Applied Catalysis A: General 464–465 (2013) 243–252

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

# Tailored copper nanoparticles in ordered mesoporous KIT-6 silica: Preparation and application as catalysts in integrated system for NO removal with products of methanol decomposition

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## ARTICLE INFO

*Article history:*
Received 11 April 2013
Received in revised form 27 May 2013
Accepted 5 June 2013
Available online 14 June 2013

*Keywords:*
OMCVD technique
Copper nanoparticles supported on KIT-6
Methanol decomposition
SCR of NO with CO
SCR of NO with CO and $CH_4$

## ABSTRACT

First time a combined wet impregnation (WI)-organometallics chemical vapor deposition (OMCVD) strategy was applied for loading of 3–7 wt.% copper in mesoporous silica KIT-6 matrix nanoparticles with tailored particle size. XRD, HRTEM, nitrogen physisorption, UV–vis, XPS and temperature programmed reduction with hydrogen were used for the samples characterization and comparison with the similar materials obtained by conventional impregnation technique. The catalytic behaviour of all samples was tested in number of ecological reactions, such as methanol decomposition, selective catalytic reduction (SCR) of NO by CO and, for the first time, in SCR of NO with a mixture of CO and $CH_4$. The catalyst composition was optimized in a view of its potential application in an integrated catalytic system for the NO removal by SCR with the products of methanol decomposition. The step-wise WI-OMCVD technique is appropriate for the preparation of uniform and finely dispersed copper nanoparticles inside the mesoporous of KIT-6 silica matrix. The growth of copper particles and their catalytic behaviour is strongly controlled by the porous structure of the support.

## 1. Introduction

Copper-based catalysts have been of great interest due to their good catalytic performances in a wide range of reactions, including dehydrogenation of alcohols, isomerization, oxidation of CO and VOCs, selective hydrogenation, epoxidation, hydrogenolysis and selective catalytic reduction of NO [1–18]. Recently, mesoporous silicas have been received much attention as a catalyst support due to their high surface area, tunable pore size, shape, and topology [8,19–21 and refs. therein]. The existence of residual micropores in the inorganic walls of these mesoporous materials provides the formation of accessible and finely dispersed metal nanoparticles [10,22–24]. A challenge in the preparation of these supported catalysts is to disperse the active metal component uniformly. Generally, the traditional impregnation method provides high degree of agglomeration of copper species, especially at higher metal content [11,25,26] and the nature of the loaded species depends on the copper precursor and the type of the mesoporous silica. Vansant [11] found that copper deposited on mesoporous silicas presents in the form of isolated $Cu^{2+}$ cations, oligonuclear $[Cu–O–Cu]_n$ clusters, and bulky CuO particles. Parida [26] registered formation of crystalline CuO phase above 4 wt.% copper loading using simple impregnation of MCM-41 silica. Isolated $Cu^{2+}$ cations dominated in the case of MCM-48 modified by impregnation method, oligonuclear $[Cu–O–Cu]_n$ species predominantly exist when copper is loaded from acetylacetonate precursor by molecular design dispersion method [11], while for the large pore mesoporous silicas copper dominates in the form of isolated $Cu^{2+}$ cations, independently of the impregnation method used. Patel et al. [20] found that the support structure tends to play a major role in determination of the quantity of the active phase and they established better catalytic activity of CuO supported on SBA-15 and MCM-41 in comparison with KIT-6 and MCM-48 analogues in NO reduction with CO. Alternatively, OMCVD is often applied for deposition of metals and offers many advantages in comparison to other methodologies, but the main problems here are related to the poor control in the metal loading [27,28]. In our previous study [29] we reported

