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Chromium-modified cobalt molybdenum nitrides as catalysts for ammonia synthesis

Abstract: The influence of chromium compounds on the properties of cobalt molybdenum nitrides was studied. $CoMoO_4$ obtained by precipitation from cobalt and molybdenum salts was modified by the addition of chromium(III) nitrate. A mixture of cobalt-molybdenum nitrides, Co_2Mo_3N and Co_3Mo_3N, was formed by ammonolysis of modified $CoMoO_4$. The concentration of Co_2Mo_3N decreases with increasing chromium content. The specific surface area of cobalt molybdenum nitrides consisting of 2 wt% of Cr atoms increased by 50% in comparison to pure cobalt molybdenum nitrides. The catalytic activity of obtained catalysts in ammonia synthesis process decreases with rising of chromium concentration.

Keywords: cobalt molybdenum nitride; catalyst; ammonia; chromium; promoter.

1 Introduction

Various forms of iron catalysts based on magnetite [1, 2] or wustite [3, 4] are still the most widely used in ammonia plants. The high energy consumption of the ammonia synthesis based on the iron catalysts is an incentive for the search of novel catalysts which will be effective at lower temperatures or under lower pressure.

An alternative material, ruthenium supported on carbon, is already commercialized [5] and some others materials are promising e.g. cobalt molybdenum nitrides [6], carbon supported cobalt [7, 8], Co-Ce-Ba catalysts [9] or $CoRe_4$ catalysts [10].

Theoretical studies have proven that cobalt molybdenum nitride, Co_3Mo_3N, is potentially the most active catalyst for ammonia synthesis [11]. Experiments have shown that cesium or potassium promoted cobalt molybdenum nitride is more active in the ammonia synthesis process than the industrial iron catalyst [6, 12, 13]. The admixture of alkali metals has a beneficial effect on the activity of the catalyst but at the expense of a less developed porous structure and lower thermal stability [12, 14].

One plausible way to limit the detrimental effect of alkali metals on the specific surface area is the addition of a co-promoter. This assumption is based on the similarities between the structure and behavior of the present catalysts and iron catalysts for ammonia synthesis. In case of the latter, the admixture of aluminum or calcium oxides results in the formation of a well-developed porous structure which is a base for the active catalyst. Therefore, the proper choice of a co-promoter is crucial for the best catalytic action of the catalysts considered. In view of the model devised for the surface of iron catalyst [15] the oxides of multivalent metals can play the role of structural promoters. In this paper, the admixture of chromium compounds to cobalt molybdenum nitrides is examined and their influence on the phase composition, structural properties and catalytic activity of Co-Mo-N catalysts is studied.

2 Experimental

The precursor of catalysts was precipitated from hot water solutions of cobalt(II) nitrate $Co(NO_3)_2 \cdot 6H_2O$ and ammonium heptamolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The

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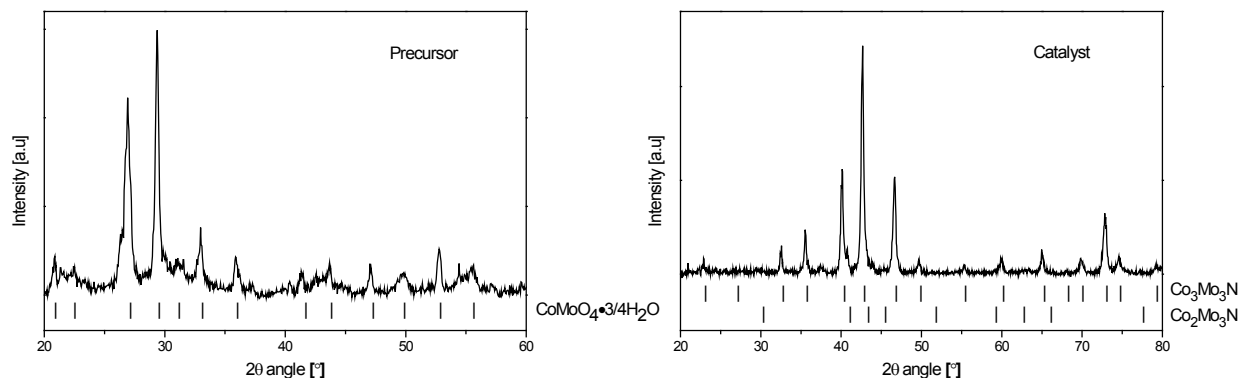
Figure 1: X-ray diffraction pattern of the precursor containing 2.0 wt% of chromium (left) and of the same sample after ammonolysis (right).

