Molybdenum-based catalysts for the decomposition of ammonia: In situ X-ray diffraction studies, microstructure, and catalytic properties

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ABSTRACT

The ammonia decomposition reaction over molybdenum-based catalysts is an example for the complex influence of different factors, such as phase composition, size of crystalline domains, or defect concentration, on the catalytic behavior of a material. In situ powder diffraction allows the direct analysis of how catalysts change during a reaction with respect to the atomic structure or microstructure in terms of defects or size changes. In this article, the influence of catalyst treatment such as pre-reduction or ball milling on the catalytic properties is discussed in detail.

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1. Introduction

Ammonia is an excellent hydrogen carrier, and therefore, the decomposition of ammonia would be an elegant way to generate hydrogen for fuel cell applications without formation of CO_x. On the other hand, ammonia can be used directly as feed for solid oxide fuel cells. Up to now, the benchmark catalyst is ruthenium dispersed on carbon nanotubes [1,2]. The activity is significantly influenced by the appropriate choice of promoters which are added to the supported catalysts [3]. Due to economical aspects, the substitution of noble metal catalysts by metal oxides is under discussion. As an example, iron oxide-based materials have been studied as catalysts for ammonia decomposition [4]. Since several years, compounds, such as molybdenum carbides and nitrides, are considered as potential catalysts for several catalytic reactions [5–8] or as catalyst supports [9]. The formation of molybdenum nitrides by nitridation of molybdenum oxides under ammonia flow was the topic of a large number of publications. Heating MoO_3 in NH_3 atmosphere is one way to obtain molybdenum nitrides with high surface areas [10–14]. The formation of different intermediates, such as molybdenum bronze, molybdenum oxynitrides, and molybdenum nitrides with different stoichiometries, makes this system quite complicated. Even though many aspects of the nitridation of MoO_3 have already been studied in detail, there are many open questions, especially with respect to catalysis. Aim of our work was to correlate the catalytic activity of molybdenum-based

catalysts with structure and/or phase changes monitored by in situ powder diffraction. Another topic of interest was the influence of microstructure properties on the catalytic performance of such catalysts. For this purpose, also ball-milled catalyst precursors have been investigated.

2. Experimental

2.1. Catalyst preparation

Commercial MoO_3 (MoO_3-C) (Merck, purity 99%) was used as starting material for the synthesis of catalysts for the conversion of ammonia. A second type of MoO_3 samples was prepared by impregnation and subsequent calcination of porous carbon with an aqueous solution of molybdic acid (H_2MoO_4, min 83% of MoO_3, Riedel de Haën) according to the literature [15]. For the preparation, either 7 mL of saturated aqueous molybdic aqueous solution or 7 mL of a 0.96 M phosphomolybdic acid hydrate (puriss. p.a.) (PMA) aqueous solution was added dropwise under stirring to 15 g of an as-received activated carbon (GPAK-500, Gel-type purchased from CarboTex GmbH). The impregnated carbon was then calcined for 2 h at 550 °C in air with a heating rate of 4 °C min^{-1}. The samples obtained by this procedure are denoted as MoO_3-G.

2.2. Ball milling

Ball milling of MoO_3-C was performed in a Retsch MM2000 mixer mill equipped with tungsten carbide vials. One ball of the

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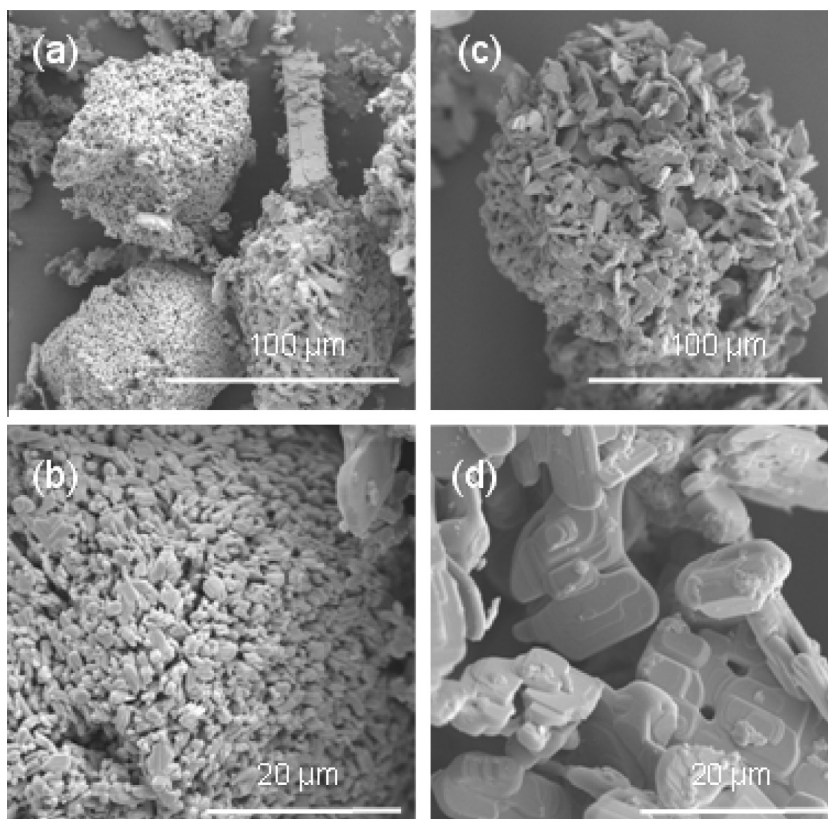
Fig. 1. SEM images of sample (a) and (b) MoO$_3$-C and of sample MoO$_3$-G (c, d).