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http://dx.doi.org/10.1016/j.apcata.2013.06.006

a new method for synthesis of copper nanoparticles with tailored size on conventional silica support. The method is based on the stepwise OMCVD of bis-(hexafluoroacetylacetonate) copper (II) hydrate ($Cu(hfac)_2$) precursor under hydrogen atmosphere onto a parent material, which was obtained by simple incipient wetness impregnation technique (WI). It was found that the application of $Cu(hfac)_2$ precursor required presence of hydrogen to assure the deposition of copper in metallic state [29,30] and the precursor decomposition is promoted by the contact with the metallic surfaces [29,31] which leads to controlled growth of copper particles. The aim of the current paper is to apply this new strategy for the loading of copper nanoparticles with tailored size in mesoporous silica KIT-6 host matrix, where the mass transfer should be of crucial importance for its realization. XRD, HRTEM, Nitrogen physisorption, UV–vis, XPS and temperature programmed reduction with hydrogen (TPR) were used for the samples characterization and comparison with the similar materials obtained by conventional impregnation technique. The catalytic behaviour of the obtained materials was tested in reactions with a potential application in environmental protection, such as methanol decomposition, selective reduction of NO with CO (CO-SCR), and simultaneous reduction of NO with a mixture of CO and $CH_4$ (CO, $CH_4$-SCR) [32–42].

## 2. Experimental

### 2.1. Catalyst preparation

Mesoporous KIT-6 silica was prepared according the procedure described elsewhere [43] using Pluronic P123 triblock-co-polymer (EO20PO70EO20) as structure-directing agent. The template was removed by calcination in air at 823 K for 6 h. A series of materials, denoted as *n*Cu/KIT-6(A), where *n* is the amount of copper in mass %, were obtained using the following procedure. The initial 3Cu/KIT-6(A) sample was prepared by WI of silica support with 0.4 M aqueous solution of $Cu(NO_3)_2{\cdot}6H_2O$ (Sigma–Aldrich) and further consecutive treated in air at 620 K and in hydrogen at 773 K for 1 h for each procedure. The 5Cu/KIT-6(A) sample was obtained from 3Cu/KIT-6(A) by OMCVD of $Cu(hfac)_2$ as described in [29]. In details, the catalyst 3Cu/KIT-6(A) was placed in a round bottomed flask with an open holder on the bottom where $Cu(hfac)_2$ precursor was loaded to avoid any direct contact with the catalyst before sublimation. The powder was gently mixed by a rotary evaporator at 403 K in $H_2$ (800 mbar) for 3 h placing the flask inside an oil bath. After deposition, the catalyst was slowly heated (1.5 K $min^{-1}$) up to 623 K in $H_2$. The 6Cu/KIT-6(A) and 7Cu/KIT-6(A) samples were prepared repeating the deposition/decomposition steps procedure using as a starting material the one obtained previously. Alternatively, a series of samples denoted as *n*Cu/KIT-6(B) with similar *n* amount of copper was obtained by WI of KIT-6 support with water solution of copper nitrate. After the decomposition of nitrate precursor in air at 773 K for 2 h the samples were treated in hydrogen at 523 K for 2 h.

The copper content determined by atomic absorption spectroscopy (AAS) for each sample is summarized in Table 1.

