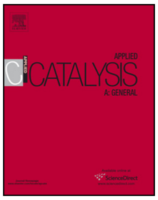
Applied Catalysis A: General 514 (2016) 114–125

Contents lists available at ScienceDirect

Applied Catalysis A: General

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



Effect of nitric oxide on the formation of cobalt–aluminum oxide structure from layered double hydroxide and its further transformation during reductive activation

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ARTICLE INFO

Article history:
Received 23 October 2015
Received in revised form 9 January 2016
Accepted 11 January 2016
Available online 14 January 2016

Keywords:
Cobalt
Layered double hydroxide
Nitric oxide
Fischer–Tropsch synthesis

ABSTRACT

The presence of nitric oxide NO in the gas phase was shown to decrease the decomposition rate of the hydrotalcite-like Co–Al LDH phase in the catalysts prepared by co-precipitation or deposition on Al_2O_3 under the condition of urea hydrolysis. The decrease in LDH decomposition rate is related to the formation of a more crystallized phase of the spinel-like Co–Al oxide due to the ability of nitric oxide to transfer oxygen in consecutive reactions of the oxidation to NO_2 and reduction to NO. The difference in the coherent scattering domain size of the catalyst samples precalcined in the presence of NO or in a pure inert gas is retained at all consecutive steps of the reductive heat treatment in hydrogen: after the formation of a cubic phase of the (Co, Al)O oxide and its reduction to metallic cobalt. The observed changes in the degree of crystallinity and dispersion of the active metal exert only a slight effect or even no effect on the activity of the catalysts in Fischer–Tropsch synthesis. Noteworthy are a lower selectivity for methane and a greater fraction of olefins in the products obtained on the catalysts precalcined in a flow of inert gas containing 3% NO.

1. Introduction

Cobalt-containing catalysts, in particular the cobalt–aluminum ones, have attracted considerable attention over several decades primarily due to their activity in Fischer–Tropsch synthesis (FTS). The active component of cobalt-containing FTS catalysts is represented by metallic cobalt nanoparticles. The optimal size of metallic cobalt particles providing maximum activity and selectivity of a catalyst in the process ranges from 5 to 10 nm [1–5]. In this connection, many researchers are searching for the methods of stabilizing such cobalt particles on the oxide supports. The search is hindered by the ability of cobalt cations to form difficultly reducible mixed oxides with aluminum and silicon cations. For example, Co^{2+} cations in cobalt metasilicate CîSiO$_3$ can be reduced in flowing hydrogen only at 900–920 °C, in cobalt orthosilicate Co_2SiO_4 at 970–980 °C [6,7], and Co^{2+} cations in the tetrahedral positions of stoichiometric cobalt aluminate $CoAl_2O_4$ are reduced at temperatures above 950 °C [8]. At the same time, although the presence of a small amount of impurity Al^{3+} cations in cobalt oxide decreases the fraction of cobalt reduced to a metallic state, it may also facilitate the stabilization of disperse metal particles due to their decoration with the oxide Al^{3+}-containing clusters [9]. In this connection, the problem is not to completely prevent the formation of mixed cobalt and aluminum species but rather to diminish the dissolution of cobalt cations in the support oxide, which leads to the formation of a mixed oxide enriched with aluminum.

The formation of mixed cobalt–aluminum oxide can occur not only during the deposition/precipitation of cobalt species from a solution but also at the subsequent calcination of the catalyst precursor. The formation of mixed cobalt–aluminum oxide upon calcination of Co–Al hydroxocarbonates is accompanied by the oxidation of a substantial part of Co^{2+} cations to Co^{3+}, which proceeds even if calcination is performed in a flow of inert gas [10,11]. In this connection, regulation of the oxidation state of cobalt cations during calcination of the catalyst precursor can be an efficient way for controlling the phase composition of oxide precursor, the degree of cobalt reduction to metallic state, and the dispersion of active component after catalyst reduction.

It was shown in [12–15] that the presence of nitric oxide, NO, strongly affects the decomposition of cobalt nitrate and hence the size of Co_3O_4 cobalt oxide crystallites and the degree of their inter-

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http://dx.doi.org/10.1016/j.apcata.2016.01.012

action with the support. As a result, the processes of reductive activation of the catalysts synthesized by impregnation of various cobalt nitrate supports as well as the particle size of active metal in the reduced catalyst are sensitive to the presence of nitric oxide NO at the step of preliminary calcination of the catalyst precursor. The study [14] showed by means of in-situ XAS that nitric oxide changes the mechanism of Co nitrate decomposition. The interaction of the Co nitrate and nitric oxide occurs at below 100 °C and gives the intermediate Co hydroxynitrate phase, which afterwards decomposes progressively starting from 110 °C.

According to [16], the presence of NO moderates the decomposition of Ni nitrate supported on the ordered mesoporous silica SBA-15; it was supposed that NO serves as a mild reducing agent that scavenges oxygen. Thus, thermal decomposition makes it possible to obtain a smaller particle size of the oxide. The next study of the same authors [12] demonstrated a similar effect of NO on thermal decomposition of Co nitrate supported on SiO_2. A smaller particle size of the oxide and hence of metallic cobalt produced by its reduction led to a high activity of the catalysts in Fischer–Tropsch synthesis irrespective of a considerable decrease in the fraction of reducible cobalt.

