



Optimization of the preparation procedure of cobalt modified silicas as catalysts in methanol decomposition

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ABSTRACT

Novel modified "chemisorption–hydrolysis" technique and conventional "incipient wetness impregnation" procedure were compared for loading of cobalt species on mesoporous silica supports. Effect of cobalt amount, pH of the precursor solution, duration of the "chemisorption" procedure and pretreatment medium, as well as topological characteristics of the mesoporous silica support were investigated. The state of the loaded cobalt species was studied by XRD, FTIR, FTIR of adsorbed pyridine, UV–vis, XPS and TPR methods and their catalytic properties were elucidated in methanol decomposition to hydrogen and carbon monoxide. The "incipient wetness impregnation" technique facilitates the formation of finely dispersed spinel cobalt oxide species. Their catalytic activity could be significantly increased by hydrogen pretreatment, but the effect is more pronounced when mesoporous silica with ordered pseudo 1D pore structure (SBA-15) is used as a support. The modified "chemisorption–hydrolysis" procedure facilitates the formation of strongly interacting with the support cobalt species, which are stable under the reduction conditions. Their properties could be regulated during the modification procedure, by varying the cobalt content and pH of the impregnated solution as well as by the duration of the "chemisorption" procedure.

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1. Introduction

Recently, cobalt based materials opened new prospects to the fabrication of novel electronic and magnetic devices and for the development of effective catalysts for some important industrial processes, such as alkene epoxidation [1], reforming of methane [2] or ethanol [3], ethane hydroformylation [4], Fischer–Tropsch synthesis (FTS) [5–7], hydrogenation of aromatics [8] or aldehydes [9], NO_x removal [10]. They have been considered as a suitable alternative to the high cost noble metal based catalysts for the elimination of toxic compounds from the automobile exhaust and industrial emissions via combustion [11–15]. It is known that the amount of cobalt loading, its dispersion, oxidative state, phase composition and reducibility could strongly affect the catalytic process. That is why the synthesis of efficient catalysts with desired properties is a problem strongly related to the control of the overall state of cobalt

species in them. Up to now, the application of mesoporous silicas as a support of stable metal oxide nanoparticles has been widely discussed in view of the specific features of these materials evolving from their high specific surface area, pore volume and tunable pore size, shape and connectivity [16–20]. Ordered mesoporous silicas with uniform pores and different pore structures, such as MCM-41 [21–29], MCM-48 [23,27,30], SBA-15 [1,14,21,22,29–35], HMS [33], KIT-6 and KIT-5 [14] have been studied as a host matrix of cobalt oxide particles as well. Up to now, the scientists focused their attention to clarify the influence of the metal particle size [22,31,36–40] and support pore diameter [6,22,30,29,41–47] on the catalytic behavior of these materials, but to the best of our knowledge, the data on the relation between them are rather scarce. It was established [36] that the size of Co_{fcc} nanoparticles decreases when the support pore size decreases, whereas the size of Co_{hcp} ones remains constant. In our previous study we established the facilitated effect of the formation of well-crystallized spinel Co₃O₄ nanoparticles on their catalytic activity in total oxidation of ethyl acetate [14]. It was reported that their formation is promoted when ordered mesoporous silicas with larger mesopores are used as a host matrix of

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cobalt species. Khodakov et al. [22] found that Co/SBA-15 catalysts are more active and selective toward C_{5+} hydrocarbons formation during the FTS process than Co/MCM-41, which was ascribed to the higher reducibility of larger Co_3O_4 particles, formed in the larger pores of the SBA-15 support. However, Wang et al. [48] observed a low FTS activity and high methane selectivity for highly dispersed Co/SBA-15 catalysts, prepared from cobalt acetate and cobalt acetylacetonate precursors. The obtained data strongly suggested that the preparation method used, in particular its efficiency to control the particles size and their interaction with the support, is a powerful approach for the regulation of the catalysts design.

The aim of the present paper is to compare the state and catalytic behavior of cobalt species loaded on mesoporous silicas with respect to the differences in the preparation procedure and textural characteristics of the mesoporous silica support. A conventional incipient wetness impregnation technique and a modified “chemisorption–hydrolysis” (CH) procedure [49] are applied for the samples modification. Since the good results obtained through the employment of CH methodology for gaining highly dispersed copper oxide on SiO_2 catalyst using $[Cu(NH_3)_4]^{2+}$ as chemisorbing species, we focused our attention to use the same methodology for the preparation of Co/ SiO_2 materials. In order to stabilize cobalt ions in aqueous solution at higher pH, we individuated $[Co(NH_3)_6]^{3+}$ as a good candidate for the synthesis, preventing the precipitation of Co in alkaline conditions. $[Co(NH_3)_6]Cl_3$ was already reported for the deposition of Co on silica and carbon through strong electrostatic adsorption [50,51]. Alternatively, in this study in order to avoid the presence of chloride ions, we started from Co(II) nitrate and through oxidation we obtained the hexaammonia Co(III) precursor. We used this procedure in order to have a stable and high soluble Co precursor in alkaline conditions [50]. In the present study, high surface area mesoporous silicas with ordered porous structure (SBA-15, KIT-6) and non-ordered mesoporous silica (SiO_2) were used as a support of cobalt species. The catalytic behavior of the samples was tested in methanol decomposition to hydrogen and CO due to the increasing interest in this reaction as a source of alternative clean and efficient fuel [52 and references therein].

