



Effect of mesoporous silica topology on the formation of active sites in copper supported catalysts for methanol decomposition



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ABSTRACT

Modified incipient wetness impregnation procedure was applied for deposition of finely dispersed CuO or metallic copper particles into ordered mesoporous silica host matrix (KIT-6 and SBA-15). This modified procedure consists of number of consecutive impregnation steps with copper nitrate solution with changeable concentration and soft drying under vacuum procedures. Nitrogen physisorption, XRD, UV–vis, TEM–EDXS, FTIR of probe molecules (CO, NO and N₂) and TPR were applied for characterization of copper state in the matrix. The obtained materials were tested as catalysts in methanol decomposition. Selected catalytic experiments were carried out under very low coverage of the surface with ¹¹C-radiolabelling methanol. In situ FTIR study of methanol decomposition was also performed. It was found that the catalytic behaviour of copper, supported on mesoporous materials, depends in a complex way on the dispersion and accessibility of copper species within the host matrix. They can be tuned by copper loading and pore topology of the support. The optimal catalytic activity in methanol decomposition is achieved at about 8 and 15 wt.% copper content for the SBA-15 and KIT-6 mesoporous supports, respectively.

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1. Introduction

Recently, hydrogen and hydrogen-rich gases have attracted much attention as promising alternative source of energy for fuel cells and low-emission automobile applications [1–6]. On-board production of hydrogen from a liquid fuel is considered as a good alternative due to safety storage and no requirement of new automobile infra-structures. Methanol is one of the best candidates, because it could convert into hydrogen at relatively low temperatures via catalytic decomposition, steam reforming or autothermal reforming processes with high efficiency due to its high hydrogen to carbon ratio. In last decade, the interest to methanol significantly increased due to the possibility to obtain methanol from renewable sources such as biomass, waste products or carbon dioxide from the atmosphere. Many studies were performed on dehydrogenation of methanol over copper containing catalysts, especially on the catalysts of methanol synthesis. However, Cheng et al. [7,8]

established that the conventional Cu/ZnO based methanol synthesis catalysts had good initial activity in methanol decomposition reaction was quickly deactivated. They reported that Ba, Si and Mn oxides promoted the activity of copper catalysts, while Cr oxides improved their stability [7]. The role of CO₂ for stabilization of the activity of Cu based catalysts was also reported in [8]. Up to now, much effort has been attached to control the behaviour of copper catalysts via understanding the nature of the catalytic sites and mechanism of the reaction [9 and refs. therein]. Millar et al. [10] demonstrated that methanol adsorption on Cu/SiO₂ resulted in the formation of methoxide groups, which after heating, transformed to CO₂ and CO via methyl formate. Clarke et al. [11] confirmed the formation of adsorbed methoxide, formaldehyde, methylenebisoxo, and formate groups on copper. Latter, Fisher and Bell [12] reported that depending on the presence of methanol in the gas phase, surface methoxide species could decompose either to CO₂ and H₂ via formaldehyde and formate intermediates or to CO and H₂ via methyl formate ones. It was found that the formation of methyl formate intermediate from methanol showed low sensitivity to the state of metal copper, while its further decomposition to CO and hydrogen depends on the state of metal copper in

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the catalysts [7,13]. Greeley and Mavrikakis [14] demonstrated that the abstraction of single hydrogen atom from methoxide species was the rate-limiting step in the reaction. Minyukova et al. [13] assumed that the methyl formate selectivity could be close to 1 at low methanol conversion but the selectivity decreased with the conversion increase. Many authors believed that all three copper states, Cu^{2+} , Cu^+ , and Cu^0 , are active in methanol decomposition [13], but Domokos et al. [15] and Morikawa [16] concluded that only Cu^{2+} ions are responsible for the dehydration of methanol to methyl formate, while Guerreiro et al. [17] assumed Cu^0 instead of Cu^{2+} as active site. Guerreiro et al. [18] stressed on the critical limit of copper particle size which can ensure methanol dehydrogenation. However it was found that the amount of supported copper had a strong effect on the catalyst efficiency and the state of active phase could be modified in a wide range by the preparation method used [19 and refs. therein]. The application of direct synthesis technique typically results in relatively low copper loading, while the traditional impregnation method [20–22] usually provides agglomeration of copper species on the silica surface, especially at high metal content. Chen et al. [23] found that the grafting method resulted predominantly in the formation of Cu^+ ions, while a partial destruction of support structure occurred when homogeneous deposition precipitation method was used. The predominant formation of oligomeric Cu–O–Cu species was found by molecular design method, while isolated Cu^{2+} ions dominated by the impregnation method [24]. Recently, mesoporous silica revealed good prospects as a host matrix of tunable nanoscale metal/metal oxide particles due to their unequal pore structure characteristics [24–27 and refs. therein]. In our previous study we demonstrated better copper dispersion of copper loaded on hexagonal MCM-41 compared to cubic MCM-48 mesoporous silica [28], while negligible effect of pore structure on the state of copper species has been established when copper precursor strongly interacted with the surface functionality [29]. Patel et al. [30] supposed that for the copper catalysts prepared by impregnation technique, the pore volume and surface area of mesoporous silica supports had a lower dominance on the copper dispersion than the pore topology.