### 2.2. Catalyst characterization

Copper content in the samples was determined by atomic absorption spectroscopy (AAS) with a Perkin Elmer-3100 Spectrometer using air-acetylene flame. Specific surface area and pore size distribution were measured through nitrogen adsorption–desorption isotherms at 77 K using a conventional volumetric apparatus. Surface areas were calculated on the basis of the BET equation, whereas the pore size distribution was estimated based on the Pierce method [44], using the adsorption branches of the isotherms. The amount of micropores was elucidated by the method of Dubinin–Radushkevich [45] and its distribution by the SE method [46]. Prior to the analysis, the samples were outgassed at 573 K until the residual pressure was less than $10^{-2}$ Pa. The powder X-ray diffraction spectra were recorded within the range from $1^\circ$ to $80^\circ$ $2\theta$ with a step of $0.05^\circ$ $2\theta$ and counting time 1 s/step on Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation and LynxEye detector. TEM micrographs of the samples from Series A were collected by a ZEISS LIBRA 200 FE HRTEM. The TEM micrographs of the samples from Series B were performed by TEM JEOL 2100 with an accelerating voltage of 200 kV. Samples were gently ground in an agate mortar and dispersed in isopropyl alcohol for 15 min in ultrasonic bath. A drop of each fine suspension was then deposited on a holey carbon film supported on a standard copper grid. TEM analyses were performed after complete evaporation of the solvent overnight. The frequency counts of metal NPs with respect to the diameter were evaluated from several pictures representative of the catalyst. The UV–vis spectra of the powder samples were recorded using a Jasco V-650 spectrophotometer equipped with a diffuse reflectance unit. The IR spectra (KBr pellets) were recorded on a Bruker Vector 22 FTIR spectrometer at a resolution of 1–2 $cm^{-1}$, accumulating 64–128 scans. The XPS measurements were done in the UHV chamber of a ESCALAB-Mk II (VG Scientific) electron spectrometer with a base pressure of $1 \times 10^{-8}$ Pa. The photoelectron spectra were excited using unmonochromatized Al $K\alpha_{1,2}$ radiation ($h\nu = 1486.6$ eV). The C1s peak (285.0 eV) was used as internal standard for calibrating the binding energies (BE ± 0.2 eV). Photoelectron spectra of the C 1s, O 1s, Cu 2p and Si 2p core levels and the Cu *LMM* Auger lines were recorded. The composition and chemical surrounding of the samples were investigated on the basis of the areas and binding energies of C 1s, O 1s, Si 2p and Cu $2p_{3/2}$ photoelectron peaks and Scofield's [47] photo-ionization cross-sections. Modified Auger parameter $\acute{\alpha}_{Cu}$ which is defined as $\acute{\alpha}_{Cu}$ = KE (Cu $L_3M_{4,5}M_{4,5}$) + BE (Cu $2p_{3/2}$), where KE (Cu $L_3M_{4,5}M_{4,5}$) is the kinetic energy of the Cu $L_3M_{4,5}M_{4,5}$ and BE (Cu $2p_{3/2}$) is the binding energy of the Cu $2p_{3/2}$ peak.

The temperature-programmed reduction-thermogravimetric (TPR-TG) analyses were performed with a Setaram TG 92 instrument. Before the experiments, the samples were oxidized in air at 623 K for 1 h. Typically, 40 mg of the sample were placed in a microbalance crucible and heated in a flow of 100 $cm^3$ $min^{-1}$ $H_2$ in Ar (1:1) up to 773 K at 5 K $min^{-1}$. The weight loss during the reduction was calculated on the base of TPR-TG curves and the values were normalized to the same catalyst weight (40 mg).

### 2.3. Catalytic tests

Methanol conversion was carried out in a fixed bed flow reactor (0.055 g of catalyst) and argon being used as a carrier gas (50 $cm^3$ $min^{-1}$). The methanol partial pressure was 1.57 kPa. The catalysts were tested under conditions of a temperature-programmed regime within the range of 350–770 K with heating rate of 1 K $min^{-1}$. On-line gas chromatographic analyses were performed on HP apparatus equipped with flame ionization and thermo-conductivity detectors, on a PLOT Q column, using an absolute calibration method and a carbon based material balance. The product selectivity was calculated as $Xi/X \times 100$, where X*i* was the current yield of the product *i* and X was methanol conversion.

Catalytic activity tests of CO-SCR and CO, $CH_4$-SCR were performed using an integrated quartz micro-reactor and mass spectrometer system (CATLAB, Hiden Analytical, UK). The system features a fast-response, low thermal mass furnace with integrated air-cooling, a precision Quadrupole Mass Spectrometer, and a quartz inert capillary with "hot zone" inlet for continuous close-coupled catalyst sampling with minimal dead volume and memory