



# $^{11}\text{C}$ -radiolabeling study of methanol decomposition on copper oxide modified mesoporous SBA-15 silica

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## ARTICLE INFO

### Article history:

Received 8 December 2010

Received in revised form 14 February 2011

Accepted 22 February 2011

Available online 26 February 2011

### Keywords:

Copper oxide modified SBA-15

Methanol decomposition

$^{11}\text{C}$ -radiolabeling study

## ABSTRACT

$^{11}\text{C}$ -radiolabeling technique is applied to investigate methanol decomposition on copper oxide modified SBA-15. Nitrogen physisorption, XRD, FTIR, UV–vis and TPR techniques are used for catalyst characterization. Selective adsorption coverage of the catalytic active sites with  $^{11}\text{C}$ - and  $^{12}\text{C}$ -methanol molecules is carried out and the products of their conversion are followed. The mechanism of methyl formate, methylal and  $\text{CO}_2$  formation from methanol is discussed.

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## 1. Introduction

Over two decades methanol decomposition has been in the focus of intensive investigation both from the theoretical point of view, as a reverse reaction of methanol synthesis, and practical interest, as a potential alternative clean fuel for vehicles, gas turbines and fuel cells [1]. It was reported that copper containing materials, particularly in nanoscale range [2], are efficient and low cost catalysts for methanol decomposition. Recently, mesoporous silicas have demonstrated great advantages as a host matrix of nanosized metal/metal oxide particles due to their high specific surface area and well-developed ordered pore structure [3]. SBA-15 silica, which structure characterizes with hexagonally packed cylindrical mesopores with tunable size and concomitantly microposity, is among the most frequently studied members of these materials [4].

The problem with the control of the catalytic processes is closely related to the knowledge of their mechanism. However, nowadays despite the intensive investigations on the mechanism of methanol decomposition on copper containing catalysts by various techniques, it is hard to find a clear study, which relates the products distribution to the catalyst state [[5–17] and refs. there in]. It was demonstrated that on metallic copper the decomposition proceeds through methoxide species [12], which decompose to formaldehyde [6,8] or dioxymethylene intermediates [5]. Harikumar [13] reported that formate species is mostly produced on  $\text{Cu}^{1+}$ -rich sur-

face, while Poulston [14] suggested their decomposition to  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{H}_2\text{O}$  on  $\text{CuO}$ . It was found that copper-based catalysts provide a selective formation of methylal (DMM) when the reaction is carried out in liquid phase, while methyl formate (MF) is selectively formed in the gas-solid reaction [15] at low conversion of methanol [5]. Harikumar [13] considered that  $\text{Cu}^{2+}$  are active sites in MF formation from methanol, while Guerreiro [18] reported the activity of  $\text{Cu}^0$  and  $\text{Cu}^{1+}$  in this reaction.

The aim of the current study is to highlight some controversial points of methanol decomposition on copper oxide modified mesoporous SBA-15 silica, discussing the relation between the various catalytic sites and the obtained products. The investigation is carried out using novel high sensitive  $^{11}\text{C}$ -labeling technique under selective coverage of the catalyst surface with labeled and non-labeled methanol. The advantages of similar approach were already demonstrated in our recent investigations related to methanol decomposition on iron, vanadium and nickel modified MCM-41 mesoporous materials [19–22].

## 2. Experimental

### 2.1. Materials

Mesoporous SBA-15 silica ( $\text{BET} = 661 \text{ m}^2/\text{g}$ , total pore volume =  $0.89 \text{ cc/g}$ , average pore diameter =  $7 \text{ nm}$ ) was synthesized according to [4]. Copper oxide (10 wt.%) was loaded using incipient wetness impregnation technique from corresponding acetylacetonate precursor in toluene and its further decomposition in air at  $773 \text{ K}$  for 2 h.

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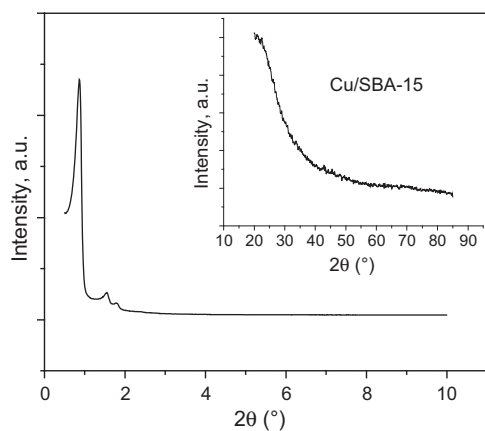


Fig. 1. XRD patterns of copper modified SBA-15.

## 2.2. Methods of investigation

Powder XRD was carried out on a Stadi-P diffractometer of the STOE & Cie GmbH (transmission geometry). Nitrogen physisorption was conducted at 77 K on a Quantachrome Quadrasorb SI MP. FTIR measurements were done on a Bruker IFS25 spectrometer. The UV-vis spectra were recorded on PerkinElmer Lambda 900 UV/vis/NIR Spectrometer. The TPR/TG (temperature-programmed reduction/thermogravimetric) analysis was performed in a Setaram TG92 instrument in a flow of  $H_2$  in Ar (1:1) at 5 K/min.

