Thermochimica Acta 584 (2014) 31–35

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Short Communication

Thermal analysis coupled with mass spectrometry as a tool to determine the cobalt content in cobalt catalyst precursors obtained by co-precipitation

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ARTICLE INFO

Article history:
Received 9 December 2013
Received in revised form 11 March 2014
Accepted 21 March 2014
Available online 29 March 2014

Keywords:
Thermal analysis
TG-MS
Co content determination
Cobalt catalyst
Co-precipitation

ABSTRACT

The cobalt content in catalyst precursors obtained by co-precipitation containing oxide forms of Co and Ce or Co and La was determined by thermal analysis coupled with mass spectrometry. The described methodology is based on two types of thermogravimetric measurements: in an inert atmosphere (TG-MS(Ar)) which allowed us to determine the content of Co_3O_4 and in a reducing atmosphere (TG-MS(H_2)) which specifies the metallic cobalt content in the samples. The effective determination of the active phase (Co) content in the cobalt–cerium catalyst precursor (Co/Ce) is possible by providing only one of the described measurements: TG-MS(Ar) or TG-MS(H_2). The cobalt–lanthanum material (Co/La) requires combining both measurements. Results were validated by a comparison with the results of ICP-OES analysis and demonstrated good accuracy. The phase composition of the samples was confirmed by XRPD.

1. Introduction

Thermal analysis is nowadays an essential tool for material research and development. Its application includes studies of, among others: minerals, metals, ceramics, polymers, organic and inorganic substances, as well as pharmaceuticals [1,2]. This method of observation of the changes taking place in materials due to temperature increase or decrease provides many opportunities for detailed characterization of the tested materials: their composition and purity, thermal stability, and kinetics of the occurring changes [3–7]. In the case of catalysts, the information about behavior of these materials at high temperatures is particularly significant. Nowadays, thermal analysis allows researchers to simulate industrial processes – the furnace of a thermobalance is treated as the reactor in which the conditions are similar to those in the real reactors.

In the case of catalysts obtained by co-precipitation [8,9], which usually contain two or more components, analysis of transformations occurring during the temperature changes is very helpful in determination of the chemical composition of these contacts. Thermogravimetric measurements are carried out in various gaseous atmospheres but the gas composition is an important parameter in determining the type of changes that occur in the sample. Thermal decomposition may occur in an atmosphere of inert gas or air, whereas a reduction of samples takes place in hydrogen [5,10]. These reactions can be used to analyze the composition of multicomponent catalytic materials. Based on the analysis of the various stages of sample mass change, which are directly connected with specific reactions or changes, both qualitative and quantitative analysis of the composition can be made. In addition, the coupling of thermal analysis with mass spectrometry enables the observation of gaseous products which evolve during the changes, which greatly facilitates the assignment of a sample mass change to a specific transformation, and thus allows the precise identification of the components of the studied materials [11–13].

This paper reports thermogravimetric measurements coupled with mass spectrometry which aim to determine the Co content in the precursors of catalyst for ammonia synthesis obtained by co-precipitation. The precursors of these catalysts consist of the oxidized forms of: the active phase (cobalt) and promoters (cerium or lanthanum). The complex composition of these materials results in major difficulties in its precise determination, especially for contacts containing cobalt and lanthanum, due to the possibility of their interaction and formation of mixed phases. A methodology for determining the Co content in these materials using two types of thermogravimetric measurements: in an inert atmosphere

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http://dx.doi.org/10.1016/j.tca.2014.03.026
0040-6031/

(TG-MS(Ar)) and in a reducing atmosphere (TG-MS(H_2)), is presented. The first allowed us to determine the content of the cobalt oxide phase, whereas the second: metallic cobalt content in the catalyst samples. The experimental results were compared with the results of ICP-OES analysis.

2. Experimental information

2.1. Preparation procedure

Preparation of the catalysts was based on the co-precipitation method described previously [8,9]. The study considered two types of catalyst systems: containing cobalt and cerium, as well as cobalt and lanthanum. The initial step was to obtain a mixture of cobalt and cerium or cobalt and lanthanum carbonates in fixed proportions by co-precipitation using K_2CO_3 as the precipitating agent. Mixtures with appropriate amounts of $Co(NO_3)_2{\cdot}6H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ or $Co(NO_3)_2{\cdot}6H_2O$ and $La(NO_3)_3{\cdot}6H_2O$ were dissolved in distilled water and warmed to approximately 90 °C. Then, a warm solution of K_2CO_3 was slowly added. The obtained participate was filtered under reduced pressure (about 0.04 MPa) and washed with cold distilled water until the pH was neutral. The material was then dried (120 °C, overnight) and calcined at 800 °C (24 h). As a result, a mixture of either Co_3O_4 and CeO_2 or Co_3O_4 and La_2O_3 was obtained. The obtained materials were marked with symbols: Co/Ce (catalyst containing cobalt and cerium) and Co/La (catalyst with cobalt and lanthanum). All compounds used during the preparation had a purity greater than 99%.