The aim of the current investigation is to prepare copper supported mesoporous silica catalysts for methanol decomposition varying the copper loading in a wide range (1.5–25 wt.%) by simple modification of the traditional incipient wetness impregnation technique. This modified technique includes “step-wise” loading of copper phase by number of consecutive impregnations with copper nitrate solution with changeable concentration followed by soft drying procedure under vacuum. Mesoporous silica type SBA-15 and KIT-6, which structures represent ordered cylindrical mesopores, arranged in hexagonal and cubic symmetry respectively, are compared as host matrices [31,32]. Nitrogen physisorption, XRD, UV–vis, TEM–EDXS, FTIR of probe molecules (CO, NO and N_2) and H_2 -TPR were applied for the characterization of the copper state. In order to highlight the state of copper active sites more precisely, ^{13}C -methanol radiolabelling technique and in situ FTIR study of methanol conversion were applied.

2. Experimental

2.1. Materials

Mesoporous silica type SBA-15 and KIT-6 were synthesized using tetraethylorthosilicate (TEOS) as a silica source and Pluronic P123 triblock-co-polymer (EO20PO70EO20) as structure-directing agent according to the procedures described in [31,32], respectively. A series of copper modifications of these silicas were prepared by modified incipient wetness impregnation technique

(MWI). The method included “step-wise” copper deposition by alternating sequence of number incipient wetness impregnation and vacuum drying cycles. Aqueous solution of copper nitrate was used as a precursor. The concentration of the impregnated solutions, the number of “impregnation-drying” cycles and the drying temperature were varied and the data for the procedures are summarized in Table 1. Samples with copper loading in the range of 1.5–25 wt.% were obtained (Table 1). For comparison, selected samples containing 8 wt.% Cu were prepared using conventional one-step incipient wetness impregnation technique (WI). The precursor was decomposed after calcination in air at 763 K for 2 h. The samples were denoted as $x\text{CuO/S}$, where x was the copper content (as wt.%) and S was SBA-15 or KIT-6 support. Separately, portions of the modifications thus obtained were reduced in a flow of 50 vol.% H_2 in Ar at 523 K for 2 h and the obtained reduced samples thus obtained were denoted as $x\text{Cu/S}$. For comparison, the studied catalysts were compared to a commercial copper catalyst for low-temperature water gas shift reaction (Haldor Topsøe), denoted as CC.

2.2. Methods of catalyst characterization

The specific surface area (S_{BET}) and porosity of the materials were calculated from nitrogen adsorption–desorption isotherm collected at 77 K on a BELSORB-mini II apparatus (BEL Japan Inc.) Prior to the measurements, the samples were outgassed for 2 h at 250 °C. S_{BET} was calculated applying the Brunauer, Emmet and Teller (BET) equation for N_2 relative pressure in range of $0.05 < P/P_0 < 0.30$. Pore size distribution was determined by Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherm. Powder X-ray diffraction patterns were collected within the range of $5.3\text{--}80.0^\circ 2\theta$ on a Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation and using a LynxEye detector. Low-angle part of the patterns was collected from 0.3° to $8.0^\circ 2\theta$ using the knife-edge anti-scatter screen attachment of the primary beam. The average crystallite size was evaluated according to Scherrer equation.

The UV–vis spectra were recorded on Jasco V-650 UV–vis spectrophotometer equipped with a diffuse reflectance unit.

The TEM measurements were performed at 200 kV with an aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS), equipped with a JED-2300 (JEOL) energy-dispersive X-ray-spectrometer (EDXS) for chemical analysis. The aberration corrected STEM imaging High-Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF) were performed with a spot size of approximately 0.1 nm, probe current of 120 pA, convergence angle of $30\text{--}36^\circ$ and collection semi-angles for HAADF and ABF of $90\text{--}170$ mrad and $11\text{--}22$ mrad, respectively. The sample was deposited without any pretreatment on a holey carbon supported Ni-grid (mesh 300) and transferred to the microscope.

FTIR spectra in the region of skeletal vibrations were recorded on a Bruker Vector 22 spectrometer at a resolution of $1\text{--}2\text{ cm}^{-1}$, accumulating 64–128 scans and KBr pellets technique.

FTIR spectra of probe molecules were recorded with a Nicolet 6700 spectrometer accumulating 64 scans at a spectral resolution of 2 cm^{-1} . Self-supporting pellets (ca. 10 mg cm^{-2}) were prepared from the powdered samples and treated in situ in a purpose-made IR cell allowing measurements at ambient and lower temperature. The cell was connected to a vacuum-adsorption apparatus with a residual pressure below 10^{-3} Pa. Prior to the adsorption of probe molecules, the samples were activated by calcination in air at 673 K for 1 h and evacuation at 723 K for 1 h. Reduced samples were obtained by flowing with H_2 (10 kPa) at 523–723 K for 1 h followed by evacuation at 673 K. Samples treated with methanol (for details see below) were also characterized in situ. The experiments on adsorption of probe molecules (CO, NO and N_2) were performed at

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