



New approach to the preparation of highly dispersed transition metals sulfides and nitrides



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ABSTRACT

Gas–solid reactions leading to bulk or supported nitride and sulfide catalysts conventionally involve inter-action of oxide precursors with NH_3 or H_2S flow. Addition of gaseous oxygen acceptors, such as carbon tetrachloride, to the treatment gas flow changes the reaction pathway and opens new possibilities for the preparation of highly divided sulfides and nitrides. Thus, sulfidation or nitridation of the electropositive transition metals oxides becomes possible under relatively soft conditions. Otherwise, novel original 2D and hollow morphologies become available. Latest achievements using this approach are reviewed and original results are presented for the preparation of sulfides and nitrides. A critical analysis of the possibilities and limitations of the new approach is provided with emphasis on the preparation of highly divided catalytic materials.

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1. Introduction

The preparation step is fundamental for accessing desired properties of inorganic materials. Many recent breakthroughs in the materials science began from finding novel preparation techniques. Extending the scope of available synthetic strategies is crucial, with emphasis on the properties tuning. Nanodispersed sulfides and nitrides of transition metals are important classes of modern inorganic materials, presenting great interest as catalysts [1–3] lubricants [4], photocatalysts [5,6], anodes for Li-ion batteries [7,8], photovoltaics and many others. For all these applications, highly dispersed solids are desirable, characterized by intense contact of a material surface with the environment. Beside the small size, control of nanoparticles shape is of paramount importance. To meet these criteria, a great number of novel preparation techniques have been developed, using a variety of reaction conditions and precursors. Such innovative preparation techniques proposed to prepare nitrides and sulfides include laser ablation [9,10], chemical vapor deposition [11,12], solution syntheses assisted with a surfactant, ultrasound [13,14], microwave power [15,16], and many others. The precursors applied include transition metals carbonyls [17], volatile chlorides [18,19], thiosalts [20,21] and various metalloorganic compounds with sulfur- or

nitrogen-containing ligands [22,23]. The corresponding synthetic procedures often involve glove box reactions excluding any contact of the precursors with air or moisture.

However, industrial catalysis with sulfides and the envisaged applications of nitrides are large scale processes involving many kilograms or even tons of a solid catalyst. To get a newly developed synthesis route at least potentially viable for the industrial applications, severe constraints should be immediately foreseen on the set of admitted precursors and procedures. Among the precursors, oxides and oxo-salts of transition metals are particularly readily available and easy to handle. Thus, alkali earth molybdates or tungstates in micro- and nanodispersed form have been prepared using various methods such as molten salt [24], microwave/hydrothermal [25] and metathesis in aqueous and non-aqueous solvents [26]. Meanwhile such materials are not studied as precursors for the preparation of catalysts. As with the preparation procedures for sulfides and nitrides, solid–gas reactions of oxides with H_2S and NH_3 are by far the most convenient and conventionally applied in the catalysis field to obtain highly dispersed sulfide [27–29] or nitride [30,31] catalysts, respectively.

While being the most widely used, solid–gas reactions have strong limitations, both thermodynamically and kinetically. Thus, for catalysis with early transition metals sulfides and nitrides preparation of dispersed materials represents a challenge. Many sulfides and nitrides of early transition metals are hardly available in the nanodispersed state which hampers their use in catalysis. Indeed, to obtain sulfides or nitrides of relatively electropositive

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metals such as tantalum, high temperatures should be applied, hardly compatible with further catalytic applications.

The present paper gives an account of a recently proposed approach, which allows considerable extending of the possibilities of preparation of sulfide and nitride catalysts by means of solid–gas reactions. Technically it represents a simple add-on to the standard sulfidation or nitridation procedures. Conceptually, in the most general terms it consists in admitting of an additional reagent to the gas phase, which would withdraw oxygen from an oxide precursor by means of an acid–base mechanism. Oxygen acceptor considered in this paper is carbon tetrachloride CCl_4 .

In the following sections we shall briefly outline the previously published and ongoing research and provide original data on the preparation of bulk and supported sulfides and (oxy)nitrides achieved using this approach.

2. Experimental

2.1. Reaction setup and preparation of solid materials

The materials used as precursors for sulfidation and nitridation included P25 titanium oxide from Degussa and commercial Ta_2O_5 , Na_2MoO_4 , LiTaO_3 , MoO_3 and WO_3 , from Aldrich. Supported $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst was prepared by impregnation of gamma alumina ($220\text{ m}^2/\text{g}$) with ammonium heptamolybdate to obtain 10 wt.% molybdenum loading. Alkali earth molybdates and tungstates were prepared from the metathesis of alkali earth nitrates and alkali molybdates or tungstates in ethylene glycol.

