Microporous and Mesoporous Materials 164 (2012) 93–98

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

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

Preparation and *in situ* spectroscopic characterization of Cu-clinoptilolite catalysts for the oxidative carbonylation of methanol

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ARTICLE INFO

Article history:
Available online 26 June 2012

Keywords:
Cu-clinoptilolite
In situ FTIR spectroscopy
Dimethyl carbonate

ABSTRACT

Cu-containing natural and synthetic clinoptilolite were prepared by Cu cation exchange and impregnation with copper nitrate solution. The samples were characterized and tested for the synthesis of dimethyl carbonate. The state of Cu(I) and Cu(II) species was proved by *in situ* FTIR spectroscopy using CO and NO as probe molecules. The observed bands of νCu(I)–CO and νCu(II)–NO modes are relatively broad indicating a location of the Cu cations at several sites in the zeolite lattice. Cu-clinoptilolite catalysts oxidize CO and NO to a certain extent even at room temperature where CO_2 is partly captured in the zeolite cavities.

The interaction of the catalysts with $MeOH/CO/O_2$ gas mixtures was studied by *in situ* FTIR spectroscopy and *operando* DRIFTS/MS. Oxygenated products like dimethoxy methane and methyl formate were found besides CO_2 in the gas phase while formate, methyl formate and methoxy species were adsorbed at the catalyst surface. In contrast to Cu-Y catalysts no dimethyl carbonate formation could be detected. Obviously, the different channel system of clinoptilolite and the distinct lower BET surface area are disadvantageous concerning dimethyl carbonate formation.

1. Introduction

Clinoptilolite is the most abundant natural zeolite [1] showing a framework structure with a two-dimensional channel system and a recognized cation exchange capacity as main application [2]. Its exchange reactions with Cu(II) cations have drawn the attention of few researchers [3–8] and have been reviewed by Caputo and Pepe [9]. The ongoing effort to remove metals and treat wastewater and polluted water has stimulated the operation of the exchange phenomenon. In this field, the main task has been the achievement of a high efficiency and capacity of clinoptilolite from different deposits upon copper removal [10–15].

The characterization of Cu-containing clinoptilolite by spectroscopic methods has received little attention in the literature. Diffuse reflection spectra served to stablish the positions of the Cu(II) exchanged cations [3], and the cation influence on IR vibrations of modified natural clinoptilolite was investigated by Rodríguez-Fuentes et al. [16].

Clinoptilolite is, in addition, a potential heterogeneous catalyst. However, only few studies concerning the application of Cu-containing clinoptilolite in heterogeneous catalyzed reactions have been reported. Impregnated or exchanged with Cu, clinoptilolite has shown catalytic activity in the SCR with ammonia [17], in the oxidation of *p*-xylene [18], of CH_4, C_3H_6, CO, and methanol [19], in the decomposition of NO [20], in the joint conversion of NO_x and CO_x [21], in the vapor phase oxidation of ethanol [22], and in the total oxidation of toluene [23].

It is known that several Cu containing zeolite catalysts have been applied for the synthesis of dimethyl carbonate (DMC) by the oxidative carbonylation of methanol (MeOH), where promising results were achieved with Cu-Y zeolites [24–26]. DMC is an attractive chemical with versatile applications [27,28] which requires an increasing production level. However, the traditional synthesis route of DMC comprises the use of the toxic and hazardous phosgene as reagent. Insofar, the development of an environmentally benign preferable gas phase process for DMC synthesis would be an interesting alternative.

Against this background, the possible use of Cu-modified clinoptilolite samples for DMC synthesis was taken into account considering the broad availability of clinoptilolite.

For this reason, Cu-modified natural clinoptilolite samples were prepared, characterized, and tested for DMC synthesis. For comparative studies a synthetic clinoptilolite sample was modified in the same way. We present here the results of mainly *in situ* spectroscopic investigations of two selected Cu-modified (exchanged and impregnated) natural and synthetic clinoptilolite samples, respectively. The investigations comprise the adsorption of CO

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http://dx.doi.org/10.1016/j.micromeso.2012.06.025

and NO for the characterization of Cu(I) and Cu(II) sites as well as the study of the oxidative carbonylation of methanol (MeOH) by *in situ* FTIR spectroscopy and *operando* DRIFTS/MS.

