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Carbothermal reduction of SiO_2 promoted with tungsten and morphology of WC-W_2C-β-SiC nanostructured composite material

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ABSTRACT

This paper presents the results of a study on the influence of tungsten as a structure promoter in the carbothermal reduction of silica. The morphology and surface structure of the obtained materials were analyzed using XRD, SEM-EDS, TEM and FTIR techniques. Surface area and porosity were evaluated on the basis of low temperature adsorption of nitrogen. The WC-W_2C-β-SiC nanostructured composite material formed from the carbothermal reduction of SiO_2 promoted with tungsten had a larger surface area ($25.8\,m^2\,g^{-1}$) in comparison to that measured for a β-SiC sample obtained by the simple carbothermal reduction of silica. Based on the results of this research, tungsten promoted carbothermal reduction of silica appears as a relatively simple procedure for obtaining valuable materials with a sufficiently high surface area to be used in catalysis.

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1. Introduction

Silicon carbide (SiC) is well known for its hardness and high melting point. Moreover, its high thermal conductivity, resistance to oxidation and reduction at elevated temperatures, limited reactivity towards metals commonly used as active catalytic phases and high mechanical strength, make SiC suitable as a catalyst support or even as a new kind of catalyst. Due to these properties, SiC supported catalysts have been successfully applied in a range of reactions, including selective oxidation of hydrogen sulfide [1], partial oxidation of methane [2,3], methane reforming [4,5], Fischer–Tropsch synthesis [6,7], liquid phase esterification of acetic acid with *n*-butanol [8] and hydrogen production from cellulose pyrolysis [9].

In particular, SiC high thermal conductivity has been shown to provide higher catalyst stability in comparison to more commonly used oxide supports, such as silica and alumina. The extremely high stability as a function of time on stream reported for SiC supported Ni catalysts used in the partial oxidation of methane has been attributed to the high thermal conductivity of SiC. Efficient heat transfer from the catalyst prevents the formation of hot spots on the catalyst surface and associated phenomena such as carbon

deposition, changes in catalyst selectivity in the undesired direction and catalyst sintering [3,10,11].

The chemical inertness of SiC means that it is possible to regenerate deactivated catalysts by burning off carbonaceous deposit on the catalyst surface. It has been shown that an Ni/SiC catalyst used in the partial oxidation of methane can be easily regenerated by this method [2,6,11]. In Ni/SiC catalysts the reaction between the active metal and the SiC support is considerably limited after calcination at 1273 K, whereas in a Ni/Al_2O_3 or Ni/SiO_2 catalyst the process results in substantial deactivation. It has been shown that in the case of Ni/SiC catalysts a thin Si–O layer forms on the SiC surface, which effectively hampers the reaction of Ni with the SiC support even after calcination at 1273 K. As a result, only NiO phase is formed on the Ni/SiC surface during calcination, which can be reduced at relatively low temperatures below 1000 K [12]. Finally, SiC is also capable of having a synergistic effect in Co/SiC catalysts, leading to improved CO conversion and product selectivity in Fischer–Tropsch processes compared to cobalt catalysts supported on alumina or titania [13,14].

Disadvantages of SiC include partial oxidation, forming SiO_2, and considerable sintering in atmospheres of air or steam at 1273 K, restricting the application of SiC as a catalyst support [15].

Moreover, to be successfully applied as a catalyst support, SiC should have a sufficiently high specific surface area, in the range of $20–100\,m^2\,g^{-1}$. Since SiC obtained by direct reaction of molten silicon and carbon has a low specific surface area of $10–19\,m^2\,g^{-1}$ [16], other methods of SiC preparation have been proposed.

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One such alternative method, which is frequently employed to obtain SiC with a specific surface area appropriate for use as a catalyst support, is carbothermal reduction using silicon xerogel as a silicon precursor. For example, the carbothermal reduction of silicon xerogel in an inert atmosphere at elevated temperatures has been reported to produce nanostructured SiC with a specific surface area of $76 \, m^2 \, g^{-1}$ [17]. SiC with a specific surface area of $112 \, m^2 \, g^{-1}$ has been reportedly obtained using the modified sol–gel process with nickel nitrate as a pore-adjusting reagent [18].

Other studies in the literature have shown that the morphology of SiC synthesized by carbothermal reduction depends on the compounds which are used as carbon sources. SiC has been shown to reflect the cellular morphology of charcoal precursor when wood-derived charcoal soaked with silica sol is used as a substrate [19]. This approach enables the production of high-porosity SiC, which preserves the woodlike microstructure of the porous biocarbon template [20]. Using water, glass and different carbon precursors, Gou et al. obtained various nanostructured forms of SiC with specific surface areas of between 45 and $81 \, m^2 \, g^{-1}$ [21]. Strauch and co-workers synthesized mesoporous silicon carbide with a specific surface area of $660 \, m^2 \, g^{-1}$ using the carbothermal process and plant material as a substrate [22].

Another method, based on the thermal decomposition of triethylsilane or silicone oil at autogenic pressure, yielded SiC nanoparticles with high specific surface areas of $150 \, m^2 \, g^{-1}$ (with triethylsilane) and $563 \, m^2 \, g^{-1}$ (with silicone oil) [23]. Additional advantages of this method are that only one substrate is required and the process occurs under relatively mild temperature conditions. High surface area SiC may also be obtained by the gas solid reaction of SiO vapor and activated charcoal, referred to as shape memory synthesis (SMS), as elaborated by Ledoux and co-workers [24–26]. The main advantage of the SMS method is the possibility of using different forms of carbon precursor, yielding SiC powders with specific surface areas in the range of $15–50 \, m^2 \, g^{-1}$.