purple precipitate obtained via vacuum filtration was rinsed twice with distilled water and once with ethanol and then dried overnight at 150°C. Chromium was introduced to the dry precursor by impregnation with chromium(III) nitrate $Cr(NO_3)_3 \cdot 9H_2O$ dissolved in distilled water. The water was removed by vacuum evaporation at 70°C and samples with chromium concentration between 1 and 5 wt% were prepared. The chromium-promoted precursors were reduced in a horizontal steel reactor under ammonia flow at 700°C for 5 hours to obtain an active form of the catalysts.

The phase composition of the obtained materials was analyzed by X-ray diffraction (XRD) using a Philips X'pert MPD diffractometer with Cu K_a ($\lambda_{\alpha1}$=0,154056 nm, $\lambda_{\alpha2}$=0,154439 nm) monochromatized radiation. A full-pattern fit based on the Rietveld method was applied to calculate the weight fractions of the identified phases. Data required for initialization of Rietveld refinement was retrieved from the ICDD PDF-4+ database. The specific surface area of the catalysts was measured by a volumetric method utilizing the Brunauer–Emmett–Teller (BET) model with use of Quantachrome Quadrasorb SI-Kr/MP. Prior to measurements, the samples were degassed for 6 hours at 400°C. The activity test was performed in the test setup described in details elsewhere [14]. Samples were put in separated channels of the reactor and activated under a hydrogen-nitrogen atmosphere (N_2:H_2 = 1:3; 0.1 MPa). Activity tests were performed under 10 MPa at 400°C. The ammonia concentration in the outlet stream was measured by a Siemens ULTRAMAT 6 NDIR analyzer. After the first activity tests, the catalysts were kept under a hydrogen-nitrogen atmosphere (ambient pressure, 650°C) for 24 hours to test their thermal stability. Subsequently, the activity test was repeated.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

The phase analysis of chromium-modified precursors indicates that all materials contain only cobalt molybdate hydrate, which corresponds with the $CoMoO_4 \times 3/4\ H_2O$ structure reported elsewhere [16, 17]. Although chemical analysis proved the presence of chromium in the samples, the crystallographic phases containing chromium have not been identified. After ammonolysis, cobalt molybdate hydrate was transformed into a black product which was identified as a mixture of two crystallographic phases, both being cobalt molybdenum nitrides: Co_3Mo_3N [18] and Co_2Mo_3N [19]. No chromium-containing phases have been found in the active form of the catalysts. In Figure 1 X-ray diffraction patterns for the sample containing 2 wt% of chromium obtained before and after reduction under ammonia are presented.

Rietveld analysis was used to estimate the weight fractions of Co_3Mo_3N and Co_2Mo_3N phases in all prepared materials and the weight percentage of Co_2Mo_3N is presented in Figure 2. The sample without chromium admixture contains about 18 wt% of Co_2Mo_3N. The admixture of chromium compounds results in a loss of the Co_2Mo_3N weight fraction to about 4-5 wt% observed in the range between 2 wt% and 5 wt% of Cr in the catalyst. The presence of chromium atoms affects the stability of cobalt molybdenum nitrides seemingly leading to the formation of the catalysts with lower Co_2Mo_3N content.

