

**COMPOSITE OXIDE SUPPORT, SUPPORTED CATALYST, AND
HYDROGENATED NITRILE BUTADIENE RUBBER AND PREPARATION
METHOD THEREFOR AND USE THEREOF**

5 Technical Field

The present invention relates to a composite oxide support and a preparation method therefor, a supported catalyst and a preparation method therefor, as well as hydrogenated nitrile butadiene rubber and a preparation method therefor and an application thereof.

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Background Art

Nitrile butadiene rubber (NBR) is a copolymer polymerized from acrylonitrile and butadiene monomers, which shows excellent oil resistance, high wear resistance, good heat resistance, and strong adhesion. It has drawbacks such as poor low
15 temperature resistance, poor odor resistance, low insulation performance, and low elasticity. NBR is widely used in the preparation of various oil resistant rubber articles, in fields such as automobiles, aviation, and petroleum.

Hydrogenated nitrile butadiene rubber (HNBR) is a product obtained by the catalytic selective hydrogenation of unsaturated olefin segments in the hydrocarbon
20 chain of nitrile butadiene rubber (NBR). HNBR has excellent characteristics such as good oil resistance, heat resistance, chemical corrosion resistance, odor resistance, high tear resistance, and wear resistance.

Currently, the main industrial production method for HNBR is solution
25 hydrogenation process, which primarily includes homogeneous hydrogenation and heterogeneous hydrogenation. Homogeneous hydrogenation refers to the catalytic hydrogenation of a polymer under certain reaction conditions where the active component of the catalyst is dispersed in the polymer solution in the form of molecules. In homogeneous hydrogenation, the reactant and the catalyst are uniformly mixed, the reaction conditions are easy to control, and the resulting product has stable
30 performance. However, a common drawback of the homogeneous solution

hydrogenation method is the difficulty in separating the catalyst from the product. Although a variety of technologies have been developed to address this issue, for example, using ion exchange resins for ion exchange of precious metals, utilizing the complexation of stannous chloride with rhodium catalyst for aqueous phase extraction and recovery of precious metal rhodium, and employing temperature-controlled phase transfer catalysts, these methods are difficult to completely remove the residual precious metal catalyst in the polymer or may produce gel to affect the quality of the product, and the cost of large-scale industrialization is extremely high. The residue of precious metals in hydrogenation products will increase production costs and waste precious metal resources on one hand. On the other hand, it will lead to the accelerated aging rate of HNBR and affect the mechanical processing performance of the polymer.

Compared with homogeneous hydrogenation catalytic systems, heterogeneous catalytic reaction systems use supported precious metal catalysts, which can effectively solve the problem of separating the catalyst from hydrogenated products. This not only enables the recycling of precious metal catalysts but also effectively avoids the residue of precious metals in the polymer. At present, the preparation of supported catalysts still relies on the traditional impregnation method, which leads to a large particle size of the active component, and a significant decrease in the number of active centers. Additionally, due to the weak interaction between the active component and the support, it is easy to cause the detachment and loss of precious metals from the support surface after a strong stirring reaction, which reduces the availability of the catalyst and affects the performance of the hydrogenation product. Zeon Corporation uses SiO₂ as a support to load Pd metal for the hydrogenation of NBR, with a one-pass hydrogenation degree of over 95%. Nevertheless, the catalyst performs poorly in repeated use, for example, the activity begins to decrease in the second use, and the activity decreases significantly in the third to fourth use, and the degree of hydrogenation decreases significantly.

The homogeneous catalytic hydrogenation method achieves a high degree of hydrogenation, but the catalyst separation is difficult and the cost is increasing. The heterogeneous catalyst hydrogenation method for the saturation of polymers results in

an insufficiently high degree of hydrogenation. Moreover, there is a phenomenon of active component loss during the stirring process of the reactor or the effect of repeated use of the catalyst is poor, and the degree of hydrogenation is significantly decreased. Therefore, there is a need to develop a catalyst and related use methods that not only ensure a high degree of hydrogenation and easy separation/recovery of the catalyst, but also guarantee the repeated use of the heterogeneous catalyst.

Currently, all the aforementioned catalysts use precious metals such as rhodium, palladium, ruthenium, osmium, platinum, and iridium as active components. There is no disclosure in the prior art of supported heterogeneous catalysts for NBR that use non-precious metals as active components while simultaneously possessing high activity, high selectivity, and high stability.

Contents of the Invention

Directed to the aforementioned problems in the prior art, the present invention provides a novel composite oxide support. The composite oxide support has the surface characteristics that its infrared (IR) spectrum shows three characteristic peaks in the range of 610-720 cm^{-1} and three characteristic peaks in the range of 2840-2970 cm^{-1} . The support can significantly improve the dispersion of active component on the catalyst surface and control the size of the atomic clusters of the active component to be no larger than 5 nm, thereby remarkably enhancing the hydrogenation activity of the catalyst. Additionally, the novel multifunctional supported non-precious metal catalyst of the present invention uses SiO_2 microspheres as the support and non-precious metals as the main active components, and has small particle sizes. By adopting a method of synergistic cooperation with homogeneous catalysts, the present invention ensures the hydrogenation saturation of polymer materials at relatively low temperatures and pressures, and the resulting hydrogenated polymer products (e.g., HNBR) achieve a high degree of hydrogenation. Furthermore, the supported catalyst of the present invention can be reused multiple times, and the catalyst composition can be easily separated and recovered. More notably, the use of non-precious metals as active components for preparing the supported catalyst avoids the problem of precious metal

active component loss, further improves the recoverability of the catalyst, and significantly reduces the cost of the catalyst, thereby lowering the production cost of hydrogenated polymers (e.g., HNBR).

A first aspect of the present invention is to provide a composite oxide support, characterized in that it comprises SiO₂ and a Group IVB metal oxide, wherein the Group IVB metal oxide is TiO₂ and/or ZrO₂. the composite oxide support has the surface characteristics that its infrared (IR) spectrum shows three characteristic peaks in the range of 610-720 cm⁻¹ and three characteristic peaks in the range of 2840-2970 cm⁻¹. In the present invention, the IR spectrum measurement conditions are as follows: a Nicolet iS50 IR spectrometer is used; the sample preparation and scanning are performed in attenuated total reflection mode; the scanning range is 4000-400 cm⁻¹; the resolution is 4 cm⁻¹; and the number of scans is 32. For example, as shown in Figure 1, the composite oxide support according to the present invention has the surface characteristics that its IR spectrum shows three characteristic peaks in the range of 610-720 cm⁻¹ and three characteristic peaks in the range of 2840-2970 cm⁻¹.

In some embodiments of the composite oxide support according to the present invention, the composite oxide support has the surface characteristics that its IR spectrum shows three characteristic peaks in the range of 620-710 cm⁻¹ and three characteristic peaks in the range of 2850-2960 cm⁻¹.

In some embodiments of the composite oxide support according to the present invention, the composite oxide support has the surface characteristics that its IR spectrum shows characteristic peaks at 620±1 cm⁻¹, 649±1 cm⁻¹, and 708±1 cm⁻¹; and/or the composite oxide support has the surface characteristics that its IR spectrum shows characteristic peaks at 2850±1 cm⁻¹, 2919±1 cm⁻¹, and 2955±1 cm⁻¹.

In some embodiments of the composite oxide support according to the present invention, the composite oxide support is obtained by subjecting a composite oxide support precursor comprising SiO₂ and a Group IVB metal oxide to surface treatment using an impregnation solution containing an organic cationic quaternary ammonium salt.

In some embodiments of the composite oxide support according to the present

invention, the organic cationic quaternary ammonium salt is a C₆ and longer (C₆+) long-chain alkyl quaternary ammonium salt, preferably a C₆+ long-chain alkyl quaternary ammonium halide salt. Preferably, the halogen is Cl, Br, or I, with Cl being more preferred. More preferably, the C₆+ long-chain alkyl group is a C₆-C₂₄ alkyl group, more preferably C₈-C₂₂ alkyl group, further preferably C₁₀-C₂₀ alkyl group, and further more preferably C₁₂-C₁₈ alkyl group. More preferably, the organic cationic quaternary ammonium salt is at least one selected from dimethyldioctadecylammonium chloride, cetyltrimethylammonium chloride, and C₁₂₋₁₄-alkyldimethylethylbenzylammonium chloride.

In some embodiments of the composite oxide support according to the present invention, the surface treatment is impregnation and drying. That is, the entire surface treatment process of the composite oxide support precursor with the organic cationic quaternary ammonium salt does not involve any high-temperature treatment steps (e.g., at temperatures above 300°C) such as roasting, calcination, or sintering. In the IR spectrum of the composite oxide support according to the present invention, the three characteristic peaks in the range of 610-720 cm⁻¹, e.g., the three characteristic peaks in the range of 620-710 cm⁻¹, or the characteristic peaks at 620±1 cm⁻¹, 649±1 cm⁻¹, 708±1 cm⁻¹, are mainly attributed to C-halogen (e.g., C-Cl) vibrations; the three characteristic peaks in the range of 2840-2970 cm⁻¹, e.g., the three characteristic peaks in the range of 2850-2960 cm⁻¹, or the characteristic peaks at 2850±1 cm⁻¹, 2919±1 cm⁻¹, 2955±1 cm⁻¹, are mainly attributed to C-H vibrations.

In some embodiments of the preparation method of the composite oxide support according to the present invention, based on the total weight of the composite oxide support, the content of the Group IVB metal oxide is 5~25 wt%, and the content of SiO₂ is 75~95 wt%. For example, but not limited to, the content of the Group IVB metal oxide is 5~20 wt%, 5~15 wt%, 5~10 wt%, 10~25 wt%, 10~20 wt%, 10~15 wt%, 12~25 wt%, 12~20 wt%, 12~15 wt%, 15~25 wt%, 15~20 wt%, 20~25 wt% and the like; correspondingly, the content of SiO₂ is 80~95 wt%, 85~95 wt%, 90~95 wt%, 75~90 wt%, 80~90 wt%, 85~90 wt%, 75~88 wt%, 80~88 wt%, 85~88 wt%, 75~85 wt%, 80~85 wt%, 75~80 wt% and the like. Preferably, the content of the Group IVB

metal oxide is 10~25 wt% and the content of SiO₂ is 75~90 wt%. Preferably, the content of the Group IVB metal oxide is greater than 10~25 wt% and the content of SiO₂ is 75~less than 90 wt%. Preferably, the content of the Group IVB metal oxide is 11~25 wt% and the content of SiO₂ is 75~89 wt%. Preferably, the content of the Group IVB metal oxide is 12~25 wt% and the content of SiO₂ is 75~88 wt%. Preferably, the content of the Group IVB metal oxide is 15~25 wt% and the content of SiO₂ is 75~85 wt%.