The experimental setup is a modification of a standard solid–gas sulfidation/nitridation device, in which an additional gas flow is introduced (Fig. 1). A flow of nitrogen saturated with carbon tetrachloride vapor was introduced by means of including of a glass saturator bubbled through with nitrogen at a controlled temperature in the range 0–25 °C. The flow rates of gaseous ammonia for nitridation were from 30 to 500 mL/min, those of H_2S for sulfidation were from 10 to 100 mL/min. The solids (1–2 g) were treated in Pyrex (below 550 °C) or quartz (up to 800 °C) reactors.

After the reaction the solids were kept and further handled under inert gas. The materials prepared from the precursors containing alkali or alkali earth metals were washed several times with distilled water in order to remove the corresponding soluble chlorides.

2.2. Characterizations

Powder X-ray diffraction (XRD) patterns were obtained on a BRUKER diffractometer using $\text{Cu K}\alpha$ emission. The XRD patterns were analyzed using standard ICDD files. The average size of crystallites was estimated by the Scherrer equation, using

several isolated peaks for each pattern. Diffuse reflectance UV–visible spectra were measured with the AvaSpec-2048 Fiber Optic Spectrometer equipped with 2048 pixel CCD detector, in the range 250–800 nm with BaSO_4 reference. X-band (9.5 GHz) EPR spectra were recorded at 77 K on a Bruker ESP 300E spectrometer using a rectangular (TE102) EPR cavity (Bruker ER4102ST) at microwave power 1.6 mW and modulation amplitude 1 G. For quantitative analysis the EPR spectra were treated using EasySpin software [32]. Nitrogen adsorption–desorption isotherms were measured on a Micromeritics ASAP 2010 instrument. Specific surface areas were calculated using BET equation. Pore size distributions calculated using Barrett–Joyner–Hallenda (BJH) method. Prior to measurements the samples were heated in a secondary vacuum at 300 °C for 4 h. Molybdenum content in the solids was determined after dissolution in a $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture by plasma-coupled atomic emission spectroscopy (AES-ICP). The contents of carbon, hydrogen, nitrogen and sulfur (CHNS) in the solids were determined on a EA1110-CHNS instrument. Thermodynamics of reactions was calculated using HSC Chemistry® 6.0 software. The morphology of the particles was examined by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) energy dispersive spectroscopy (EDS) and selected area electron diffraction (SAED) on a JEOL 2010 microscope with an accelerating voltage of 200 kV. For TEM and HRTEM analysis, the as-synthesized nanoparticles were dispersed in ethanol by ultrasonic treatment. Then a drop of dispersion was transferred to a holey carbon film supported on a copper grid and evaporated naturally. Scanning electron microscopy was carried out on a Hitachi S800 device.

The gaseous products evolved during the treatments were studied using a mass-spectrometer VG Thermo Fisher equipped with a quadrupole analyzer (VG analyser) working in a Multiplier mode. The ionization was done by electron impact with an electron energy of 65 eV. The samples (ca. 1 g) were heated from room temperature to 700 °C in a quartz cell at the heating rate of 5°/min. A silica capillary tube heated at 180 °C continuously bled off a portion of the gaseous reaction products.

2.3. Catalytic test

Thiophene HDS tests carried out without exposure of the solids to oxygen; the sulfides were transferred to the catalytic reactor under argon. Steady state activities after 12 h on stream were compared at 300 °C. The temperature varied between 280 °C and 340 °C in order to measure kinetics and to build Arrhenius plot of the reaction rate. The properties of the solid catalysts were determined after the catalytic test. The products were analyzed using on-line gas chromatography. Reaction rate was determined using pseudo-first rate equation assuming large excess of hydrogen. In

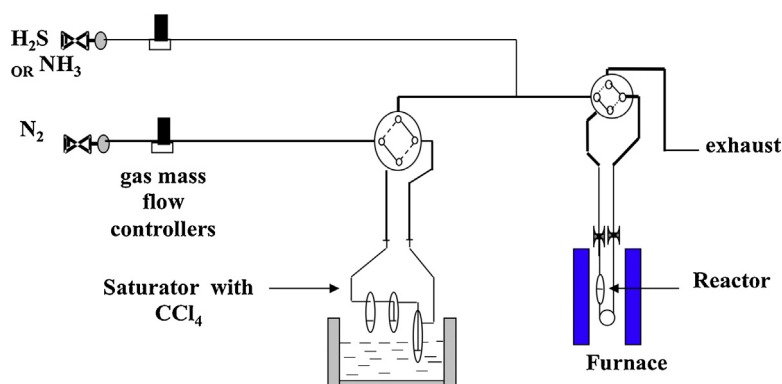


Fig. 1. Experimental setup.

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