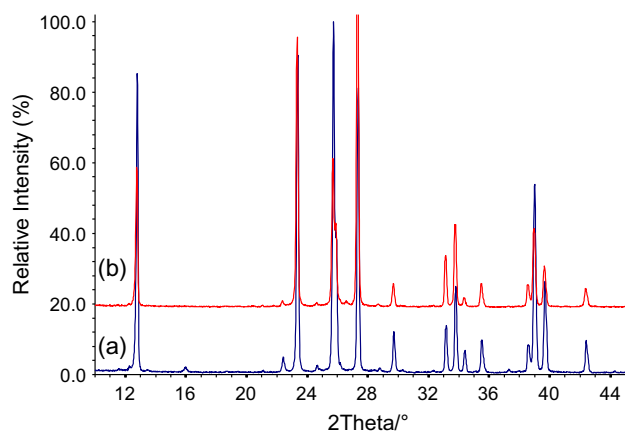**Fig. 2.** XRD patterns of (a) MoO$_3$-C and (b) MoO$_3$-G.

same material with a diameter of 5 mm was used as grinding medium. The ball-to-powder mass ratio was 8:1 and the rotational speed was 900 rpm. Samples were milled for 5 or 10 h, and after every hour, milling was suspended for 15 min.

2.3. Catalyst characterization

All samples were characterized by means of X-ray powder diffraction (XRD) at ambient conditions, in situ XRD under reaction conditions, scanning electron microscopy and transmission electron microscopy (SEM and TEM), nitrogen adsorption, and X-ray photoelectron spectroscopy (XPS). Moreover, catalytic activity was tested in a fixed-bed reactor. XRD experiments under ambient conditions were carried out in reflection geometry on a Stoe STA-

DIP θ/θ diffractometer (Bragg–Brentano geometry) using Cu K$\alpha_{1,2}$ radiation. Divergence slit was set to 0.6 mm, receiving slit was set to 0.6 mm, and the width of the horizontal mask was set to 4 mm. Data were collected in the 2θ range of 20–85° for molybdenum oxides and carbides and in the 2θ range of 30–90° for the molybdenum nitrides. In situ XRD experiments were performed on a PANalytical X'Pert diffractometer equipped with an Anton Paar XRK 900 high-temperature reaction chamber and with Cu K$\alpha_{1,2}$ radiation (40 kV, 40 mA) using the following slit configuration: primary and secondary soller slits 0.04 rad, divergence slit 0.5°, and anti-scatter slits 1°. No monochromator but a secondary Ni filter has been used. Data were collected in the 2θ range of 20–85° for molybdenum oxides and carbides and the 2θ range of 30–85° for the molybdenum nitrides. The Anton Paar reaction chamber was equipped with a Marcor® sample holder (6–10 mm diameter). Measurements were taken under pure ammonia flow with a space velocity of 15 000 mL/g$_{sample}$ h and heating from room temperature to 800 °C with a heating rate of 40 °C min^{-1}. The sample was deposited on a sieve plate (10 mm diameter, 1 mm depth) which allows the reaction gas to pass through the catalyst bed. The product gases leave the reaction chamber through an exhaust pipe under the sample.

For the analysis of the microstructure, XRD patterns were analyzed by the Whole Powder Pattern Modelling (WPPM) approach. The method is based on a direct physical modeling of the microstructure from XRD data in terms of density of specific lattice defects, shape, and size distribution of coherently diffracting domains. Domain size, domain size distribution, and dislocation density (ρ) were retrieved using the PM2K software based on the WPPM approach [16]. The Cagliotti function [17] was used to parameterize the instrumental effects and was obtained from the analysis of diffraction data of a silicon reference material (NIST SRM 640C). Domain size distribution of (spherical) domain diame-