In some embodiments of the preparation method of the composite oxide support according to the present invention, where the Group IVB metal oxide is TiO₂ and ZrO₂, the ratio of TiO₂ to ZrO₂ can vary within a wide range. For example, but not limited to, the weight ratio of TiO₂ to ZrO₂ is 0.01~100:1, 0.05~20:1, 0.1~10:1, 0.3~3:1, 0.5~2:1, 1~100:1, 1~20:1, 1~10:1, 1~3:1, 1~2:1, 0.01~1:1, 0.05~1:1, 0.1~1:1, 0.3~1:1, 0.5~1:1.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the composite oxide support has the particle size of 5~30 μm. For example, but not limited to, 5~25 μm, 5~20 μm, 5~15 μm, 5~10 μm, 10~30 μm, 10~25 μm, 10~20 μm, 10~15 μm, 15~30 μm, 15~25 μm, 15~20 μm, 20~30 μm, 20~25 μm and the like, including the range between any two values mentioned above. In the present invention, the particle size of the composite oxide support is measured in accordance with the test method specified in NB/SH/T 0951-2017, using the MS2000 laser particle size analyzer from Malvern company.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the composite oxide support has the average pore diameter of 100~1200 nm. For example, but not limited to, 100~1000 nm, 100~800 nm, 100~600 nm, 100~500 nm, 100~400 nm, 100~300 nm, 100~200 nm, 200~1200 nm, 200~1000 nm, 200~800 nm, 200~600 nm, 200~500 nm, 200~400 nm, 200~300 nm, 300~1200 nm, 300~1000 nm, 300~800 nm, 300~600 nm, 300~500 nm, 300~400 nm, 400~1200 nm, 400~1000 nm, 400~800 nm, 400~600 nm, 400~500 nm, 500~1200 nm, 500~1000 nm, 500~800 nm, 500~600 nm, 600~1200 nm, 600~1000 nm, 600~800 nm, 600~700 nm, 700~1200 nm, 700~1000 nm, 700~800 nm, 800~1200 nm, 800~1000 nm, 900~1200 nm, 900~1000 nm, 1000~1200 nm and the like, including the

range between any two values mentioned above. In the present invention, the average pore diameter of the composite oxide support is measured in accordance with the mercury intrusion porosimetry method specified in GB/T 21650.1-2008 (Determination of pore size distribution and porosity of solid materials by mercury intrusion porosimetry and gas adsorption methods — Part 1: Mercury intrusion porosimetry method), using an AutoPore IV 9500 high-performance fully automatic mercury porosimeter from Micromeritics Instrument Corporation, USA.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the composite oxide support has the specific surface area of 30~200 m²/g. For example, but not limited to, 30~150 m²/g, 30~120 m²/g, 30~100 m²/g, 30~90 m²/g, 30~80 m²/g, 30~70 m²/g, 30~60 m²/g, 30~50 m²/g, 30~40 m²/g, 50~200 m²/g, 50~150 m²/g, 50~120 m²/g, 50~100 m²/g, 50~90 m²/g, 50~80 m²/g, 50~70 m²/g, 50~60 m²/g, 80~200 m²/g, 80~150 m²/g, 80~120 m²/g, 80~100 m²/g, 80~90 m²/g, 100~200 m²/g, 100~150 m²/g, 100~120 m²/g, 120~200 m²/g, 120~150 m²/g and the like, including the range between any two values mentioned above. In the present invention, the specific surface area of the composite oxide support is measured in accordance with the mercury intrusion porosimetry method specified in GB/T 21650.1-2008 (Determination of pore size distribution and porosity of solid materials by mercury intrusion porosimetry and gas adsorption methods — Part 1: Mercury intrusion porosimetry method), using an AutoPore IV 9500 high-performance fully automatic mercury porosimeter from Micromeritics Instrument Corporation, USA.

A second aspect of the present invention is to provide a method for preparing the aforementioned composite oxide support, comprising the following steps:

(1) subjecting a SiO₂ microsphere support to a first impregnation with a solution of a Group IVB metal compound, followed by a first drying and a first roasting to obtain an oxide composite support precursor, wherein the Group IVB metal compound is a titanium-containing compound and/or a zirconium-containing compound;

(2) subjecting the composite oxide support precursor to surface treatment using an

impregnation solution containing an organic cationic quaternary ammonium salt to obtain the composite oxide support.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the impregnation solution containing the organic cationic quaternary ammonium salt comprises the organic cationic quaternary ammonium salt, a solvent, and an acid.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the organic cationic quaternary ammonium salt is a C₆+ long-chain alkyl quaternary ammonium salt, preferably a C₆+ long-chain alkyl quaternary ammonium halide salt. Preferably, the halogen is Cl, Br, or I, with Cl being more preferred. More preferably, the C₆+ long-chain alkyl group is a C₆-C₂₄ alkyl group, more preferably C₈-C₂₂ alkyl group, further preferably C₁₀-C₂₀ alkyl group, and further more preferably C₁₂-C₁₈ alkyl group. More preferably, the organic cationic quaternary ammonium salt is at least one selected from dimethyldioctadecylammonium chloride, cetyltrimethylammonium chloride, and C₁₂₋₁₄-alkyldimethylethylbenzylammonium chloride.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the solvent is at least one selected from deionized water, methanol, ethanol, acetone, methyl ethyl ketone, tetrahydrofuran, o-xylene, p-xylene, and pyridine. Preferably, the solvent is at least one selected from o-xylene, p-xylene, and pyridine. More preferably, the solvent is o-xylene or pyridine.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the acid is at least one selected from hydrochloric acid, sulfuric acid, nitric acid, and citric acid. Preferably, the acid is hydrochloric acid. More preferably, the concentration of the acid is 1~98.3 wt%.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the concentration of the quaternary ammonium salt in the impregnation solution containing the organic cationic quaternary ammonium salt is 0.1~10 wt%. More preferably, the weight ratio of the organic cationic quaternary ammonium salt, solvent, and acid is 1:10~19:1~3. For example, the weight of 1 mL of

37 wt% concentrated hydrochloric acid in the example is 1.18 g.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the surface treatment is impregnation and drying. Preferably, the impregnation conditions include: a temperature of 20~60°C and a time of 0.5~8 h; the drying conditions include: a temperature of 50~120°C and a time of 2~10 h. The entire surface treatment process of the composite oxide support precursor with the organic cationic quaternary ammonium salt does not involve any high-temperature treatment steps (e.g., at temperatures above 300°C) such as roasting, calcination, or sintering. Thus, the groups of the organic cationic quaternary ammonium salt and the acid (e.g., amino groups, hydrogen ion, halide ions, alkyl groups, etc.) can be retained on the composite oxide support, and these groups can interact with the active components, thereby promoting the dispersion of the active components.

In the present invention, the SiO₂ microsphere support can be impregnated simultaneously with a solution of a titanium-containing compound and/or a zirconium-containing compound, followed by drying and roasting to obtain a composite oxide support of SiO₂ with TiO₂ and/or ZrO₂. Alternatively, the SiO₂ microsphere support can first be impregnated with a solution of a titanium-containing compound, followed by drying and roasting, and then impregnated with a solution of a zirconium-containing compound, followed by drying and roasting to obtain the composite oxide support of SiO₂ with TiO₂ and/or ZrO₂. Alternatively, the SiO₂ microsphere support can first be impregnated with a solution of a zirconium-containing compound, followed by drying and roasting, and then impregnated with a solution of a titanium-containing compound, followed by drying and roasting to obtain the composite oxide support of SiO₂ with TiO₂ and/or ZrO₂.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the SiO₂ microsphere support has the particle size of 5~30 μm. For example, but not limited to, 5~25 μm, 5~20 μm, 5~15 μm, 5~10 μm, 10~30 μm, 10~25 μm, 10~20 μm, 10~15 μm, 15~30 μm, 15~25 μm, 15~20 μm, 20~30 μm, 20~25 μm and the like, including the range between any two values mentioned

above. In the present invention, the particle size of the SiO₂ microsphere support is measured in accordance with the test method specified in NB/SH/T 0951-2017, using the MS2000 laser particle size analyzer from Malvern company.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the SiO₂ microsphere support has the average pore diameter of 100~1200 nm. For example, but not limited to, 100~1000 nm, 100~800 nm, 100~600 nm, 100~500 nm, 100~400 nm, 100~300 nm, 100~200 nm, 200~1200 nm, 200~1000 nm, 200~800 nm, 200~600 nm, 200~500 nm, 200~400 nm, 200~300 nm, 300~1200 nm, 300~1000 nm, 300~800 nm, 300~600 nm, 300~500 nm, 300~400 nm, 400~1200 nm, 400~1000 nm, 400~800 nm, 400~600 nm, 400~500 nm, 500~1200 nm, 500~1000 nm, 500~800 nm, 500~600 nm, 600~1200 nm, 600~1000 nm, 600~800 nm, 600~700 nm, 700~1200 nm, 700~1000 nm, 700~800 nm, 800~1200 nm, 800~1000 nm, 900~1200 nm, 900~1000 nm, 1000~1200 nm and the like, including the range between any two values mentioned above. In the present invention, the average pore diameter of the SiO₂ microsphere support is measured in accordance with the mercury intrusion porosimetry method specified in GB/T 21650.1-2008 (Determination of pore size distribution and porosity of solid materials by mercury intrusion porosimetry and gas adsorption methods — Part 1: Mercury intrusion porosimetry method), using an AutoPore IV 9500 high-performance fully automatic mercury porosimeter from Micromeritics Instrument Corporation, USA.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the SiO₂ microsphere support has the specific surface area of 30~200 m²/g. For example, but not limited to, 30~150 m²/g, 30~120 m²/g, 30~100 m²/g, 30~90 m²/g, 30~80 m²/g, 30~70 m²/g, 30~60 m²/g, 30~50 m²/g, 30~40 m²/g, 50~200 m²/g, 50~150 m²/g, 50~120 m²/g, 50~100 m²/g, 50~90 m²/g, 50~80 m²/g, 50~70 m²/g, 50~60 m²/g, 80~200 m²/g, 80~150 m²/g, 80~120 m²/g, 80~100 m²/g, 80~90 m²/g, 100~200 m²/g, 100~150 m²/g, 100~120 m²/g, 120~200 m²/g, 120~150 m²/g and the like, including the range between any two values mentioned above. In the present invention, the specific surface area of the SiO₂ microsphere support is measured in accordance with the mercury intrusion porosimetry

method specified in GB/T 21650.1-2008 (Determination of pore size distribution and porosity of solid materials by mercury intrusion porosimetry and gas adsorption methods — Part 1: Mercury intrusion porosimetry method), using an AutoPore IV 9500 high-performance fully automatic mercury porosimeter from Micromeritics Instrument Corporation, USA.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the composite oxide treated with the quaternary ammonium salt has the surface characteristics that its IR spectrum shows three characteristic peaks in the range of 610-720 cm^{-1} and three characteristic peaks in the range of 2840-2970 cm^{-1} . The IR spectrum measurement can be conducted under the following conditions: a Nicolet iS50 IR spectrometer is used, the sample preparation and scanning are performed in attenuated total reflection mode, the scanning range is 4000-400 cm^{-1} , the resolution is 4 cm^{-1} , and the number of scans is 32.