The catalytic activity of non-promoted cobalt molybdenum nitrides is relatively high and comparable to the activity of industrial iron catalysts [6]. Promotion with cesium or potassium compounds makes this catalyst much more active than reference iron catalysts [6, 13] even though the specific surface area of catalysts promoted with alkali metals is lower than non-promoted ones. The main role of chromium considered in this paper is to stimulate formation of a well-developed porous structure. Therefore,
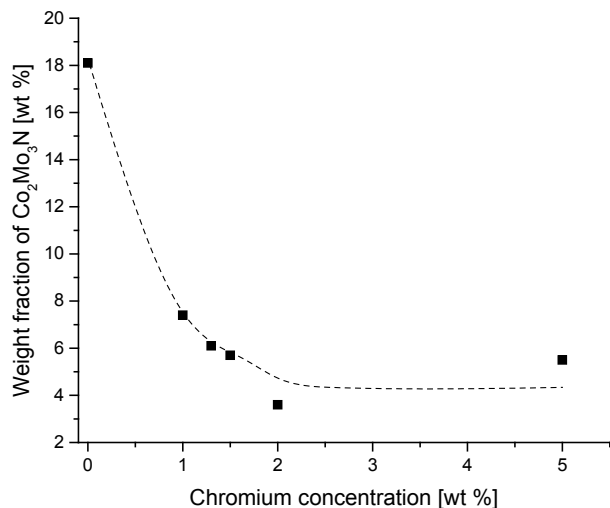
Figure 2: The weight fraction of Co_2Mo_3N phase calculated upon XRD data as a function of chromium concentration in the sample. A dashed line is for an eye-guidance only.
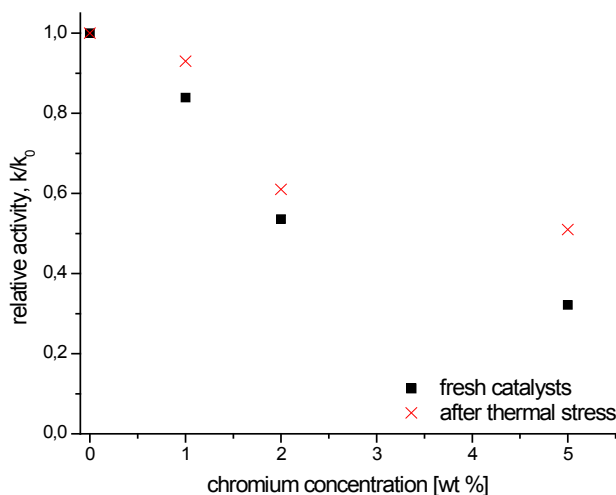

Figure 4: The activity of the catalysts as a function of chromium concentration in the sample.
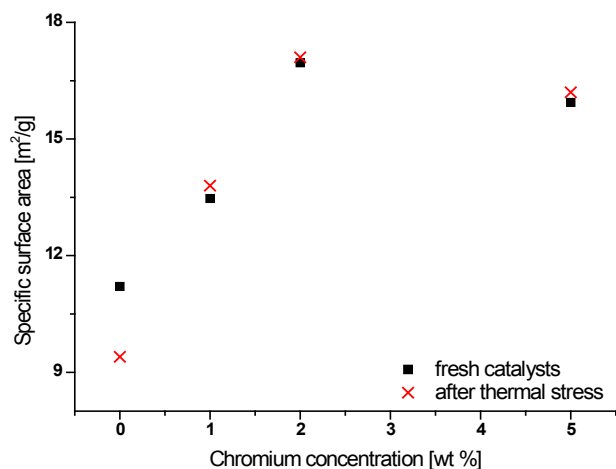

Figure 3: The specific surface area of the catalysts as a function of chromium concentration in the sample.

the beneficial influence of that promoter on the formation of the high surface area of cobalt molybdenum nitrides is a key factor of the present study. After ammonolysis, the surface area of each catalyst was measured by volumetric methods and the results are shown in Figure 3. The specific surface area of the non-promoted catalyst is about 11 m^2/g. The structure of chromium-promoted catalysts is better developed and their specific surface area is increased to about 17 m^2/g for the sample promoted with 2 wt% of Cr. In comparison to non-promoted catalyst, the surface area of the latter catalyst is about 50 % higher.

Long run of a catalytic reaction usually has a detrimental effect on the porous structure of the catalyst.

Regarding the metallic catalysts, it is usually due to sintering of the crystallites and leads to the decrease of the specific surface area. This process results in a limited lifetime and thermal stability of the catalyst. Therefore, to simulate thermal stress and aging the Co-Mo-N catalysts were heated up to 650°C for 12 hours after the activity test. The specific surface area was measured again after repeated activity test and results are shown in Figure 3. The specific surface area of the non-promoted Co-Mo-N catalyst decreased to about 9.5 m^2/g. A similar effect has been reported previously for Co-Mo-N catalysts promoted with cesium [14] and was ascribed to the sintering process. The specific surface area remains stable for the catalysts promoted with chromium which indicates that the admixture of chromium compounds to Co-Mo-N catalysts not only promotes the development of the porous structure but also increases thermal stability.

