

REPARATION AND CHARACTERIZATION OF MESOPOROUS SILICATES FUNCTIONALIZED BY COBALT SALT SOLUTION FOR THE DECOMPOSITION OF VOLATILE ORGANIC COMPOUNDS

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ABSTRACT

Among volatile organic compounds (VOCs), toluene is one of the targeted components, which is produced from petrochemical industry. The transition metal-containing mesoporous silicate materials are appropriate candidates for VOC oxidation. In this contribution we present the effect of the post-synthesis modification of mesoporous silicate KIL-2 with different cobalt salts via incipient wetness impregnation. Cobalt oxide species of different nature (Co_3O_4 , Co^{2+} and Co-silicate like species) are formed as a result of different interactions with the support KIL-2, depending on the nature of the salt precursor. These species possess diverse reducibility and dispersion. Functionalized Co-containing samples were characterized by X-ray powder diffraction (XRD), N_2 physisorption, scanning electron microscopy (SEM), temperature-programmed reduction (TPR), diffuse reflectance UV-Vis and FT-IR spectroscopy.

Keywords: cobalt, post-synthesis functionalization, mesoporous silicates, toluene oxidation, VOC decomposition.

INTRODUCTION

Volatile organic compounds are the main class of air pollutants, emitted from various industrial processes and their release into the atmosphere can cause serious environmental problems. The decomposition of VOCs is essential for the control of air quality and for the protection of the environment. A catalytic total oxidation has been considered as the most appropriate method for VOCs removal. Recently, many efforts have been made to design low-cost catalysts of high activity and selectivity for VOCs elimination [1, 2]. For example, transition metal oxides deposited on mesoporous silicate support are good candidates. The precursor used for the functionalization of the mesoporous support materials influences the type and distribution of the deposited metal oxide species and their catalytic behavior in the total oxidation of VOCs.

Cobalt supported catalysts are highly efficient in some important processes, such as the Fischer-Tropsch synthesis, NO_x removal, partial oxidation of olefins and hydrodesulfurization. They are also considered as a suitable alternative to the high cost noble metal based catalysts for the toxic compounds elimination from the exhausted automobile and industrial emissions via combustion. Efforts to improve the catalytic behaviour are focused on the impregnation of cobalt on various supports, such as silica, alumina, titanium oxide, magnesia and zeolites [3].

The present work reports on the investigation regarding the preparation and characterization of Co-containing mesoporous KIL-2 silicates. The effect of the impregnation

by different cobalt salts on the formation of cobalt oxides of different nature, reducibility and dispersion on the silicate support were studied.

EXPERIMENTAL

The mesoporous disordered silicate KIL-2 [4] was prepared by a two-step synthesis using the reactants in a 1 TEOS : 0,5 TEA : 0,1 TEAOH : 11 H₂O molar ratio. In the first step tetraorthosilicate (TEOS 98 %, Acros) and triethanolamine (TEA 99 %, Fluka) were stirred for 30 minutes. Next, demineralized water was added to the above mixture, followed by the addition of tetraethylammonium hydroxide (TEAOH 20 %, Acros). The solution was mixed with a magnetic stirrer to obtain a homogeneous gel. The final gel was aged overnight at room temperature and then dried in an oven at 50 °C for 24 h. In the second step the gel was solvothermally treated in ethanol in a Teflon-lined stainless autoclave at 150 °C for 48 h. The template was removed by calcination at 500 °C for 10 h under air flow.

Cobalt was supported onto KIL-2 by incipient wetness impregnation with solutions of different cobalt(II) salts: cobalt(II) acetyl acetonate, cobalt(II) nitrate and cobalt(II) acetate, designated as Co(AcAc), Co(N) and Co(Ac), respectively. The Co loading was about 6 wt. %. The obtained samples were then calcined for 2 h in air at 500 °C.

RESULTS AND DISCUSSION

Comparison of SEM images of KIL-2 (Fig. 1) and Co(Ac)KIL-2 (Fig. 2) samples do not show any difference in morphology, while the SEM images of Co(AcAc)KIL-2 (Fig. 3) and Co(N)KIL-2 (Fig. 4) show the presence of Co₃O₄ nanoparticles.