In the present invention, the SiO_2 microsphere support can be obtained commercially (e.g., from Shandong Bangkai Materials Co., Ltd., J&K Scientific, Shanghai Aladdin Biochemical Technology Co., Ltd., etc.) or self-made.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the titanium-containing compound is at least one selected from titanium sulfate, metatitanic acid, titanium tetrachloride, and tetrabutyl titanate. For example, titanium sulfate or titanium tetrachloride can be dissolved in water; metatitanic acid can be dissolved in a dilute sulfuric acid solution; or tetrabutyl titanate can be dissolved in an ethanol solution.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the zirconium-containing compound is at least one selected from zirconium tetrachloride, zirconium sulfate, zirconium nitrate, zirconyl chloride, and zirconium oxalate. For example, the aforementioned zirconium compounds can be dissolved in water.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the concentration of the titanium-containing compound and/or zirconium-containing compound in the solution of the

titanium-containing compound and/or zirconium-containing compound is 0.1~1.0 mol/L. For example, but not limited to, 0.1~0.8 mol/L, 0.1~0.6 mol/L, 0.1~0.4 mol/L, 0.2~1.0 mol/L, 0.2~0.8 mol/L, 0.2~0.6 mol/L, 0.2~0.4 mol/L, 0.3~1.0 mol/L, 0.3~0.8 mol/L, 0.3~0.6 mol/L, 0.3~0.4 mol/L, 0.4~1.0 mol/L, 0.4~0.8 mol/L, 0.4~0.6 mol/L, 0.5~1.0 mol/L, 0.5~0.8 mol/L, 0.5~0.6 mol/L and the like, including the range between any two values mentioned above.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the molar ratio of the SiO₂ microsphere support to the Group IVB metal-containing compound is 3~40:1, e.g., 4~26:1, 5~30:1, 6~39:1, wherein, the amount of the SiO₂ microsphere support is calculated as Si, and the amount of the titanium-containing compound and/or zirconium-containing compound is calculated as titanium and/or zirconium elements.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the conditions for the first impregnation include: a temperature of 20~60°C and a time of 0.5~8 h.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the conditions for the first drying include: a temperature of 105~130°C and a time of 2~8 h.

In some embodiments of the preparation method of the composite oxide support according to the present invention, the conditions for the first roasting include: a temperature of 450~650°C and a time of 3~8 h.

A third aspect of the present invention is to provide a supported catalyst, comprising: the aforementioned composite oxide support, and an active component Cu and its oxide supported on the support; the particle size of the copper atomic clusters of the active component is no larger than 5 nm; based on the total weight of the supported catalyst, the content of Cu and its oxide calculated as CuO is 5~25 wt%, preferably 8~25 wt%, more preferably 10~25 wt%, and even more preferably 12~25 wt%.

In some embodiments of the supported catalyst according to the present invention, the supported catalyst has the particle size of 5~30 μm. For example, but not limited to,

5~25 μm , 5~20 μm , 5~15 μm , 5~10 μm , 10~30 μm , 10~25 μm , 10~20 μm , 10~15 μm , 15~30 μm , 15~25 μm , 15~20 μm , 20~30 μm , 20~25 μm and the like, including the range between any two values mentioned above. In the present invention, the particle size of the catalyst is measured in accordance with the test method specified in NB/SH/T 0951-2017, using the MS2000 laser particle size analyzer from Malvern company.

In some embodiments of the supported catalyst according to the present invention, the supported catalyst has the average pore diameter of 100~1200 nm. For example, but not limited to, 100~1000 nm, 100~800 nm, 100~600 nm, 100~500 nm, 100~400 nm, 100~300 nm, 100~200 nm, 200~1200 nm, 200~1000 nm, 200~800 nm, 200~600 nm, 200~500 nm, 200~400 nm, 200~300 nm, 300~1200 nm, 300~1000 nm, 300~800 nm, 300~600 nm, 300~500 nm, 300~400 nm, 400~1200 nm, 400~1000 nm, 400~800 nm, 400~600 nm, 400~500 nm, 500~1200 nm, 500~1000 nm, 500~800 nm, 500~600 nm, 600~1200 nm, 600~1000 nm, 600~800 nm, 600~700 nm, 700~1200 nm, 700~1000 nm, 700~800 nm, 800~1200 nm, 800~1000 nm, 900~1200 nm, 900~1000 nm, 1000~1200 nm and the like, including the range between any two values mentioned above. In the present invention, the average pore diameter of the catalyst is measured in accordance with the mercury intrusion porosimetry method specified in GB/T 21650.1-2008 (Determination of pore size distribution and porosity of solid materials by mercury intrusion porosimetry and gas adsorption methods — Part 1: Mercury intrusion porosimetry method), using an AutoPore IV 9500 high-performance fully automatic mercury porosimeter from Micromeritics Instrument Corporation, USA.

In some embodiments of the supported catalyst according to the present invention, the supported catalyst has the specific surface area of 30~200 m^2/g . For example, but not limited to, 30~150 m^2/g , 30~120 m^2/g , 30~100 m^2/g , 30~90 m^2/g , 30~80 m^2/g , 30~70 m^2/g , 30~60 m^2/g , 30~50 m^2/g , 30~40 m^2/g , 50~200 m^2/g , 50~150 m^2/g , 50~120 m^2/g , 50~100 m^2/g , 50~90 m^2/g , 50~80 m^2/g , 50~70 m^2/g , 50~60 m^2/g , 80~200 m^2/g , 80~150 m^2/g , 80~120 m^2/g , 80~100 m^2/g , 80~90 m^2/g , 100~200 m^2/g , 100~150 m^2/g , 100~120 m^2/g , 120~200 m^2/g , 120~150 m^2/g and the like, including the

range between any two values mentioned above. In the present invention, the specific surface area of the catalyst is measured in accordance with the mercury intrusion porosimetry method specified in GB/T 21650.1-2008 (Determination of pore size distribution and porosity of solid materials by mercury intrusion porosimetry and gas adsorption methods — Part 1: Mercury intrusion porosimetry method), using an AutoPore IV 9500 high-performance fully automatic mercury porosimeter from Micromeritics Instrument Corporation, USA.

In some embodiments of the supported catalyst according to the present invention, the particle size of the copper atomic clusters of the active component is 2~5 nm, which is characterized by transmission electron microscopy (TEM) and measured according to the scale bar.

In some embodiments of the supported catalyst according to the present invention, the supported catalyst is substantially free of precious metals such as rhodium, palladium, ruthenium, osmium, platinum, and iridium. The phrase "substantially free of" means that the content of precious metals (e.g., rhodium, palladium, ruthenium, osmium, platinum, and iridium) in the supported catalyst is less than 1 wt%, preferably less than 0.5 wt%, preferably less than 0.2 wt%, preferably less than 0.1 wt%, and preferably 0 wt%. Preferably, the supported catalyst is completely free of precious metals such as rhodium, palladium, ruthenium, osmium, platinum, and iridium.

In some embodiments of the supported catalyst according to the present invention, the supported catalyst is substantially free of non-precious metals (such as cobalt, nickel, molybdenum, zinc, and iron) other than copper, titanium, and zirconium. The phrase "substantially free of" means that the content of non-precious metals (such as cobalt, nickel, molybdenum, zinc, and iron) other than copper, titanium, and zirconium in the supported catalyst is less than 1 wt%, preferably less than 0.5 wt%, preferably less than 0.2 wt%, preferably less than 0.1 wt%, and preferably 0 wt%. Preferably, the supported catalyst is completely free of non-precious metals (such as cobalt, nickel, molybdenum, zinc, and iron) other than copper, titanium, and zirconium.

In some embodiments of the supported catalyst according to the present invention, the supported catalyst is substantially free of metals other than copper, titanium, and

zirconium. The phrase "substantially free of" means that the content of metals other than copper, titanium, and zirconium in the supported catalyst is less than 1 wt%, preferably less than 0.5 wt%, preferably less than 0.2 wt%, preferably less than 0.1 wt%, and preferably 0 wt%. Preferably, the supported catalyst is completely free of metals other than copper, titanium, and zirconium.

A fourth aspect of the present invention is to provide a method for preparing the aforementioned supported catalyst, comprising the following steps: subjecting the aforementioned composite oxide support to a second impregnation with a solution of a soluble copper salt, followed by a second drying and a second roasting.

In some embodiments of the preparation method of the supported catalyst according to the present invention, the molar ratio of the composite oxide support to the soluble copper salt is 1:0.03~0.6, for example, 1:0.03~0.4, 1:0.04~0.25, 1:0.05~0.32, or 1:0.06~0.5. The molar amount of the composite oxide support is calculated as Si, and the soluble copper salt is calculated as Cu element.

In some embodiments of the preparation method of the supported catalyst according to the present invention, the soluble copper salt is at least one selected from copper chloride, copper sulfate, copper nitrate, copper acetate, and disodium cupper ethylenediaminetetraacetate (EDTA-Cu-15).

In some embodiments of the preparation method of the supported catalyst according to the present invention, the conditions for the second impregnation include: a temperature of 20~60°C and a time of 0.5~8 h.

In some embodiments of the preparation method of the supported catalyst according to the present invention, the conditions for the second drying include: a temperature of 105~180°C and a time of 2~8 h.

In some embodiments of the preparation method of the supported catalyst according to the present invention, the conditions for the second roasting include: a temperature of 450~650°C and a time of 3~8 h.

In some embodiments of the preparation method of the supported catalyst according to the present invention, the amounts of the SiO₂ microsphere support and

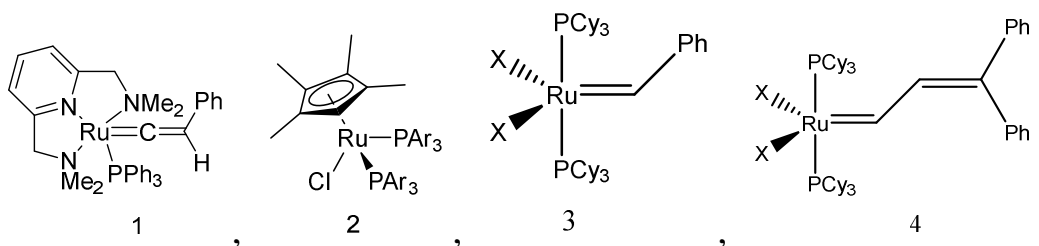
the solution of the titanium-containing compound are such that, based on the total weight of the prepared composite oxide support of SiO₂ with TiO₂ and/or ZrO₂, the content of TiO₂ and/or ZrO₂ is 5~25 wt%, and the content of SiO₂ is 75~95 wt%.

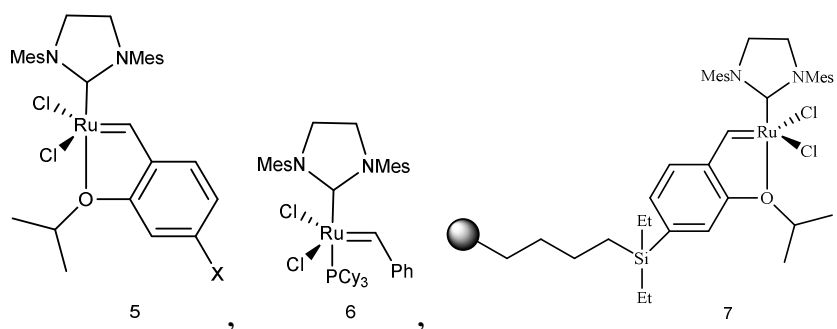
In some embodiments of the preparation method of the supported catalyst according to the present invention, the amount of the soluble copper salt used for the second impregnation of the composite oxide support of SiO₂ with TiO₂ and/or ZrO₂ is such that, based on the total weight of the supported catalyst, the content of CuO calculated as CuO is 5~25 wt%. For example, but not limited to, 5~20 wt%, 5~15 wt%, 5~10 wt%, 10~25 wt%, 10~20 wt%, 10~15 wt%, 12~25 wt%, 12~20 wt%, 12~15 wt%, 15~25 wt%, 15~20 wt%, 20~25 wt% and the like.