The activity of the present catalysts was measured at 400°C during the ammonia synthesis reaction carried out under the pressure of 10 MPa. The relative activity, k/k_0, i.e. the activity of a specific catalyst related to the activity of the non-promoted Co-Mo-N catalyst is shown in Figure 4. Despite the significant increase of the specific surface area for the catalysts promoted with chromium, their catalytic activity is inferior in comparison to the non-promoted Co-Mo-N catalyst. Although the surface area of the catalysts containing 2.0 wt% of chromium increased by 50% the catalytic activity of that catalyst is about 50% lower than the activity of the reference catalyst and catalysts with higher chromium concentration (5 wt%) are even less active. These observations imply that the

application of chromium compounds as the only promoter for Co-Mo-N catalysts is inefficient. However, the relative activity of chromium-modified catalysts is higher after the thermal stability test (Figure 4). In comparison to the pure cobalt molybdenum nitrides, the promoted catalysts are more stable under prolonged thermal stress.

The effect of chromium regarded herein is similar to the way the promoters like aluminum or calcium influence the properties of iron catalysts for ammonia synthesis. Their presence results in an increased thermal stability and extended lifespan of iron catalyst [1]. However, if they are used as an exclusive promoter it makes the iron catalyst virtually inactive in comparison to the iron catalyst promoted with alkali metals [20]. This effect was elucidated assuming the formation of a homogenous structure on the metal surface, in which oxygen atoms are directly bound to the iron substrate, while promoter atoms are located on the top-most layer [15]. In this layer, the relation between the number of oxygen and promoter atoms is strictly established and dependent on promoter valence state. In contrast to alkali metals which are bound to only one oxygen atom, elements like calcium or aluminum require two or three oxygen atoms in the vicinity, and as a result the whole metal surface is covered with oxygen atoms and there are no free adsorption sites. On the other hand, the presence of oxygen atoms has a beneficial effect on the formation of the surface area of the catalyst. The clean metal surface due to a high surface energy tends to sinter but the formation of metal-oxygen bonds partially balances out this trend.

Chromium nitrate added to the precursor of Co-Mo-N catalysts is transformed into chromium oxide during ammonolysis of catalysts' precursor. The presence of chromium oxides on the surface of the precursor was earlier proven by X-ray photoelectron spectroscopy (XPS) studies [17]. Since the formation of the crystallographic phases containing chromium atoms was not proven by XRD analysis it is assumed that this element mostly occupies the catalysts' surface. The effects of chromium admixture resemble the influence of calcium or aluminum in iron catalysts for ammonia synthesis. It is suggested that the main role of chromium oxide in Co-Mo-N catalysts is to change the surface energy of the system promoting the formation of a well-developed porous structure and limiting the tendency to sintering. Simultaneously the abundance of oxygen atoms, which are required to complement chromium presence on the surface, results in the reduction of the number of free adsorption sites and considerably limits the activity of the catalysts.

The main goal of the present study was achieved since chromium compounds indeed promote the development of the porous structure of Co-Mo-N catalysts. However, the materials studied herein are intended to work as a catalyst for ammonia synthesis and the inferior catalytic activity is a serious disadvantage. In view of the surface model referred to above [15], a synergetic effect of the multivalent element and alkali metal may result in the formation of a highly active catalyst with a decent surface area.

4 Conclusions

The admixture of chromium compounds to the catalysts based on cobalt molybdenum nitrides influences the structural and catalytic properties of these materials. With increasing chromium concentration the weight fraction of the Co_2Mo_3N phase decreases. Although the overall catalytic activity of chromium-promoted catalysts is lower than pure cobalt molybdenum nitrides, their structural parameters are enhanced. In the promoted catalysts the specific surface area is increased by about 50%. Furthermore, the thermal stability of the promoted catalysts is superior to non-promoted material.

Conflict of interest: Authors declare no conflict of interest.

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