2. Experimental

2.1. Samples preparation

Ordered mesoporous SBA-15 and KIT-6 silicas with pore volume of $1.1\text{ cm}^3/\text{g}$, average pore size diameter of 7.8 nm and BET surface area of 924 and $829\text{ m}^2/\text{g}$, were synthesized according to the procedures described in Refs. [53,54] respectively. A commercial mesoporous material (SiO_2 , DAVISIL from Grace Davison) with BET surface area of $529\text{ m}^2/\text{g}$; pore volume $0.88\text{ cm}^3/\text{g}$ and average pore size diameter 5.4 nm was also used as a cobalt support. Cobalt oxide was supported by incipient wetness impregnation (WI) of the supports with aqueous solution of cobalt nitrate, followed by drying in ambient atmosphere overnight and its further decomposition in air at 773 K for 2 h. A modified “chemisorption–hydrolysis” procedure was also applied for SiO_2 modification. The needed amount of $Co(NO_3)_2 \cdot 6H_2O$ was dissolved into a water solution containing NH_4NO_3 (mol NH_4NO_3 /mol Co = 10/1) under stirring. The solution was cooled at 273 K and slowly a 30% solution of H_2O_2 and NH_4OH were added. Finally, the temperature was increased to 333 K and after 2.5 h the solution was cooled down to room temperature and the pH was adjusted to 9 or 10 with 28% solution of NH_4OH , before adding the support (SiO_2). The silica suspension was kept under stirring for 0.5 or 24 h and then it was diluted with water at 273 K and filtered. The solid was washed with water, dried overnight at 373 K and calcined in air at 773 K for 1 h.

The samples were denoted as $Co/S.a(m)$, where S was a type of silica support, a was the type of the preparation procedure and m was the Co loading (wt%). Additionally, it was denoted whether the samples were pre-treated with hydrogen (red) or used in the catalytic test (cat).

2.2. Methods of investigation

Cobalt content in the samples was determined by atomic absorption spectroscopy on Atomic Absorption Spectrometer 3100 – PerkinElmer; flame: acetylene/air. Powder X-ray diffraction patterns were collected within the range from 5.3° to 80° 2θ with a constant step 0.02° 2θ on Bruker D8 Advance diffractometer with $Cu\ K_\alpha$ radiation and LynxEye detector. Low-angle part of the patterns was collected from 0.3° to 8° 2θ using the knife-edge anti-scatter screen attachment of the primary beam. Phase identification was performed with the Diffractionplus EVA using ICDD-PDF2 Database. The IR spectra (KBr pellets) were recorded on a Bruker Vector 22 FTIR spectrometer at a resolution of $1\text{--}2\text{ cm}^{-1}$, accumulating 64–128 scans. The UV–vis spectra were recorded on the powder samples using a Jasco V-650 UV–vis spectrophotometer equipped with a diffuse reflectance unit. The analysis was performed in static condition on a sample disk (10 mg) placed inside a measurement cells that allowed evacuation and pretreatment in temperature under vacuum and controlled atmosphere. The FTIR studies of pyridine adsorption were carried out with a BioRad FTS40 spectrophotometer equipped with mid-IR DTGS detector. The measurements were performed after activation of the samples at 773 K in air for 20 min followed by evacuation for 40 min and eventual reduction in hydrogen at the same temperature for 40 min. The absorption of pyridine was performed at room temperature and all spectra were recorded at room temperature after pyridine desorption at selected temperatures. The XPS analyses were performed on a SSX 100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized micro focused Al X-ray source (powered at 20 mA and 10 kV). The samples powder pressed in small stainless steel troughs of 4 mm diameter were placed on an aluminum conductive carousel. The pressure in the analysis chamber was around 10^{-6} Pa. The angle between the surface normal and the axis of the analyzer lens was 55° . The analyzed area was approximately 1.4 mm^2 and the pass energy was set at 150 eV. In these conditions, the full width at half maximum (FWHM) of the Au $4f_{7/2}$ peak of a clean gold standard sample was about 1.6 eV. A flood gun set at 8 eV and a Ni grid placed 3 mm above the sample surface were used for charge stabilization. Data treatment was performed with the Casa XPS program (Casa Software Ltd., UK), some spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after subtraction of a non linear baseline. Molar fractions were calculated using peak areas normalized on the basis of acquisition parameters and sensitivity factors provided by the manufacturer. The TPR/TG (temperature-programmed reduction/thermogravimetric) analyses were performed in a Setaram TG92 instrument. Typically, 40 mg of the sample were placed in a microbalance crucible and heated in a flow of 50 vol.% H_2 in Ar ($100\text{ cm}^3\text{ min}^{-1}$) up to 773 K at 5 K min^{-1} and a final hold-up of 1 h. The weight loss during the reduction was calculated on the base of TPR-TG curves and the values were normalized to one and the same catalyst weight (40 mg).

2.3. Catalytic experiments

Methanol conversion was carried out in a fixed bed flow reactor (0.055 g of catalyst, three times diluted with grounded glass), argon being used as a carrier gas (50 ml min^{-1}). The methanol partial pressure was 1.57 kPa. The catalysts were tested under

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