A fifth aspect of the present invention is to provide a catalyst composition, comprising a homogeneous catalyst and the aforementioned supported catalyst.

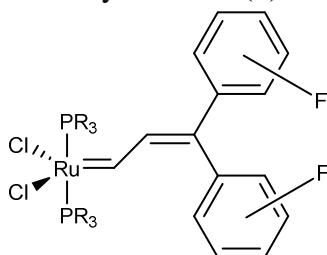
In some embodiments of the catalyst composition according to the present invention, any homogeneous catalyst commonly used in the art can be employed. Examples include transition metal ruthenium carbene complexes, Grubbs catalysts (e.g., catalysts for olefin metathesis), triphenylphosphine, and triphenylphosphine chlorides of platinum-group metals. Preferably, the homogeneous catalyst comprises triphenylphosphine and triphenylphosphine chloride of a platinum-group metal.

Specifically, transition metal ruthenium carbene complex catalysts include, but are not limited to, structures represented by the following Formula (1) to Formula (7):





The structure of Grubbs catalysts includes, but is not limited to, the one represented by Formula (8):



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In some embodiments of the hydrogenation method for HNBR according to the present invention, the triphenylphosphine chloride of the platinum-group metal is rhodium triphenylphosphine chloride and/or ruthenium triphenylphosphine chloride.

10 In some embodiments of the hydrogenation method for HNBR according to the present invention, the weight ratio of triphenylphosphine to the triphenylphosphine chloride of the platinum-group metal is 2~5:1. Examples include, but are not limited to, 2~5:1, 2~4:1, and 2~3:1.

15 In some embodiments of the hydrogenation method for HNBR according to the present invention, the weight ratio of the supported catalyst to the homogeneous catalyst is 1:0.01~0.3. Examples include, but are not limited to, 1:0.05~0.3, 1:0.1~0.3, 1:0.15~0.3, 1:0.16~0.3 and the like.

20 A sixth aspect of the present invention is to provide a hydrogenation method of a polymer, comprising: dissolving the polymer in an organic solvent, then adding the aforementioned catalyst composition, and reacting the polymer with hydrogen in the presence of the catalyst composition. The hydrogenation method is typically carried

out in a reactor, wherein the polymer dissolved in the organic solvent is first added to the reactor, then the catalyst composition is added, subsequently, the reactor is closed, and hydrogen is introduced to displace air, allowing the polymer to react with hydrogen in the presence of the catalyst composition.

5 In some embodiments of the hydrogenation method of the polymer according to the present invention, the amount of the supported catalyst accounts for 5~20 wt% of the polymer, for example, 5~20 wt%, 5~15 wt%, 5~10 wt%, 10~20 wt%, 10~15 wt%, 15~20 wt% and the like.

10 In some embodiments of the hydrogenation method of the polymer according to the present invention, the reaction conditions include: a temperature of 30~90°C, a hydrogen pressure of 5~10 MPa, and a time of 5~10 h.

15 In some embodiments of the hydrogenation method of the polymer according to the present invention, the amount of the organic solvent used to dissolve the polymer is such that the content of the polymer in the organic solvent is 0.1~10 wt%, for example, 0.1~10 wt%, 0.1~8 wt%, 0.1~6 wt%, 0.1~4 wt%, 0.1~2 wt%, 0.1~1 wt%, 0.5~10 wt%, 0.5~8 wt%, 0.5~6 wt%, 0.5~4 wt%, 0.5~2 wt%, 0.5~1 wt%, 1~10 wt%, 1~8 wt%, 1~6 wt%, 1~4 wt%, 1~2 wt%, 3~10 wt%, 3~8 wt%, 3~6 wt%, 3~4 wt%, 5~10 wt%, 5~8 wt%, 5~6 wt%, 7~10 wt%, 7~8 wt%, 8~10 wt%, 9~10 wt% and the like, based on the total weight of the polymer and the solvent.

20 In some embodiments of the hydrogenation method of the polymer according to the present invention, the polymer is an unsaturated copolymer of a conjugated diene and a copolymerizable monomer. The conjugated diene is at least one selected from butadiene, isoprene, piperylene, and 2,3-dimethylbutadiene, preferably butadiene and/or isoprene, and more preferably butadiene. The copolymerizable monomer is at
25 least one selected from acrylonitrile, methacrylonitrile, styrene, propyl acrylate, butyl acrylate, propyl methacrylate, and butyl methacrylate, preferably acrylonitrile and/or methacrylonitrile, and more preferably acrylonitrile.

30 In some embodiments of the hydrogenation method of the polymer according to the present invention, the polymer is NBR. In the art, NBR refers to a copolymer polymerized from acrylonitrile and butadiene monomers.

In some embodiments of the hydrogenation method of the polymer according to the present invention, there is no particular restriction on the type of NBR, i.e., the hydrogenation method of the present invention can be used for the hydrogenation of almost all types of NBR. For example, NBR can be obtained commercially (e.g., from Zeon Corporation, with grades such as DN series, 1000x132, 1001CG, 10001LG, 1031, 1041, 1041L, 1042, 1002, 1032J, 1022x59, 1052J, 1032-45, 1092-80, 1043, N917, 1094-80, 1014, 1034-60; or from Qilu Petrochem.) or self-made.

For example, the acrylonitrile content of NBR may be 15~55 wt%, for example, 19~51 wt%, 20~55 wt%, 25~55 wt%, 30~55 wt%, 35~55 wt%, 40~55 wt%, 45~55 wt%, 20~50 wt%, 25~50 wt%, 30~50 wt%, 35~50 wt%, 40~50 wt%, 45~50 wt%, 20~45 wt%, 25~45 wt%, 30~45 wt%, 35~45 wt%, 40~45 wt%, 20~40 wt%, 25~40 wt%, 30~40 wt%, 35~40 wt%, 20~35 wt%, 25~35 wt%, 30~35 wt%, 20~25 wt%, 20~30 wt%, and 25~30 wt%, including the range between any two values mentioned above.

For example, the Mooney viscosity (ML, 100°C, 1+4) of NBR may be 20~100, for example, 20~40, 20~60, 20~80, 25~35, 25~55, 25~75, 25~95, 30~50, 30~70, 30~90, 35~45, 35~65, 35~85, 40~60, 40~80, 40~100, 45~55, 45~75, 45~95, 50~70, 50~90, 55~65, 55~85, 60~80, 60~100, 65~75, 65~95, 70~90, 75~85, 80~100, 85~95, and 90~100, including the range between any two values mentioned above.

In some embodiments of the hydrogenation method of the polymer according to the present invention, the organic solvent is at least one selected from chlorobenzene, acetone, methyl ethyl ketone, tetrahydrofuran, dichloromethane, chloroform, cyclohexanone, ethyl acetate, and dimethylformamide.

In some embodiments of the hydrogenation method of the polymer according to the present invention, the aforementioned hydrogenation method of the polymer further comprises: after the completion of the reaction, recovering the supported catalyst by filtration or centrifugation, and recovering the homogeneous catalyst by ion exchange using an ion exchange resin.

In some embodiments of the hydrogenation method of the polymer according to the present invention, the degree of hydrogenation is at least 90%. Examples include,

but are not limited to, at least 91%, at least 92%, at least 93%, at least 94%, at least 95%, at least 96%, at least 97%, at least 98%, at least 99%. The degree of hydrogenation is measured in accordance with SH/T 1762-2008/ISO 14558:2000.

5 In some embodiments of the hydrogenation method of the polymer according to the present invention, the selectivity is at least 98%. Examples include, but are not limited to, at least 99%, at least 99.1%, at least 99.2%, at least 99.3%, at least 99.4%, at least 99.5%, at least 99.6%, at least 99.7%, at least 99.8%, at least 99.9%, 100%. The selectivity is measured by IR spectroscopy using a Nicolet 560 FTIR spectrometer from Nicolet Instrument Corporation, USA.

10 A seventh aspect of the present invention is to provide a hydrogenated polymer, preferably HNBR, obtained by the aforementioned hydrogenation method.

15 In some embodiments of the hydrogenated polymer, preferably HNBR, according to the present invention, the degree of hydrogenation of the hydrogenated polymer, preferably HNBR, is at least 90%. Examples include, but are not limited to, at least 91%, at least 92%, at least 93%, at least 94%, at least 95%, at least 96%, at least 97%, at least 98%, at least 99%. The degree of hydrogenation is measured in accordance with SH/T 1762-2008/ISO 14558:2000.

20 In some embodiments of the HNBR according to the present invention, the HNBR shows excellent properties such as good oil resistance, heat resistance, chemical corrosion resistance and odor resistance, as well as high tear strength and wear resistance.

25 An eighth aspect of the present invention is to provide applications of the aforementioned composite oxide support, the composite oxide support obtained by the aforementioned preparation method of the composite oxide support, the aforementioned supported catalyst, the supported catalyst obtained by the aforementioned preparation method of the supported catalyst, the aforementioned catalyst composition, the hydrogenated polymer obtained by the aforementioned hydrogenation method, or the aforementioned hydrogenated polymer in rubber articles

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or their manufacturing, particularly in HNBR articles or their manufacturing.

Advantages of the present invention:

(1) Modifying the composite support of SiO₂ and Group IVB metal oxide with an impregnation solution containing an organic cationic quaternary ammonium salt can significantly improve the dispersion of the active component on the catalyst surface and control the size of Cu atomic clusters of the active component to be no larger than 5 nm, thereby remarkably enhancing the hydrogenation activity of the catalyst.

(2) The supported catalyst prepared based on the composite support of SiO₂ and Group IVB metal oxide treated with an organic cationic quaternary ammonium salt has a pore structure suitable for the hydrogenation of macromolecules such as NBR. TiO₂ and/or ZrO₂ on the support surface can improve the hydrogenation activity of the catalyst, and the catalyst shows good hydrogenation activity and stability.

(3) The synergistic cooperation of the supported catalyst of the present invention with a homogeneous catalyst enables the hydrogenation saturation of polymer materials at relatively low temperatures and pressures, and the resulting hydrogenated polymer (e.g., HNBR) products achieve a high degree of hydrogenation.

(4) After the completion of the reaction, the supported catalyst is recovered by filtration or centrifugation, and the homogeneous catalyst is recovered by ion exchange using an ion exchange resin, which ensures that the supported catalyst can be reused multiple times, and the catalysts are easy to separate and recover.