A detailed study of NO effect on the evolution of supported catalysts Co/SiO_2 and Co/Al_2O_3 [17] verified the increase in the interaction degree of cobalt oxide with the support oxide in the presence of NO, which gave a broader reduction profile (a slower reduction) of the CoO cobalt oxide phase and resulted in the formation of smaller metal particles as compared to the catalysts calcined in air flow. In the present work, in situ STA-MS and SR-XRD were used to reveal the effect exerted by the presence of NO in the calcination medium on the formation of cobalt oxide from Co–Al hydrotalcites of various anionic composition, which were obtained by precipitation of cobalt cations on aluminum oxides or by co-precipitation of cobalt and aluminum cations. A particular emphasis was made on the subsequent reductive activation of cobalt as well as on its adsorption and catalytic properties in the reduced sate.

2. Experimental

2.1. Sample preparation

The catalysts were prepared by thermal treatment in a flow of inert gas or in an inert gas containing 3 vol.% NO of the precursor species represented by aluminum oxide and Co–Al hydroxocompounds, which were synthesized by the following methods: (1) deposition by precipitation of cobalt cations on aluminum oxide under the conditions of urea hydrolysis, (2) co-precipitation of cobalt and aluminum cations from a nitrate solution with a soda solution.

Solutions of cobalt nitrate and aluminum oxide γ-Al_2O_3 or δ-Al_2O_3 were employed. The alumina modifications were obtained by thermal treatment of aluminum hydroxide A-64 (JSC Angarsk Catalysts and Organic Synthesis Plant) in air for 2 h at 700 and 910 °C, respectively. The formation of γ-Al_2O_3 or δ-Al_2O_3 oxide was confirmed by X-ray diffraction data. Specific surface area of the supports, as determined by the BET method, was equal to 165 m^2/g for γ-Al_2O_3 and 127 m^2/g for δ-Al_2O_3. The catalysts were prepared using supports with the grain size 0.25–0.50 mm.

2.1.1. Deposition by precipitation of cobalt cations under the conditions of urea hydrolysis

From cobalt nitrate solutions on γ- or δ-Al_2O_3 (deposition by precipitation with urea, DPU) [18] was carried out using solution with initial cobalt nitrate concentration of 0.075 M and urea concentration of 0.3 M (samples Co/GAO and Co/DAO) or $[Co^{2+}] = 0.166$ M and $[(NH_2)_2CO] = 0.5$ M (samples Co/GAO-II and Co/DAO-II). Aluminum oxide was introduced to reactor according to atomic ratio Co:Al = 0.29 for Co/GAO and Co/DAO, and Co:Al = 0.71 for Co/GAO-II and Co/DAO-II. The specified amounts of alumina and urea were added to a solution of cobalt nitrate under stirring, the mixture was heated to 90 °C and held under these conditions at a constant volume of the suspension for 23 h. Upon completion of the synthesis, the precipitate was separated from the mother liquor, washed with distilled water, and dried under an IR lamp at ca. 50 °C for 10–15 h. The resulting composition of the catalyst precursors are reported and discussed hereinafter (see Table 1 in Section 3.1).

2.1.2. Cobalt and aluminum cations were co-precipitated

With a Na_2CO_3 solution from 10% solutions of cobalt and aluminum nitrates with atomic ratio Co:Al = 1. The samples were precipitated at pH 7.3 ± 0.2 and a temperature of 65–70 °C. The resulting precipitate was washed with distilled water to decrease sodium content to 0.01 wt.%, and then dried under an IR lamp at ca. 50 °C for 10–15 h.

2.2. In situ XRD and SR-XRD

The XRD study was carried out on an X'TRA (Thermo Electron Corporation, Switzerland) diffractometer using CuKα radiation with a reflected beam monochromator. In situ XRD analysis was made with the use of synchrotron radiation (SR) at the Siberian Synchrotron and Terahertz Radiation Centre. The study was performed with a high-precision X-ray diffractometer mounted on the extraction channel of the VEPP-3 electron storage ring (beamline No. 6). The high-precision X-ray diffractometer comprised a monochromator, a collimation system, and a position-sensitive detector. The single reflection Ge(1 1 1) crystal monochromator deflected a monochromatic beam upward by ca. 30° in the vertical plane, thus providing the degree of monochromatization $\lambda\Delta/\lambda \sim (2 \div 3)\cdot 10^{-4}$. The operating radiation wavelength was $\lambda = 1.731$ Å. The diffractometer was equipped with an XRK-900 high-temperature reactor chamber (Anton Paar, Austria). The sample was loaded in an open holder, which allowed the reaction mixture to pass through the bulk of the sample, and placed in the reactor chamber. The chamber was arranged on the diffractometer so that the monochromatic beam of synchrotron radiation fell on the sample surface at an angle of ca. 15°. X-ray diffraction patterns of the catalyst were recorded in an angle range of 28–60 °C at a storage time of 1 min. The temperature ramp rate during thermal treatment of the catalyst in an inert gas Ne or in an inert gas Ar containing 3 vol.% of nitric oxide (Ar + NO) was 3–5°/min; and upon reduction in hydrogen, 2°/min. Gas flow rates were maintained at 60–90 mL/min. The sample was heated to 250 °C in an inert atmosphere, held at this temperature for 1 h, then cooled to 30 °C, and reduced by heating in hydrogen to 700 °C.

2.3. Thermal analysis studies

Thermal analysis was carried out on a Netzsch STA-449 thermograph in a 40 mL/min argon flow at a heating rate of 10 °C/min. The released gases were analyzed on a Stanford Research System UGA-200 mass spectrometer. The content of NO_x oxides generated by decomposition of nitrate anion was estimated from the mass spectrometer signal at 30 a.m.u. (NO), the content of CO_2 formed by decomposition of carbonate anion—at 44 a.m.u. (CO_2), and the amount of released water (dehydration and dehydroxylation processes)—from the signal at 18 a.m.u.

Thermal reduction curves for oxide catalysts were recorded using a gas mixture of hydrogen in argon (50% H_2 or 7.5% H_2). Gas