SiC may also be synthesized through the reaction of nickel-loaded activated carbon with silicon tetrachloride and hydrogen. In the final step of this process, SiC with surface areas ranging from 30 to $80 \, m^2 \, g^{-1}$ can be formed via the Vapour Liquid Solid (VLS) mechanism from $SiCl_4$ and CH_4 [15,27,28].

In the present study, nanostructured material with WC, W_2C and β-SiC as the main components was prepared by the simple annealing of a mixture of carbon and silica doped with tungsten oxide at $1550\,°C$ in argon atmosphere. The obtained WC-W_2C-β-SiC composite material was analyzed using XRD, SEM-EDS, TEM and FTIR techniques. Low-temperature N_2 adsorption/desorption measurements were used to determine its specific surface area and porosity.

2. Material and methods

2.1. Material synthesis

Graphitized carbon Vulcan XC72 (Cabot Co.) and silica Kieselgel 60 (Merck) were used as substrates for the carbothermal process of silicon carbon formation. The mass ratio of SiO_2 to carbon was set at 1:5 in the substrate mixture. The substrates were mixed in a ball mill for 30 min with a rotation speed of 350 rotations per minute (rpm) using zirconia balls. The mixture was then annealed at $1550\,°C$ for 90 min in a graphite furnace (VSL10/18 Degussa Wolfgang, Hanau, Germany) under Ar flow ($1 \, dm^3$/min). The heating rate was $30\,°C \, min^{-1}$.

The starting mixture used for the tungsten-assisted carbothermal reduction of SiO_2 was prepared by mixing WO_3 (Fluka) with graphitized carbon Vulcan XC72 (Cabot Co.) and silica Kieselgel 60 (Merck). This mixture was ball milled for 30 min at a speed of 350 rpm using zirconia balls. The amount of WO_3 in the starting mixture was adjusted to obtain 5 wt% of W in the mixture of substrates. Annealing was carried out at $1550\,°C$ in a graphite furnace (VSL10/18 Degussa Wolfgang, Hanau, Germany) under Ar flow ($1 \, dm^3$/min). The heating rate was $30\,°C \, min^{-1}$. Two annealing times were applied: 90 and 270 min.

For reasons of simplicity, the composite material obtained directly after the annealing of graphitized carbon and silica will be referred to as composite A, while the products of W-promoted carbothermal reduction of SiO_2 after reaction durations of 90 and 270 min will be designated, respectively, as composite B and composite C.

2.2. Characterization

Room temperature powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer in the Bragg–Brentano reflection geometry. Copper Cu Kα radiation from a sealed tube was used. Data were collected in the 2θ range of 5–90° with a step of 0.0167° and an exposure per step of 20 s. The samples were spun during data collection to minimize preferred orientation effects. A PANalytical X'Celerator detector based on Real Time Multiple Strip technology and capable of simultaneously measuring intensities in the 2θ range of 2.122° was used. For qualitative analysis, the PANalytical High Score Plus software package was used combined with the International Centre for Diffraction Data (ICDD) powder diffraction file (PDF-2 ver. 2009) database of standard reference materials. The average crystallite sizes of the nanostructures were determined according to the Scherrer formula ($d = K\lambda/\beta\cos\theta$), where λ is the wavelength of the X-ray (Cu Kα), β is the integral breadth of a reflection (in radians 2θ) located at 2θ Bragg angle, K is a shape factor (0.9) and θ is the angle of diffraction.

The specific surface area (SSA) of the samples was determined using Micromeritics ASAP 2020 equipment. SSA analysis was based on the Brunauer–Emmett–Teller (BET) model of N_2 low temperature adsorption and with the assumption that nitrogen molecules covered $0.162 \, nm^2$ of the adsorbent surface. The size and volume of pores with radiuses between 0.85 and 150.00 nm were determined using Barrett–Joyner–Halenda (BJH) desorption cumulative volume of pores and BJH desorption average pore radius. Prior to the analysis, the samples were placed in a measurement ampoule and degassed for 4 h at $300\,°C$.

Fourier transform infrared (FTIR) spectra were collected using an IRTracer-100 FTIR (Shimadzu) spectrometer equipped with a liquid nitrogen-cooled MCT detector and the KBr wafer technique. The samples and KBr were first ground into powders (the mass ratio of KBr to sample was 300), before being physically mixed until uniform and pressed into wafers. IR absorption spectra were collected in the range from 4000 to $700 \, cm^{-1}$. Before each measurement, the background was recorded on KBr. A resolution of $4.0 \, cm^{-1}$ was used throughout the investigation. One hundred twenty eight scans were taken to achieve a satisfactory signal-to-noise ratio.

The microstructure of the samples was characterized using a scanning electron microscope (Hitachi S-4700, Japan) equipped with an energy dispersive X-ray spectrometer (EDS, Thermo NORAN, USA). SEM images were reordered using a secondary electron (SE) detector. Energy Dispersive Spectrometry (EDS) enabled qualitative analysis of the elements present in micro-areas of the sample.

Transmission electron microscopy (TEM) observations were carried out on a scanning-transmission electron microscope Hitachi STEM HD2700 with an accelerating voltage of 200 kV and equipped with the EDS system. The specimens were prepared by depositing powder on a Cu TEM-grid with a holey carbon film.