(5) By using the supported catalyst and the hydrogenation method for hydrogenated polymers (e.g., HNBR) according to the present invention, the supported catalyst for hydrogenation of NBR using non-precious metals as active components is prepared for the first time. This avoids the problem of precious metal active component loss, further improves the recoverability of the catalyst, and significantly reduces the cost of the catalyst, thereby lowering the production cost of hydrogenated polymers (HNBR).

Description of Figures

Figure 1 is the IR spectrum of the composite oxide support in Example 1 of the present invention.

Figure 2 is the TEM image of the supported catalyst A in Example 13 of the present invention.

5 Figure 3 is the IR spectrum of the non-surface-treated $\text{TiO}_2\text{-SiO}_2$ composite support in Comparative Test Example 1.

Figure 4 is the IR spectrum of the surface-treated SiO_2 support in Comparative Test Example 5.

10 Figure 5 is a comparative diagram of the IR spectra of the supports in Example 1, Comparative Test Example 1, and Comparative Test Example 5.

Detailed description of the invention

To facilitate a better understanding of the present invention, it will be described in detail below with reference to examples. These examples are for illustrative purposes only and are not intended to limit the scope of application of the present invention.

In the following examples and comparative examples:

(1) SiO_2 microsphere support was purchased from Shandong Bangkai Materials Co., Ltd.

20 (2) Dimethyldioctadecylammonium chloride was purchased from J&K Scientific, with a CAS number of 61789-80-8.

(3) Cetyltrimethylammonium chloride was purchased from J&K Scientific, with a CAS number of 112-02-7.

(4) C_{12-14} alkyldimethylethylbenzylammonium chloride was purchased from J&K Scientific, with a CAS number of 85409-23-0.

25 (5) The content of Cu and its oxides calculated as CuO was analyzed using the Optima 8300 ICP atomic emission spectrometer from the Platinum Elmer (PE) company, USA, according to the standard JY/T 0567-2020.

30 (6) The content of TiO_2 was measured using a spectrophotometer. The principle is as follows: in sulfuric acid solution, Ti^{4+} reacts with hydrogen peroxide to form a yellow complex. Titanium dioxide reacts with hot sulfuric acid to form titanyl sulfate,

which then reacts with hydrogen peroxide to form a stable orange-yellow complex $[\text{TiO}(\text{H}_2\text{O}_2)]^{2-}$. The measurement was conducted at 430 nm using a UV-2100 spectrophotometer from Unico company.

(7) Similarly, the content of ZrO_2 was measured using a spectrophotometer.

(8) IR spectra were measured using a Nicolet iS50 IR spectrometer under the following conditions: the sample preparation and scanning were performed in attenuated total reflection mode, the scanning range was $4000\text{--}400\text{ cm}^{-1}$, the resolution was 4 cm^{-1} , and the number of scans was 32.

(9) TEM characterization conditions: The catalyst was observed using a Jem-3010 high-resolution transmission electron microscope at an accelerated voltage of 200 KV for HR-TEM characterization. Before test, the sample was fully ground into powder, a small amount of the sample was added to absolute ethanol and placed in an ultrasonic cleaner (model PS-10, Shenzhen Jiekang Ultrasonic Cleaner Co., Ltd.) for ultrasonic separation for 15~20 min. Finally, the suspension was drawn with a dropper and continuously dropped onto a microgrid, followed by natural drying.

(10) The particle size of the copper atomic clusters of the active component was characterized by transmission electron microscopy (TEM) and measured according to the scale bar.

【Example 1】

85 g of SiO_2 microsphere support (particle size: $20\text{ }\mu\text{m}$, average pore diameter: 110 nm, specific surface area: $78\text{ m}^2/\text{g}$) was impregnated with 420 mL of an aqueous solution of titanium sulfate with a concentration of 0.45 mol/L at 25°C for 6 h, the precipitate was dried at 110°C for 6 h and then roasted at 550°C for 5 h, to obtain a $\text{TiO}_2\text{--SiO}_2$ composite support with a TiO_2 content of 15 wt% (and an SiO_2 content of 85 wt%).

5 g of dimethyldioctadecylammonium chloride, to which 95 g of o-xylene was added, was mixed uniformly with 10 mL of hydrochloric acid (mass fraction: 37 wt%) to prepare an impregnation solution. The $\text{TiO}_2\text{--SiO}_2$ composite support was impregnated with the impregnation solution at 20°C for 2 h, and then dried at 60°C for 12 h, to obtain a $\text{TiO}_2\text{--SiO}_2$ composite oxide support.

The composite oxide support obtained was characterized by IR spectroscopy, and the IR spectrum thereof, i.e., the IR spectrum of the surface-treated SiO₂-TiO₂ composite oxide, is shown in Figure 1. It can be seen from the IR spectrum that the surface characteristics of the composite oxide support in Example 1 were that its IR spectrum showed three characteristic peaks in the range of 610-720 cm⁻¹ and three characteristic peaks in the range of 2840-2970 cm⁻¹. Specifically, the IR spectrum showed characteristic peaks at 620 cm⁻¹, 649 cm⁻¹, and 708 cm⁻¹; and characteristic peaks at 2850 cm⁻¹, 2919 cm⁻¹, and 2955 cm⁻¹.

【Example 2】

The preparation method of the TiO₂-SiO₂ composite support was the same as that in Example 1, except that 420 mL of a dilute sulfuric acid solution of metatitanic acid with a concentration of 0.86 mol/L was used instead of 420 mL of an aqueous solution of titanium sulfate with a concentration of 0.45 mol/L, to obtain a TiO₂-SiO₂ composite support with a TiO₂ content of 25 wt% (and an SiO₂ content of 75 wt%).

4 g of dimethyldioctadecylammonium chloride, to which 96 g of o-xylene was added, was mixed uniformly with 8 mL of hydrochloric acid (mass fraction: 37 wt%) to prepare an impregnation solution. The TiO₂-SiO₂ composite support was impregnated with the impregnation solution at 20°C for 2 h, and then dried at 60°C for 12 h, to obtain a TiO₂-SiO₂ composite oxide support.

The IR spectrum of the TiO₂-SiO₂ composite oxide support obtained was similar to that of the composite oxide support in Example 1. The surface characteristics were that the IR spectrum showed three characteristic peaks in the range of 610-720 cm⁻¹ and three characteristic peaks in the range of 2840-2970 cm⁻¹.

【Example 3】

The preparation method of the TiO₂-SiO₂ composite support was the same as that in Example 1, except that 398 mL of an aqueous solution of titanium tetrachloride with a concentration of 0.38 mol/L was used instead of 420 mL of an aqueous solution of titanium sulfate with a concentration of 0.45 mol/L, to obtain a TiO₂-SiO₂ composite support with a TiO₂ content of 12 wt% (and an SiO₂ content of 88 wt%).

3 g of dimethyldioctadecylammonium chloride, to which 97 g of o-xylene was added, was mixed uniformly with 7 mL of hydrochloric acid (mass fraction: 37 wt%) to prepare an impregnation solution. The TiO₂-SiO₂ composite support was impregnated with the impregnation solution at 20°C for 2 h, and then dried at 60°C for 12 h, to obtain a TiO₂-SiO₂ composite oxide support.

The IR spectrum of the TiO₂-SiO₂ composite oxide support obtained was similar to that of the composite oxide support in Example 1. The surface characteristics were that the IR spectrum showed three characteristic peaks in the range of 610-720 cm⁻¹ and three characteristic peaks in the range of 2840-2970 cm⁻¹.

【Example 4】

The preparation method of the TiO₂-SiO₂ composite support was the same as that in Example 1, except that 360 mL of an ethanol solution of tetrabutyl titanate with a concentration of 0.63 mol/L was used instead of 420 mL of an aqueous solution of titanium sulfate with a concentration of 0.45 mol/L, to obtain a TiO₂-SiO₂ composite support with a TiO₂ content of 18 wt% (and an SiO₂ content of 82 wt%).

2 g of dimethyldioctadecylammonium chloride, to which 98 g of o-xylene was added, was mixed uniformly with 5 mL of hydrochloric acid (mass fraction: 37 wt%) to prepare an impregnation solution. The TiO₂-SiO₂ composite support was impregnated with the impregnation solution at 20°C for 2 h, and then dried at 60°C for 12 h, to obtain a TiO₂-SiO₂ composite oxide support.

The IR spectrum of the TiO₂-SiO₂ composite oxide support obtained was similar to that of the composite oxide support in Example 1. The surface characteristics were that the IR spectrum showed three characteristic peaks in the range of 610-720 cm⁻¹ and three characteristic peaks in the range of 2840-2970 cm⁻¹.

【Example 5】

The preparation method of the TiO₂-SiO₂ composite support was the same as that in Example 1, except that 123 mL of an ethanol solution of tetrabutyl titanate with a concentration of 0.51 mol/L was used instead of 420 mL of an aqueous solution of

titanium sulfate with a concentration of 0.45 mol/L, to obtain a TiO₂-SiO₂ composite support with a TiO₂ content of 5 wt% (and an SiO₂ content of 95 wt%).

1 g of cetyltrimethylammonium chloride, to which 99 g of o-xylene was added, was mixed uniformly with 3 mL of hydrochloric acid (mass fraction: 37 wt%) to prepare an impregnation solution. The TiO₂-SiO₂ composite support was impregnated with the impregnation solution at 20°C for 4 h, and then dried at 80°C for 12 h, to obtain a TiO₂-SiO₂ composite oxide support.

The IR spectrum of the TiO₂-SiO₂ composite oxide support obtained was similar to that of the composite oxide support in Example 1. The surface characteristics were that the IR spectrum showed three characteristic peaks in the range of 610-720 cm⁻¹ and three characteristic peaks in the range of 2840-2970 cm⁻¹.

【Example 6】

The preparation method of the TiO₂-SiO₂ composite support was the same as that in Example 1, except for roasting at 650°C for 7 h instead of roasting at 550°C for 5 h, to obtain a TiO₂-SiO₂ composite support with a TiO₂ content of 15 wt% (and an SiO₂ content of 85 wt%).

5g of C₁₂₋₁₄-alkyldimethylethylbenzylammonium chloride, to which 95 g of o-xylene was added, was mixed uniformly with 10 mL of hydrochloric acid (mass fraction: 37 wt%) to prepare an impregnation solution. The TiO₂-SiO₂ composite support was impregnated with the impregnation solution at 40°C for 2 h, and then dried at 100°C for 12 h, to obtain a TiO₂-SiO₂ composite oxide support.

The IR spectrum of the TiO₂-SiO₂ composite oxide support obtained was similar to that of the composite oxide support in Example 1. The surface characteristics were that the IR spectrum showed three characteristic peaks in the range of 610-720 cm⁻¹ and three characteristic peaks in the range of 2840-2970 cm⁻¹.

【Example 7】

The preparation method is the same as that in Example 1, except that 420 mL of an aqueous solution of zirconium tetrachloride with a concentration of 0.29 mol/L was

used instead of an aqueous solution of titanium sulfate, to obtain a $\text{ZrO}_2\text{-SiO}_2$ composite support with a ZrO_2 content of 15 wt% (and an SiO_2 content of 85 wt%).