2.2. Thermogravimetric measurements

Thermogravimetric studies were performed using a Netzsch STA449C thermobalance equipped with a quadrupole mass spectrometer Netzsch QMS 403C. Samples of approximately 15 mg were used. The TG-MS(Ar) experiments were conducted by heating the samples up to 1100 °C at the constant rate of 10 °C/min in a pure (≥99.999 vol%) argon constant flow (100 ml/min). During The TG-MS(H_2) experiments the samples were heated at the constant rate of 10 °C/min in a pure (≥99.999 vol%) H_2:Ar = 1:1 mixture (100 ml/min) up to 550 °C. This temperature was maintained for 2 h. The reference crucible was empty. The mass change, temperature and selected m/z signals were monitored throughout the entire experiment. In order to avoid water physisorption all the necessary apparatus parts were kept heated to 280 °C.

2.3. Characterization studies

X-ray powder diffraction studies were carried out in order to confirm the phase composition of the obtained samples. XRPD data were collected with a Rigaku-Denki (Geigerflex) diffractometer in a Bragg–Brentano configuration using a Cu-sealed tube operating at 40 kV and 40 mA with stability of 0.01%/8 h. Measurements of each system were performed in the scattering 2Θ range of 15–100° with a 0.02° step and a counting rate 6 s/step. Diffraction profiles were obtained for both catalyst precursors and catalysts in the reduced form.

The determination of Co content in the prepared catalysts was carried out using inductively coupled plasma optical emission spectroscopy (ICP-OES). Prior to analysis samples were diluted in agua regia in an open system. ICP-OES spectrometer type iCAP 6500 DUO (Thermo Scientific) was used.

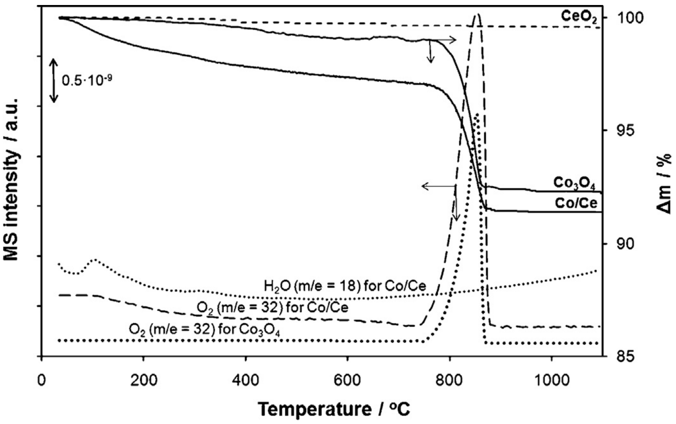

Fig. 1. TG-MS(Ar) studies of cobalt oxide, cerium oxide and the Co/Ce catalyst sample.

3. Results and discussion

3.1. Determination of the composition of the catalyst precursor containing cobalt and cerium

In order to determine the composition of the catalyst precursor containing cobalt and cerium in the oxidized form, the thermogravimetric measurements in the flow of pure argon (TG-MS(Ar)) or a mixture of argon and hydrogen in the ratio 1:1 (TG-MS(H_2)) were carried out. Each of them gave information about the content of the key catalyst component, which is cobalt. The content of the oxidized form of cobalt (Co_3O_4) was determined using TG-MS(Ar), while TG-MS(H_2) allowed us to determine the amount of metallic cobalt (active phase).

It is well known [14] that cobalt oxide Co_3O_4 is converted to CoO in the non-oxidizing atmosphere (e.g. Ar) at the temperature of about 750 °C, according to Eq. (1):

$$2Co_3O_4 = 6CoO + O_2 \quad (1)$$

This transition was observed during the blank experiment carried out for the Co_3O_4 reference sample prepared by the same procedure as the other studied systems. The results of this analysis are shown in Fig. 1. Calculations made on the basis of the mass loss (Co_3O_4 curve) connected with the oxygen emission during cobalt oxide transition confirmed that the starting material was pure Co_3O_4. In contrast to Co_3O_4, cerium oxide is stable under heating to 1100 °C in an inert atmosphere and no mass change on the TG curve was observed (see Fig. 1 – CeO_2 curve). A similar analysis, TG-MS(Ar), was carried out for the Co/Ce sample obtained by co-precipitation, which contained a mixture of Co_3O_4 and CeO_2 (see Fig. 1 – Co/Ce curve). The whole mass loss, i.e. 5.7%, resulting from the release of oxygen, was assigned to the transformation of Co_3O_4 to CoO. The MS signal of the emitted oxygen, which was recorded continuously while the sample was heated (see Fig. 1 – O_2 curve for Co/Ce), helped with the precise determination of the beginning and the end of the phase transition visible on the TG curve. On this basis the content of the Co_3O_4 phase in the sample was estimated at the level of 85.1 wt%. The remaining part was the cerium oxide, 14.9 wt%. A slight mass loss on the TG curve for Co/Ce sample was also observed at a temperature close to 100 °C, which is associated with the emission of water adsorbed on the surface of this material (see Fig. 1 – H_2O curve).

The active phase of the studied catalysts for ammonia synthesis is metallic cobalt, which forms in the catalysts as a result of the reduction carried out directly prior to activity measurements. Information about the exact content of cobalt is of great importance to conducting the reaction because results of the NH_3 synthesis