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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.

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 Co_3O_4 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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