5 g of dimethyldioctadecylammonium chloride, to which 95 g of o-xylene was added, was mixed uniformly with 10 mL of hydrochloric acid (mass fraction: 37 wt%) to prepare an impregnation solution. The $\text{ZrO}_2\text{-SiO}_2$ composite support was impregnated with the impregnation solution at 20°C for 2 h, and then dried at 60°C for 12 h, to obtain a $\text{ZrO}_2\text{-SiO}_2$ composite oxide support.

The IR spectrum of the $\text{ZrO}_2\text{-SiO}_2$ composite oxide support obtained was similar to that of the composite oxide support in Example 1. The surface characteristics were that the IR spectrum showed three characteristic peaks in the range of 610-720 cm^{-1} and three characteristic peaks in the range of 2840-2970 cm^{-1} .

【Example 8】

85 g of SiO_2 microsphere support was impregnated with 280 mL of an aqueous solution of titanium sulfate with a concentration of 0.45 mol/L at 25°C for 6 h, the precipitate was dried at 110°C for 6 h and then roasted at 550°C for 5 h. After being further impregnated with 300 mL of an aqueous solution of zirconium nitrate with a concentration of 0.14 mol/L at 25°C for 4 h, the precipitate was dried at 110°C for 8 h and then roasted at 550°C for 6 h.

A $\text{TiO}_2\text{-ZrO}_2\text{-SiO}_2$ composite support with a TiO_2 content of 10 wt%, a ZrO_2 content of 5 wt% (and an SiO_2 content of 85 wt%) was thus obtained.

5 g of dimethyldioctadecylammonium chloride, to which 95 g of o-xylene was added, was mixed uniformly with 10 mL of hydrochloric acid (mass fraction: 37 wt%) to prepare an impregnation solution. The $\text{TiO}_2\text{-ZrO}_2\text{-SiO}_2$ composite support was impregnated with the impregnation solution at 20°C for 2 h, and then dried at 60°C for 12 h, to obtain a $\text{TiO}_2\text{-ZrO}_2\text{-SiO}_2$ composite oxide support.

The IR spectrum of the $\text{TiO}_2\text{-ZrO}_2\text{-SiO}_2$ composite oxide support obtained was similar to that of the composite oxide support in Example 1. The surface characteristics were that the IR spectrum showed three characteristic peaks in the range of 610-720 cm^{-1} and three characteristic peaks in the range of 2840-2970 cm^{-1} .

【Example 9】

The preparation method of the TiO₂-SiO₂ composite oxide support was the same as that in Example 1, except that SiO₂ microsphere support with particle size of 10 μm, average pore diameter of 200 nm and specific surface area of 60 m²/g was used instead of the SiO₂ microsphere support.

The IR spectrum of the TiO₂-SiO₂ composite oxide support obtained was similar to that of the composite oxide support in Example 1. The surface characteristics were that the IR spectrum showed three characteristic peaks in the range of 610-720 cm⁻¹ and three characteristic peaks in the range of 2840-2970 cm⁻¹.

【Example 10】

The preparation method of the TiO₂-SiO₂ composite oxide support was the same as that in Example 1, except that SiO₂ microsphere support with particle size of 5 μm, average pore diameter of 120 nm and specific surface area of 75 m²/g was used instead of the SiO₂ microsphere support.

The IR spectrum of the TiO₂-SiO₂ composite oxide support obtained was similar to that of the composite oxide support in Example 1. The surface characteristics were that the IR spectrum showed three characteristic peaks in the range of 610-720 cm⁻¹ and three characteristic peaks in the range of 2840-2970 cm⁻¹.

【Example 11】

The preparation method of the TiO₂-SiO₂ composite oxide support was the same as that in Example 1, except that SiO₂ microsphere support with particle size of 30 μm, average pore diameter of 1000 nm and specific surface area of 37 m²/g was used instead of the SiO₂ microsphere support.

The IR spectrum of the TiO₂-SiO₂ composite oxide support obtained was similar to that of the composite oxide support in Example 1. The surface characteristics were that the IR spectrum showed three characteristic peaks in the range of 610-720 cm⁻¹ and three characteristic peaks in the range of 2840-2970 cm⁻¹.

【Example 12】

The preparation method of the TiO₂-SiO₂ composite oxide support was the same as that in Example 1, except that the solvent in the impregnation solution was pyridine instead of o-xylene.

The IR spectrum of the TiO₂-SiO₂ composite oxide support obtained was similar to that of the composite oxide support in Example 1. The surface characteristics were that the IR spectrum showed three characteristic peaks in the range of 610-720 cm⁻¹ and three characteristic peaks in the range of 2840-2970 cm⁻¹.

【Example 13】

100 g of the composite oxide supports prepared in Examples 1-12 were impregnated with 500 mL of an aqueous solution of copper nitrate containing 5.26-33.33 g of Cu (calculated as CuO) at 25°C for 180 min, respectively, followed by drying at 110°C for 6 h and then roasting at 500°C for 4 h, to obtain Cu/TiO₂-SiO₂ catalysts (supported catalysts A-I, L, M, N, O) with a content of Cu and its oxide calculated as CuO of 5~25 wt%. Details are shown in Table 1.

The supported catalyst A prepared was characterized by TEM, and the results are shown in Figure 2. It can be seen from Figure 2 that the active component was uniformly dispersed, the particle size of the atomic clusters of the active component was 2~5 nm, and the average particle size was 3.3 nm.

【Example 13】

100 g of the composite oxide support prepared in Example 1 was impregnated with 500 mL of an aqueous solution of copper nitrate containing 32 g of Cu at 20°C for 180 min, followed by drying at 110°C for 6 h and then roasting at 600°C for 6 h, to obtain a Cu/TiO₂-SiO₂ catalyst (supported catalyst J) with a content of Cu and its oxide calculated as CuO of 24 wt%. Details are shown in Table 1.

【Example 14】

100 g of the composite oxide support prepared in Example 1 was impregnated with 500 mL of an aqueous solution of copper nitrate containing 32 g of Cu at 30°C for 180 min, followed by drying at 110°C for 6 h and then roasting at 650°C for 7 h, to obtain a Cu/TiO₂-SiO₂ catalyst (supported catalyst K) with a content of Cu and its oxide calculated as CuO of 24 wt%. Details are shown in Table 1.

Table 1

Supported catalyst No.	Support	Content of Cu and its oxide calculated as CuO (wt%)	Particle size of copper atomic clusters of active component, nm
A	TiO ₂ -SiO ₂ (a TiO ₂ content of 15wt%) in Example 1	24	2~5
B	TiO ₂ -SiO ₂ (a TiO ₂ content of 25wt%) in Example 2	18	2~5
C	TiO ₂ -SiO ₂ (a TiO ₂ content of 12wt%) in Example 3	14	2~5
D	TiO ₂ -SiO ₂ (a TiO ₂ content of 18wt%) in Example 4	20	2~5
E	TiO ₂ -SiO ₂ (a TiO ₂ content of 15wt%) in Example 1	5	2~5
F	TiO ₂ -SiO ₂ (a TiO ₂ content of 5wt%) in Example 5	24	2~5
G	TiO ₂ -SiO ₂ (a TiO ₂ content of 15wt%) in Example 6	24	2~5
H	ZrO ₂ -SiO ₂ (a ZrO ₂ content of 15wt%) in Example 7	24	2~5
I	TiO ₂ -ZrO ₂ -SiO ₂ (a TiO ₂ content of 10wt%, a ZrO ₂ content of 5wt%) in Example 8	24	2~5

J	TiO ₂ -SiO ₂ (a TiO ₂ content of 15wt%) in Example 1	24	2~5
K	TiO ₂ -SiO ₂ (a TiO ₂ content of 15wt%) in Example 1	24	2~5
L	TiO ₂ -SiO ₂ (a TiO ₂ content of 15wt%) in Example 9	24	2~5
M	TiO ₂ -SiO ₂ (a TiO ₂ content of 15wt%) in Example 10	24	2~5
N	TiO ₂ -SiO ₂ (a TiO ₂ content of 15wt%) in Example 11	24	2~5
O	TiO ₂ -SiO ₂ (a TiO ₂ content of 15wt%) in Example 12	24	2~5

The particle size, average pore diameter, and specific surface area of the supported catalysts A-N were measured, and the results are shown in Table 2. Wherein:

The particle size was measured in accordance with the test method specified in NB/SH/T 0951-2017, using the MS2000 laser particle size analyzer from Malvern company.

The average pore diameter and specific surface area were measured in accordance with the mercury intrusion porosimetry method specified in GB/T 21650.1-2008 (Determination of pore size distribution and porosity of solid materials by mercury intrusion porosimetry and gas adsorption methods — Part 1: Mercury intrusion porosimetry method), using an AutoPore IV 9500 high-performance fully automatic mercury porosimeter from Micromeritics Instrument Corporation, USA.

Table 2

Supported catalyst No.	Particle size, μm	Average pore diameter, nm	Specific surface area, m^2/g
A	20	102	47
B	10	100	51
C	5	104	55

D	20	103	54
E	20	102	65
F	22	106	52
G	20	102	55
H	20	103	54
I	20	100	51
J	20	104	51
K	20	104	52
L	10	186	41
M	5	107	46
N	30	983	36

【Test Example 1】

To 2 L of 4 wt% of a solution of NBR in chlorobenzene (prepared by dissolving NBR in chlorobenzene), 8 g of supported catalyst A, 0.4 g of homogeneous catalyst rhodium triphenylphosphine chloride, and 1.0 g of triphenylphosphine were added, and a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following reaction conditions: temperature of 90°C, hydrogen pressure of 6 MPa, and reaction time of 8 h, whereby HNBR was obtained.

The degree of hydrogenation of the HNBR obtained was measured according to the method specified in SH/T 1762-2008/ISO 14558:2000 (for measuring unsaturation). The result showed that the degree of hydrogenation was 95.2%.

The selectivity of the HNBR obtained was measured by IR spectroscopy using a Nicolet 560 FTIR spectrometer from Nicolet Instrument Corporation, USA. The measurement results showed that the intensity of the -CN absorption peak in the IR spectrum did not decrease after hydrogenation, and no absorption peak representing -NH₂ appeared. This indicates that the -CN group remained unchanged before and after the reaction, meaning that -CN was not hydrogenated, and the selectivity was 100%. The results showed a selectivity of 100%.

【Test Example 2】

To 2 L of 4 wt% of a solution of NBR in chlorobenzene (prepared by dissolving NBR in chlorobenzene), 8 g of supported catalyst A, 0.4 g of homogeneous catalyst rhodium triphenylphosphine chloride, and 1.0 g of triphenylphosphine were added, and
5 a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following reaction conditions: temperature of 90°C, hydrogen pressure of 8 MPa, and reaction time of 6 h, whereby HNBR was obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of
10 hydrogenation was 96.1% and the selectivity was 100%.

【Test Example 3】

To 2 L of 4 wt% of a solution of NBR in chlorobenzene (prepared by dissolving NBR in chlorobenzene), 8 g of supported catalyst B, 0.4 g of homogeneous catalyst
15 rhodium triphenylphosphine chloride, and 1.0 g of triphenylphosphine were added, and a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following reaction conditions: temperature of 90°C, hydrogen pressure of 8 MPa, and reaction time of 6 h, whereby HNBR was obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of
20 hydrogenation was 93.8% and the selectivity was 100%.