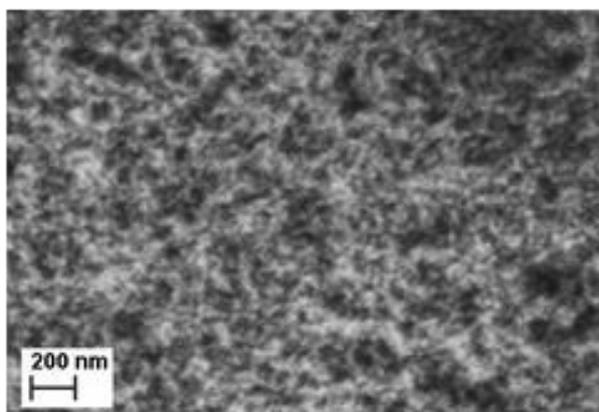


Figure 1: SEM image of KIL-2.

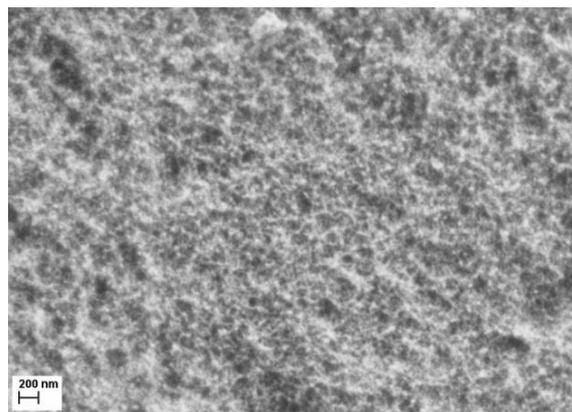


Figure 2: SEM image of Co(Ac)KIL-2.

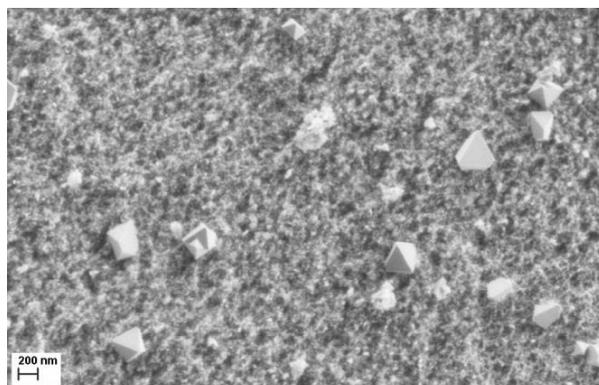


Figure 3: SEM image of Co(AcAc)KIL-2.

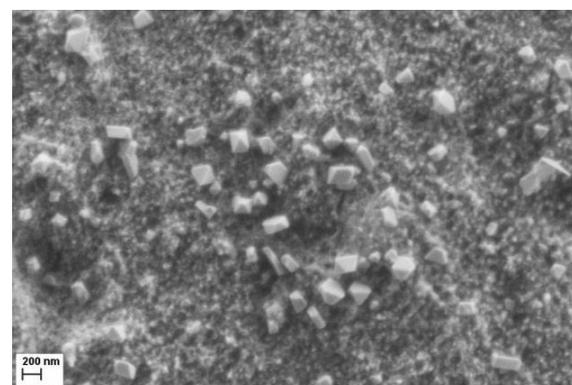


Figure 4: SEM image of Co(N)KIL-2.

The low-angle powder XRD patterns of KIL-2 indicate that KIL-2 has a disordered mesoporous structure (not shown). The XRD patterns of the Co/KIL-2 samples (Fig. 5) recorded at the wide-angle range ($5^\circ < 2\theta < 60^\circ$) confirm that cobalt oxide, Co_3O_4 , is present in the samples after calcination regardless of the salt precursor used.