## 2.3. $^{11}C$ -radiolabelling study

$^{11}C$ -radiolabeling experiments were done in apparatus equipped with closed static reactor, radiodetector and gaschromatograph with flame ionization detector (FID) and radio detectors (RD). The catalytic experiments were carried out after selective coverage of the catalyst surface with  $^{11}C$ - and/or  $^{12}C$ -methanol according to following adsorption procedures:

*Procedure (A):*  $^{11}C$ -methanol adsorption at 333 K and further desorption up to 403 K;

*Procedure (B):*  $^{11}C$ -methanol adsorption at 333 K and further desorption up to 373 K;

*Procedure (C):*  $^{12}C$ -methanol adsorption at 333 K and further adsorption of  $^{11}C$ -methanol at 333 K;

*Procedure (D):*  $^{12}C$ -methanol adsorption at 333 K, further desorption of  $^{12}C$ -methanol at 373 K and finally  $^{11}C$ -methanol adsorption at 373 K.

The catalytic test is carried out under temperature programmed regime.

Separately, desorption experiments were carried out after  $^{11}C$ -methanol adsorption at room temperature. The desorbed  $^{11}C$ -methanol after the temperature increased up to 403 K was removed by He and trapped into  $P_2O_5$  for radioactivity measuring.

## 3. Results and discussion

### 3.1. Physicochemical characterization of Cu/SBA-15

Low-angle XRD pattern of Cu/SBA-15 exhibits all reflections of  $p6mm$  SBA-15 mesophase [4], indicating its preservation during the modification (Fig. 1). No reflections of copper containing phase are registered in the wide-angle region of the patterns, demonstrating its high dispersion. The preservation of the pore structure

of the silica matrix after its copper modification is also confirmed by low-temperature nitrogen physisorption analysis (Fig. 2). The isotherms of parent and modified silica are of IV type with well-defined hysteresis loop in the 0.6–0.8 partial pressure region, typical mesoporous structure with cylindrical pores and narrow pore size distribution. The FTIR spectra of copper containing material (Fig. 3a) represent a decrease in the intensity of the bands at  $958\text{ cm}^{-1}$  and about  $3450\text{ cm}^{-1}$  in comparison with the parent SBA-15 silica, which could be an evidence for partial grafting of copper species to the silica surface with the formation of Si–O–Cu-type linkage [23,24]. The UV-vis spectra of Cu/SBA-15 (Fig. 3b) consist of absorption bands in the 250–400 nm region, which are attributable to CT transitions between Cu(II) ions and oxygen in mononuclear or oligomeric  $[Cu-O-Cu]_n$  clusters [25]. The broad band, centered at 670–750 nm, is assigned to d–d transitions of Cu(II) in CuO nanoparticles [25]. The presence of copper species in different state is also confirmed by TPR–TG experiments (Fig. 4). Generally, the reduction of bulk CuO to  $Cu^0$  is considered as one-step process and for the non-supported oxide it occurs at about 500 K [26]. In the case of supported CuO, this maximum could change its position in the range of 400–600 K, depending on the copper oxide dispersion and the nature of the support [26,27]. For the mesoporous silicas, a two-step reduction of  $Cu^{2+} \rightarrow Cu^{1+} \rightarrow Cu^0$  was also reported [28,29–31]. So, the main reduction effect, which was observed at about 470 K and the further weight loss at about 550 K (Fig. 4) could be assigned to the reduction transitions in CuO particles with different dispersion. According to the FTIR and UV-vis measurements (see above), it is not excluded the second DTG effect and the further high temperature weight loss above 750 K to be also related to the step-wise reduction of copper ions in oligomeric or isolated species, which are in strong interaction with the support. The calculated hydrogen consumption in the whole investigated temperature interval corresponds to 100% reduction of  $Cu^{2+}$  ions to metallic Cu.

### 3.2. Radiolabeling study

In order to describe the peculiarities of the surface coverage with  $^{11}C$ - and/or  $^{12}C$ -methanol after different adsorption proce-

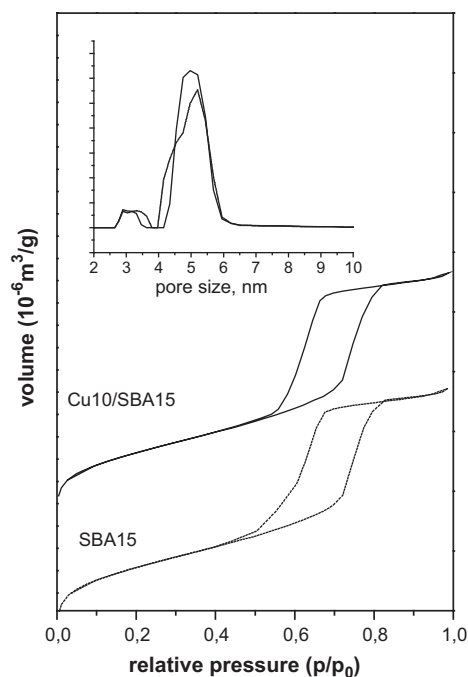


Fig. 2. Nitrogen physisorption isotherms and pore size distribution (inset) for the parent (dash line) and copper modified SBA-15.

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