【Test Example 4】

To 2 L of 3 wt% of a solution of NBR in chlorobenzene (prepared by dissolving
25 NBR in chlorobenzene), 8 g of supported catalyst C, 0.5 g of homogeneous catalyst rhodium triphenylphosphine chloride, and 1.2 g of triphenylphosphine were added, and a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following reaction conditions: temperature of 90°C, hydrogen pressure of 8 MPa, and reaction time of 6 h, whereby HNBR was obtained.

30 The HNBR obtained was measured for its degree of hydrogenation and selectivity

according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 97.1% and the selectivity was 100%.

【Test Example 5】

To 2 L of 3 wt% of a solution of NBR in chlorobenzene (prepared by dissolving NBR in chlorobenzene), 8 g of supported catalyst A, 0.4 g of homogeneous catalyst rhodium triphenylphosphine chloride, and 1.0 g of triphenylphosphine were added, and a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following reaction conditions: temperature of 90°C, hydrogen pressure of 8 MPa, and reaction time of 6 h, whereby HNBR was obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 97.6% and the selectivity was 100%.

【Test Example 6】

After the completion of the reaction in Test Example 5, the supported catalyst A was recovered by centrifugal separation, stirred and washed in the organic solvent chlorobenzene for 4 h, and then centrifugally separated. Using the same reaction conditions as those in Test Example 5, the catalyst was re-added to the reaction system to investigate its catalytic performance for hydrogenation of NBR. The experiment was conducted continuously for 4 times. The results of the degree of hydrogenation (measured according to the method in Test Example 1) and selectivity (determined by nuclear magnetic resonance: through comparing the content of -CN group in the raw material and the hydrogenated product) are listed in Table 3.

Table 3

	Reused once	Reused twice	Reused 3 times	Reused 4 times
Degree of hydrogenation	94.5%	93.6%	93.3%	92.8%
Selectivity	100%	100%	100%	100%

【Test Example 7】

To 2 L of 4 wt% of a solution of NBR in chlorobenzene (prepared by dissolving NBR in chlorobenzene), 8 g of supported catalyst D, 0.4 g of homogeneous catalyst rhodium triphenylphosphine chloride, and 1.0 g of triphenylphosphine were added, and
5 a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following reaction conditions: temperature of 90°C, hydrogen pressure of 8 MPa, and reaction time of 6 h, whereby HNBR was obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of
10 hydrogenation was 97.6% and the selectivity was 100%.

【Test Example 8】

Following the method in Test Example 1, except that supported catalyst E was used instead of supported catalyst A, HNBR was finally obtained.

15 The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 91.2% and the selectivity was 100%.

【Test Example 9】

20 Following the method in Test Example 1, except that supported catalyst F was used instead of supported catalyst A, HNBR was finally obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of
25 hydrogenation was 94.1% and the selectivity was 100%.

【Test Example 10】

Following the method in Test Example 1, except that supported catalyst G was used instead of supported catalyst A, HNBR was finally obtained.

30 The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of

hydrogenation was 95.1% and the selectivity was 100%.

【Test Example 11】

5 Following the method in Test Example 1, except that supported catalyst H was used instead of supported catalyst A, HNBR was finally obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 95.8% and the selectivity was 100%.

10 **【Test Example 12】**

Following the method in Test Example 1, except that supported catalyst I was used instead of supported catalyst A, HNBR was finally obtained.

15 The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 95.4% and the selectivity was 100%.

【Test Example 13】

Following the method in Test Example 1, except that supported catalyst J was used instead of supported catalyst A, HNBR was finally obtained.

20 The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 95.7% and the selectivity was 100%.

【Test Example 14】

25 Following the method in Test Example 1, except that supported catalyst K was used instead of supported catalyst A, HNBR was finally obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 94.8% and the selectivity was 100%.

30

【Test Example 15】

Following the method in Test Example 1, except that supported catalyst L was used instead of supported catalyst A, HNBR was finally obtained.

5 The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 95.3% and the selectivity was 100%.

【Test Example 16】

10 Following the method in Test Example 1, except that supported catalyst M was used instead of supported catalyst A, HNBR was finally obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 95.0% and the selectivity was 100%.

15 **【Test Example 17】**

Following the method in Test Example 1, except that supported catalyst N was used instead of supported catalyst A, HNBR was finally obtained.

20 The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 96.1% and the selectivity was 100%.

【Test Example 18】

25 Following the method in Test Example 1, except for the use of the following reaction conditions: temperature of 80°C, hydrogen pressure of 6 MPa, and reaction time of 8 h, HNBR was finally obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 93.9% and the selectivity was 100%.

30 **【Test Example 19】**

Following the method in Test Example 1, except for the use of the following reaction conditions: temperature of 70°C, hydrogen pressure of 6 MPa, and reaction time of 8 h, HNBR was finally obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 91.7% and the selectivity was 100%.

【Test Example 20】

Following the method in Test Example 1, except for the use of the following reaction conditions: temperature of 60°C, hydrogen pressure of 6 MPa, and reaction time of 8 h, HNBR was finally obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 90.2% and the selectivity was 100%.

【Test Example 21】

Following the method in Test Example 1, except for the use of the following reaction conditions: temperature of 50°C, hydrogen pressure of 6 MPa, and reaction time of 8 h, HNBR was finally obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 88.2% and the selectivity was 100%.

【Test Example 22】

To 2 L of 4 wt% of a solution of NBR in chlorobenzene (prepared by dissolving NBR in chlorobenzene), 8 g of supported catalyst A, 0.4 g of homogeneous catalyst rhodium triphenylphosphine chloride, and 1.2 g of triphenylphosphine were added, and a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following reaction conditions: temperature of 90°C, hydrogen pressure of 6 MPa, and reaction time of 8 h, whereby HNBR was obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 95.3% and the selectivity was 100%.

5 **【Test Example 23】**

To 2 L of 4 wt% of a solution of NBR in chlorobenzene (prepared by dissolving NBR in chlorobenzene), 8 g of supported catalyst A, 0.4 g of homogeneous catalyst rhodium triphenylphosphine chloride, and 1.6 g of triphenylphosphine were added, and a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following reaction conditions: temperature of 90°C, hydrogen pressure of 6 MPa, and reaction time of 8 h, whereby HNBR was obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 95.4% and the selectivity was 100%.

15 **【Test Example 24】**

To 2 L of 4 wt% of a solution of NBR in chlorobenzene (prepared by dissolving NBR in chlorobenzene), 8 g of supported catalyst A, 0.4 g of homogeneous catalyst rhodium triphenylphosphine chloride, and 2 g of triphenylphosphine were added, and a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following reaction conditions: temperature of 90°C, hydrogen pressure of 6 MPa, and reaction time of 8 h, whereby HNBR was obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 95.3% and the selectivity was 100%.

25 **【Test Example 25】**

To 2 L of 4 wt% of a solution of NBR in chlorobenzene (prepared by dissolving NBR in chlorobenzene), 12 g of supported catalyst A, 0.4 g of homogeneous catalyst rhodium triphenylphosphine chloride, and 1.6 g of triphenylphosphine were added, and

a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following reaction conditions: temperature of 90°C, hydrogen pressure of 6 MPa, and reaction time of 8 h, whereby HNBR was obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 98.9% and the selectivity was 100%.

【Test Example 26】

To 2 L of 4 wt% of a solution of NBR in chlorobenzene (prepared by dissolving NBR in chlorobenzene), 8 g of supported catalyst A, 0.08 g of homogeneous catalyst rhodium triphenylphosphine chloride, and 0.32 g of triphenylphosphine were added, and a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following reaction conditions: temperature of 95°C, hydrogen pressure of 8 MPa, and reaction time of 8 h, whereby HNBR was obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 91.3% and the selectivity was 100%.

【Test Example 27】

To 2 L of 4 wt% of a solution of NBR in chlorobenzene (prepared by dissolving NBR in chlorobenzene), 8 g of supported catalyst A, 0.7 g of homogeneous catalyst ruthenium triphenylphosphine chloride, and 1.5 g of triphenylphosphine were added, and a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following reaction conditions: temperature of 90°C, hydrogen pressure of 6 MPa, and reaction time of 8 h, whereby HNBR was obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 95.2% and the selectivity was 100%.

【Test Example 28】

Following the method in Test Example 1, except that supported catalyst O was used instead of supported catalyst A, HNBR was finally obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 95.7% and the selectivity was 100%.

【Comparative Test Example 1】

The non-surface-treated $\text{TiO}_2\text{-SiO}_2$ composite oxide support from Example 1 was used, with the IR spectrum, i.e., the IR spectrum of the non-surface-treated $\text{TiO}_2\text{-SiO}_2$ composite oxide support, shown in Figure 3.

Subsequently, the active component was loaded according to the method in Example 12, and a $\text{Cu/TiO}_2\text{-SiO}_2$ catalyst with a Cu content of 24 wt% was finally obtained. The particle size of the Cu atomic clusters was 20~50 nm.

Following the method in Test Example 1, HNBR was finally obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 88.2% and the selectivity was 99%.

【Comparative Test Example 2】

Using the $\text{TiO}_2\text{-SiO}_2$ composite oxide support from Example 1, following the method in Example 5 except that a solution of nickel nitrate was used instead of a solution of copper nitrate, a $\text{Ni/ZrO}_2\text{-SiO}_2$ catalyst with a Ni content of 24 wt% (supported catalyst DB1) was finally obtained. The particle size of the Ni atomic clusters was 10~30 nm.

Following the method in Test Example 1, except that supported catalyst DB1 was used instead of supported catalyst A, HNBR was finally obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 78% and the selectivity was 82.5%.

【Comparative Test Example 3】

According to the method in Test Example 1 except that only supported catalyst A was used, the specific process was as follows:

5 To 2 L of 3 wt% of a solution of NBR in chlorobenzene (prepared by dissolving NBR in chlorobenzene), 9.4 g of supported catalyst A was added, and a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following reaction conditions: temperature of 90°C, hydrogen pressure of 8 MPa, and reaction time of 6 h, whereby HNBR was obtained.

10 The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 57.6% and the selectivity was 100%.

【Comparative Test Example 4】

15 According to the method in Test Example 5 except that only homogenous catalyst was used, the specific process was as follows:

To 2 L of 3 wt% of a solution of NBR in chlorobenzene (prepared by dissolving NBR in chlorobenzene), 0.4 g of homogeneous catalyst rhodium triphenylphosphine chloride, and 1.0 g of triphenylphosphine were added, and a catalytic hydrogenation reaction was conducted in an autoclave to obtain a rubber solution under the following
20 reaction conditions: temperature of 90°C, hydrogen pressure of 8 MPa, and reaction time of 6 h, whereby HNBR was obtained.

The HNBR obtained was measured for its degree of hydrogenation and selectivity according to the methods in Test Example 1. The results showed that the degree of hydrogenation was 67.2% and the selectivity was 100%.

