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

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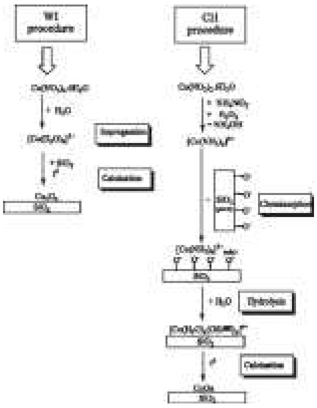
Abstract

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 pre-treatment 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.

Graphical abstract



Highlight

► Novel chemisorption–hydrolysis method for loading of cobalt on mesoporous silicas. ► Wetness impregnation facilitates formation of finely dispersed Co_3O_4 particles. ► Chemisorption–hydrolysis produces strongly interacted with the support species. ► Successful control of cobalt phase composition by varying chemisorption procedure. ► Under reduction medium pore topology of silica strongly affects catalytic activity.

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], [6], [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], [12], [13], [14], [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], [17], [18], [19], [20]. Ordered mesoporous silicas with uniform pores and different pore structures, such as MCM-41 [21], [22], [23], [24], [25], [26], [27], [28], [29], MCM-48 [23], [27], [30], SBA-15 [1], [14], [21], [22], [29], [30], [31], [32], [33], [34], [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], [37], [38], [39], [40] and support pore diameter [6], [22], [30], [29], [41], [42], [43], [44], [45], [46], [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 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 hexaamonia 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].

Section snippets

Samples preparation

Ordered mesoporous SBA-15 and KIT-6 silicas with pore volume of 1.1 cm^3/g, average pore size diameter of 7.8 nm and BET surface area of 924 and 829 m^2/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 m^2/g; pore volume 0.88 cm^3/g and average pore size diameter 5.4 nm was also used as a cobalt support. Cobalt oxide was supported by incipient wetness impregnation

X-Ray diffraction measurements

In Table 1 are summarized the data for the samples composition after the modification. It could be deduced that the prolonging of the time of the “chemisorption” step and the increase of pH of the impregnation solution during the CH procedure facilitate the preparation of samples with higher cobalt content as already reported when $Co(NH_3)_6^{3+}$ was electrostatically adsorbed on silica [50], [51]. The XRD patterns of the modified by WI method materials (Fig. 1a) represent well-defined reflections

Discussion

The modification procedure is a powerful tool to optimize the state of supported cobalt species on silica and to control their reduction and catalytic properties. Several factors, such as nature of the precursor, duration of the impregnation procedure, temperature, pH and concentration of the precursor solution could significantly affect the type of the interaction of cobalt precursor with the silica support. The further decomposition of the precursor to different cobalt species strongly

Conclusions

The “wetness impregnation” of porous silicas with cobalt nitrate precursor provides the formation of well-crystallized Co_3O_4 nanoparticles, which are in weak interaction with the support. The effect of pore topology of the support on the catalytic behavior is more pronounced after the catalysts activation in hydrogen. The restricted diffusion of the cobalt species along the pseudo 1D channel structure of SBA-15 over the 3D structure of KIT-6 preserves higher dispersion of the loaded cobalt

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References (79)

- H. Cui *et al.*
  Appl. Catal. B: Environ.
  (2010)
- E. Ruckenstein *et al.*
  Appl. Catal. A: Gen.
  (2000)
- A. Karim *et al.*
  Appl. Catal. B: Environ.
  (2010)
- K. Okabe *et al.*
  Catal. Today
  (2004)
- S.W. Ho *et al.*
  J. Catal.
  (1992)
- M. Labaki *et al.*
  Appl. Catal. B: Environ.
  (2003)
- F. Grillo *et al.*
  Appl. Catal. B: Environ.
  (2004)
- T. Tsoncheva *et al.*
  Appl. Catal. B: Environ.
  (2009)

- T. Garcia *et al.*
  Appl. Catal. A: Gen.
  (2010)
- A. Taguchi *et al.*
  Microporous Mesoporous Mater.
  (2005)
- T. Tsoncheva *et al.*
  Microporous Mesoporous Mater.
  (2006)
- R. Köhn *et al.*
  Microporous Mesoporous Mater.
  (2003)
- T. Tsoncheva *et al.*
  J. Mol. Catal. A: Chem.
  (2006)
- A.Y. Khodakov *et al.*
  J. Catal.
  (2002)
- A. Jentys *et al.*
  Catal. Today
  (1998)
- J. Panpranot *et al.*
  Catal. Today
  (2002)
- J. Panpranot *et al.*
  J. Catal.
  (2002)
- S. Suvanto *et al.*
  J. Mol. Catal. A: Chem.
  (2000)
- Y. Ohtsuka *et al.*
  Catal. Today
  (2004)
- H. Li *et al.*
  J. Mol. Catal. A: Chem.
  (2006)
- A. Martínez *et al.*
  J. Catal.
  (2003)

- A.Y. Khodakov *et al.*
  Microporous Mesoporous Mater.
  (2005)
- D. Yin *et al.*
  Microporous Mesoporous Mater.
  (2001)
- G. Laugel *et al.*
  C. R. Chimie
  (2009)
- G. Prieto *et al.*
  Appl. Catal. A: Gen.
  (2009)
- I.T. Ghampson *et al.*
  Appl. Catal. A: Gen.
  (2010)
- E. Lira *et al.*
  J. Mol. Catal. A: Chem.
  (2008)
- O. Borg *et al.*
  J. Catal.
  (2008)
- A. Khodakov
  Catal. Today
  (2009)
- J. Hong *et al.*
  Catal. Today
  (2009)
- W. Chu *et al.*
  J. Catal.
  (2007)
- D. Song *et al.*
  J. Mol. Catal. A: Chem.
  (2006)
- A.M. Saib *et al.*
  Catal. Today
  (2002)
- O. Gonzalez *et al.*
  Catal. Today
  (2009)

- Y. Wang *et al.*
  Catal. Today
  (2001)
- F. Boccuzzi *et al.*
  J. Catal.
  (1999)
- L. Jiao *et al.*
  Catal. J.
  (2008)
- G. Marbán *et al.*
  Appl. Catal. B: Environ.
  (2010)
- J. Gallardo *et al.*
  J. Non-Cryst. Solids
  (2002)

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