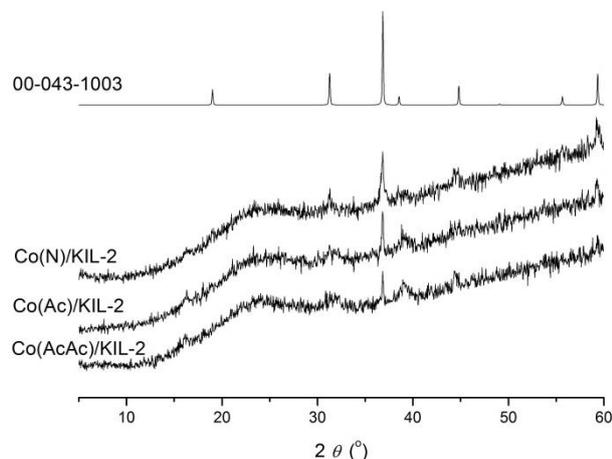


Figure 5: XRD patterns of Co/KIL-2 and reference compound Co_3O_4 (00-043-1003).

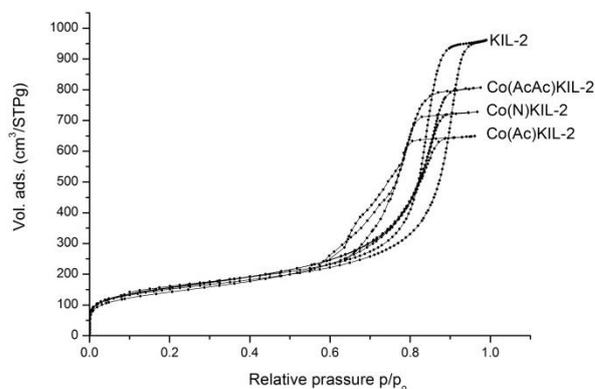


Figure 6: The nitrogen adsorption isotherms.

Nitrogen adsorption isotherms for KIL-2 and Co_3O_4 -KIL-2 materials are shown in Figure 6. The KIL-2 sample exhibits adsorption isotherm typical for KIL-2 silicate, that is the type IV isotherm with relatively narrow hysteresis loop [5]. The presence of Co_3O_4 on the KIL-2 support leads to a marked change in the shape of the hysteresis loop. Co_3O_4 nanoparticles were deposited on the KIL-2 support by using different sources of Co, i.e. cobalt(II) acetyl acetonate, cobalt(II) nitrate and cobalt(II) acetate. All hysteresis loops of the samples containing Co_3O_4 are less intensive in comparison to the original support. It can be observed that using different types of Co sources for preparing the Co_3O_4 -KIL-2 samples leads to a decreased mesopore volume from $1.137 \text{ cm}^3 \text{ g}^{-1}$ for Co(AcAc)KIL-2 to $1.024 \text{ cm}^3 \text{ g}^{-1}$ for Co(N)KIL-2 and to $0.913 \text{ cm}^3 \text{ g}^{-1}$ for Co(Ac)KIL-2. Furthermore, the second-step on the desorption branch due to the existence of Co_3O_4 nanoparticles in mesopores is evidenced for the Co(AcAc)KIL-2 and Co(N)KIL-2 samples, while for the Co(Ac)KIL-2 sample the second-step is not observed. The pore size distribution of different mesoporous materials has been determined using the BJH model, which is widely used for this type of samples [6]. The pore size distribution is determined from adsorption isotherms. The maximum, characteristic of the open mesopores of KIL-2, is the most intense and broad with the average pore diameter of 15.2 nm. The maxima characteristic for pores narrowed due to Co_3O_4 nanoparticles shift to lower pore size value: from 14.4 nm for Co(AcAc)KIL-2 to 13.8 nm for Co(N)KIL-2 and to 13.0 nm for Co(Ac)KIL-2.

Diffuse reflectance UV-Vis spectroscopy and TPR analysis were used to investigate the nature of cobalt oxide species and their reducibility in dependence on the used salt precursor. The UV-Vis spectra of Co/KIL-2 samples (not shown) reveal two broad peaks around 420 nm and 540 nm which indicate the presence of the spinel Co_3O_4 phase and Co^{2+} in tetrahedral coordination [3].

CONCLUSION

The Co-containing mesoporous KIL-2 materials have been prepared and characterized. The samples will be tested as catalysts in the oxidation reaction with toluene as a model VOC compound.

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