25

【Comparative Test Example 5】

85 g of SiO₂ microsphere support (particle size: 20 μm, average pore diameter: 110 nm) was taken.

30 5 g of dimethyldioctadecylammonium chloride, to which 95 g of o-xylene was added, was mixed uniformly with 10 mL of hydrochloric acid (mass fraction: 37 wt%)

to prepare an impregnation solution. The SiO₂ microsphere support was impregnated with the impregnation solution at 20°C for 2 h, and then dried at 60°C for 12 h.

The IR spectrum of the surface-treated SiO₂ support is shown in Figure 4.

5 It can be seen from Figure 1 and Figures 3 to 5 that after the composite oxide support is surface-treated with an impregnation solution containing an organic cationic quaternary ammonium salt, the surface characteristics of the surface-treated composite oxide support obtained are that its IR spectrum shows three characteristic peaks in the range of 610-720 cm⁻¹ and three characteristic peaks in the range of 2840-2970 cm⁻¹. In
10 contrast, neither the IR spectrum of the non-surface-treated TiO₂-SiO₂ composite oxide support nor the IR spectrum of the surface-treated SiO₂ support shows three characteristic peaks in the range of 610-720 cm⁻¹ or three characteristic peaks in the range of 2840-2970 cm⁻¹. The composite oxide support of the present invention can significantly improve the dispersion of active component on the catalyst surface and
15 control the size of the atomic clusters of the active component to be no larger than 5 nm, thereby remarkably enhancing the hydrogenation activity of the catalyst.

It can be seen from Test Examples 1-27 and Comparative Test Examples 1-4 that by adopting a method of synergistic cooperation with homogeneous catalysts, the present invention ensures the hydrogenation saturation of polymer materials at
20 relatively low temperatures and pressures, and the resulting HNBR products achieve a high degree of hydrogenation, and moreover, ensures that the supported catalyst can be reused multiple times, and the catalysts are easy to separate and recover.

The above are only preferred examples of the present invention. It should be
25 pointed out that for those skilled in the art, under the technical inspiration provided by the present invention, as common knowledge in the art, other equivalent modifications and improvements can also be made, which should also be considered as the scope of protection of the present invention.

Claims

1. A composite oxide support, characterized in that, it comprises SiO_2 and a Group IVB metal oxide, wherein the Group IVB metal oxide is TiO_2 and/or ZrO_2 , the composite oxide support has the surface characteristics that its IR spectrum shows three characteristic peaks in the range of $610\text{--}720\text{ cm}^{-1}$ and three characteristic peaks in the range of $2840\text{--}2970\text{ cm}^{-1}$.

2. The composite oxide support according to claim 1, characterized in that, the composite oxide support has the surface characteristics that its IR spectrum shows characteristic peaks at $620\pm 1\text{ cm}^{-1}$, $649\pm 1\text{ cm}^{-1}$, and $708\pm 1\text{ cm}^{-1}$; and/or the composite oxide support has the surface characteristics that its IR spectrum shows characteristic peaks at $2850\pm 1\text{ cm}^{-1}$, $2919\pm 1\text{ cm}^{-1}$, and $2955\pm 1\text{ cm}^{-1}$.

3. The composite oxide support according to claim 1, characterized in that, the composite oxide support is obtained by subjecting a composite oxide support precursor comprising SiO_2 and a Group IVB metal oxide to surface treatment using an impregnation solution containing an organic cationic quaternary ammonium salt, preferably, the surface treatment is impregnation and drying; preferably, the organic cationic quaternary ammonium salt is a C_6+ long-chain alkyl quaternary ammonium salt, preferably a C_6+ long-chain alkyl quaternary ammonium halide salt, more preferably at least one selected from dimethyldioctadecylammonium chloride, cetyltrimethylammonium chloride, and $\text{C}_{12\text{--}14}$ -alkyldimethylethylbenzylammonium chloride.

4. The composite oxide support according to any one of claims 1-3, characterized in that, based on the total weight of the composite oxide support, the content of the Group IVB metal oxide is 5~25 wt%, and the content of SiO_2 is 75~95 wt%, preferably, the content of the Group IVB metal oxide is 10~25 wt% and the content of SiO_2 is 75~90 wt%; and/or, the composite oxide support has the particle size of 5~30 μm ;

and/or, the average pore diameter of 100~1200 nm; and/or, the specific surface area of 30~200 m²/g.

5. A method for preparing the composite oxide support according to any one of claims 1-4, characterized in that, it comprises the following steps:

(1) subjecting a SiO₂ microsphere support to a first impregnation with a solution of a Group IVB metal compound, followed by a first drying and a first roasting to obtain an oxide composite support precursor, wherein the Group IVB metal compound is a titanium-containing compound and/or a zirconium-containing compound;

(2) subjecting the composite oxide support precursor to surface treatment using an impregnation solution containing an organic cationic quaternary ammonium salt to obtain the composite oxide support.

6. The method according to claim 5, characterized in that, the impregnation solution containing the organic cationic quaternary ammonium salt comprises the organic cationic quaternary ammonium salt, a solvent, and an acid;

preferably, the concentration of the quaternary ammonium salt in the impregnation solution containing the organic cationic quaternary ammonium salt is 0.1~10 wt%.

7. The method according to claim 6, characterized in that,

the organic cationic quaternary ammonium salt is a C₆+ long-chain alkyl quaternary ammonium salt, preferably a C₆+ long-chain alkyl quaternary ammonium halide salt, more preferably at least one selected from dimethyldioctadecylammonium chloride, cetyltrimethylammonium chloride, and C₁₂₋₁₄-alkyldimethylethylbenzylammonium chloride; and/or

the solvent is at least one selected from deionized water, methanol, ethanol, acetone, methyl ethyl ketone, tetrahydrofuran, o-xylene, p-xylene, and pyridine, preferably at least one selected from o-xylene, p-xylene, and pyridine, more preferably o-xylene or pyridine; and/or

the acid is at least one selected from hydrochloric acid, sulfuric acid, nitric acid, and citric acid, preferably hydrochloric acid.

8. The method according to any one of claims 5-7, characterized in that, the surface treatment is impregnation and drying, preferably, the impregnation conditions include: a temperature of 20~60°C and a time of 0.5~8 h; the drying conditions include: a temperature of 50~120°C and a time of 2~10 h.

9. The method according to any one of claims 5-8, characterized in that, the SiO₂ microsphere support has the particle size of 5~30 μm; and/or, the average pore diameter of 100~1200 nm; and/or the specific surface area of 30~200 m²/g.

10. The method according to any one of claims 5-9, characterized in that, the titanium-containing compound is at least one selected from titanium sulfate, metatitanic acid, titanium tetrachloride, and tetrabutyl titanate;

and/or, the zirconium-containing compound is at least one selected from zirconium tetrachloride, zirconium sulfate, zirconium nitrate, zirconyl chloride, and zirconium oxalate;

and/or, the concentration of the titanium-containing compound and/or zirconium-containing compound in the solution of the titanium-containing compound and/or zirconium-containing compound is 0.1~1.0 mol/L.

11. The method according to any one of claims 5-10, characterized in that, the molar ratio of the SiO₂ microsphere support to the Group IVB metal-containing compound is 3~40:1; and/or, the conditions for the first impregnation include: a temperature of 20~60°C and a time of 0.5~8 h; and/or, the conditions for the first drying include: a temperature of 105~130°C and a time of 2~8 h; and/or, the conditions for the first roasting include: a temperature of 450~650°C and a time of 3~8 h.

12. A supported catalyst, comprising: the composite oxide support according to

any one of claims 1-4, and an active component Cu and its oxide supported on the support; wherein the particle size of the copper atomic clusters of the active component is no larger than 5 nm; based on the total weight of the supported catalyst, the content of Cu and its oxide calculated as CuO is 5~25 wt%.

13. The supported catalyst according to claim 12, characterized in that, the supported catalyst has the particle size of 5~30 μm ; and/or, the average pore diameter of 100~1200 nm; and/or, the specific surface area of 30~200 m^2/g ; and/or, the particle size of the copper atomic clusters of the active component is 2~5 nm.

14. A method for preparing the supported catalyst according to claim 12 or 13, comprising the following steps: subjecting the composite oxide support according to any one of claims 1-4 or the composite oxide support obtained by the method according to any one of claims 5-9 to a second impregnation with a solution of a soluble copper salt, followed by a second drying and a second roasting.

15. The method according to claim 14, characterized in that, the molar ratio of the composite oxide support to the soluble copper salt is 1:0.03~0.6; and/or, the conditions for the second impregnation include: a temperature of 20~60°C and a time of 0.5~8 h; and/or, the conditions for the second drying include: a temperature of 105~180°C and a time of 2~8 h; and/or, the conditions for the second roasting include: a temperature of 450~650°C and a time of 3~8 h.

16. The method according to claim 14 or 15, characterized in that, the soluble copper salt is at least one selected from copper chloride, copper sulfate, copper nitrate, copper acetate, and disodium copper ethylenediaminetetraacetate.

17. A catalyst composition, comprising a homogeneous catalyst and the supported catalyst according to claim 12 or 13.

18. The catalyst composition according to claim 17, characterized in that, the homogeneous catalyst comprises triphenylphosphine and triphenylphosphine chloride of a platinum-group metal;

preferably, the triphenylphosphine chloride of the platinum-group metal is rhodium triphenylphosphine chloride and/or ruthenium triphenylphosphine chloride;

preferably, the weight ratio of triphenylphosphine to the triphenylphosphine chloride of the platinum-group metal is 2~5:1.

19. The catalyst composition according to claim 17 or 18, characterized in that, the weight ratio of the supported catalyst to the homogeneous catalyst is 1:0.01~0.3.

20. A hydrogenation method of a polymer, comprising: dissolving the polymer in an organic solvent, then adding the catalyst composition according to any one of claims 17-19, and reacting the polymer with hydrogen in the presence of the catalyst composition.

21. The hydrogenation method according to claim 20, characterized in that, the amount of the supported catalyst accounts for 5~20 wt% of the polymer.

22. The hydrogenation method according to claim 20, characterized in that, the reaction conditions include: a temperature of 30~90°C, a hydrogen pressure of 5~10 MPa, and a time of 5~10 h.

23. The hydrogenation method according to any one of claims 20-22, characterized in that, the polymer is NBR.

24. The hydrogenation method according to any one of claims 20-23, characterized in that, the organic solvent is at least one selected from chlorobenzene, acetone, methyl ethyl ketone, tetrahydrofuran, dichloromethane, chloroform, cyclohexanone, ethyl acetate, and dimethylformamide.

25. A hydrogenated polymer obtained by the hydrogenation method according to any one of claims 20-24, preferably the hydrogenated polymer is HNBR.

26. Application of the composite oxide support according to any one of claims 1-4, the composite oxide support obtained by the method according to any one of claims 5-11, the supported catalyst according to claim 12 or 13, the supported catalyst obtained by the method according to any one of claims 14-16, the catalyst composition according to any one of claims 17-19, the hydrogenated polymer obtained by the hydrogenation method according to any one of claims 20-24 or the hydrogenated polymer according to claim 25 in rubber articles or their manufacturing, particularly in HNBR articles or their manufacturing.