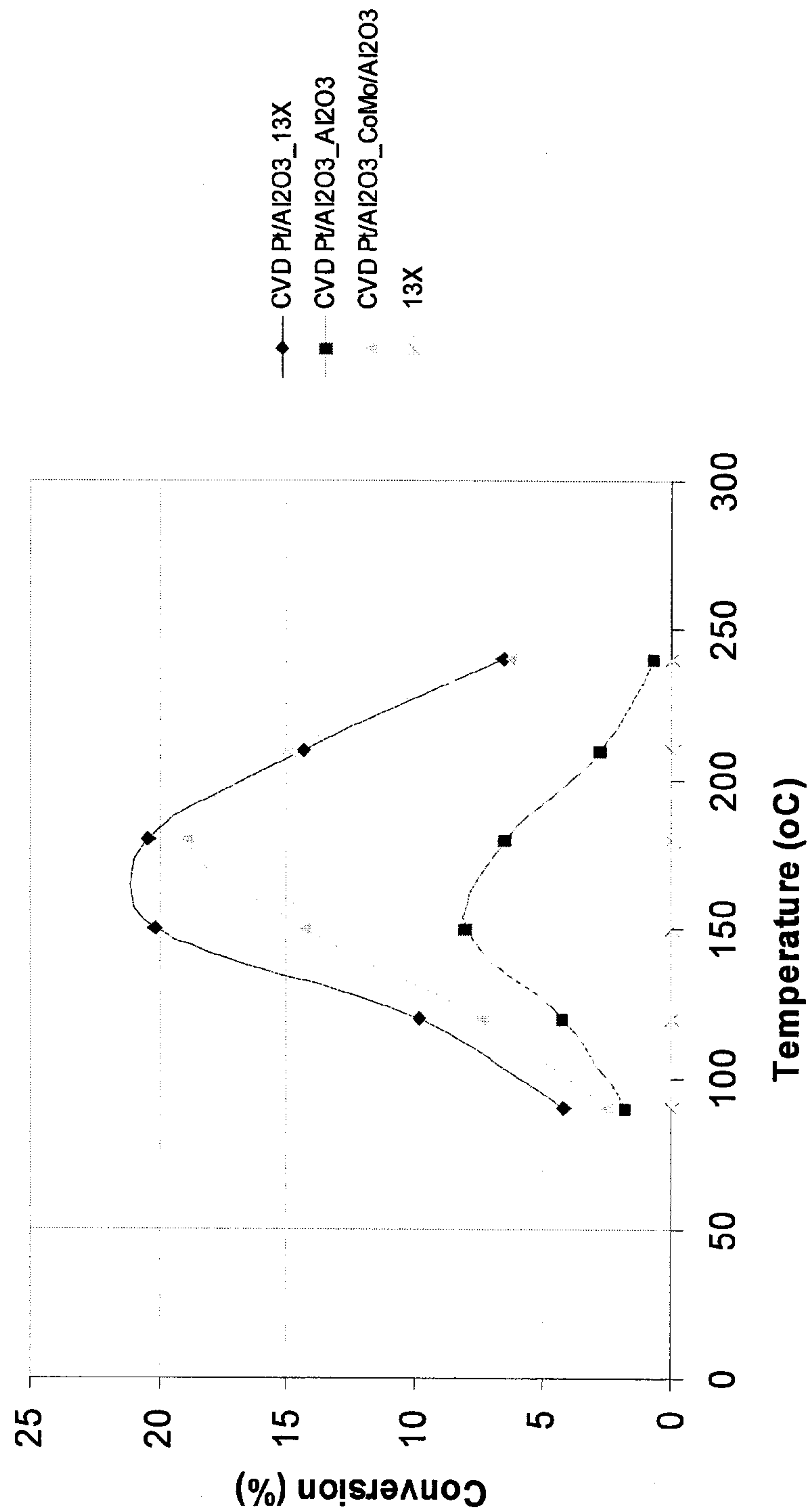


FIG. 29





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