2. Experimental

2.1. Catalyst preparation

Natural clinoptilolite (NC) was obtained from the mines at San Luis Potosí State in Mexico. The raw sample was ground to obtain a particle size of approximately 0.25–0.15 mm and washed with hydrochloric acid for 9 h. Synthetic clinoptilolite (SC) was purchased from The University of Wolverhampton in the UK. The washed and synthetic samples were modified with copper nitrate solution either by incipient wetness impregnation or ion exchange to obtain the Cu-impregnated (im) and Cu-exchanged (ex). NC_{ex} was previously ammonium-exchanged. All samples were calcined at 450 °C under synthetic air flow to convert the exchanged NH_4 form into the acid H^+ form and to decompose the copper nitrate.

2.2. Catalyst characterization

The crystal phase identification of samples was carried out by X-ray diffraction on a STADI P automated transmission diffractometer from STOE (Darmstadt, Germany) with Cu Kα_1 radiation (λ = 1.5406 Å) equipped with a linear position sensitive detector (PSD). The phase composition was determined using the program suite WinXpow (STOE) and the powder diffraction file (PDF) database of the international centre of diffraction data (ICDD).

The copper contents were determined by ICP-OES using a Varian 715 ES spectrometer. The textural characterization was achieved using the N_2 adsorption–desorption method, with an AUTOSORB-1 (Quantachrome Instruments) equipment. The specific surface areas were assessed by the Brunauer–Emmet–Teller equation. The chemical composition of the raw zeolites was determined by X-ray fluorescence spectroscopy (Spectrace Instruments).

The *in situ* FTIR measurements were carried out on a Nicolet 6700 FTIR spectrometer (Thermo Scientific). A heatable and evacuable homemade reaction cell with CaF_2 windows was used connected to a gas-dosing and evacuation system. The sample powders were pressed into self-supporting disks with a diameter of 20 mm and a weight of 50 mg.

For characterization of the Cu(I) and Cu(II) species CO and NO were used as probe molecule, respectively. The adsorption of CO and NO was carried out at room temperature after pretreatment of the catalyst samples by heating in flowing He up to 400 °C and cooling to room temperature. The respective gas mixtures (5 vol.% CO/He or 2 vol.% NO/He) were passed through the cell for 30 min. Then the cell was evacuated to remove the gas phase and the physisorbed species.

The oxidative carbonylation of MeOH was monitored by *in situ* FTIR spectroscopy in transmission mode using self-supporting wafers. For the adsorption of the $MeOH/CO/O_2$ gas mixture, 5 vol.% CO/He (35 ml/min) mixed with air (25 ml/min) or with He (25 ml/min) were passed through the MeOH saturator and then through the IR cell. After the experiment the cell was flushed with He and evacuated at reaction temperature (150 °C).

A commercial DRIFTS reaction cell (Harrick) implemented into a FTS-60A FTIR spectrometer (Bio-Rad) was used for the *operando* DRIFTS/MS measurements. The cell practically acts as fixed-bed flow reactor. The gas outlet of the reaction cell was connected to an OmniStar quadrupole mass spectrometer (Pfeiffer Vacuum). The sample was pretreated at 400 °C under a flow of He/Ar and cooled down to the reaction temperature of 150 °C. Then, the $CH_3OH/CO_2/O_2/He$ gas mixture (synthetic air: 3 ml/min and 5% CO/He: 12.5 ml/min passed through the CH_3OH saturator) was flushed through the reaction cell. The reaction was monitored 60 min at 150 °C. Afterwards the cell was flushed with He again to remove the overlaying gas phase.

Generally, difference spectra were evaluated, obtained by subtracting the spectrum of the pretreated sample from that of the respective adsorbate spectrum.

3. Results and discussion

3.1. Chemical composition, surface area, and crystallinity

The chemical composition, Cu content, BET surface area, and pore volume of the samples are shown in Tables 1 and 2. The difference in the pore volume magnitudes of SC_{ex} and SC_{im} suggests that the impregnation method favors the location of Cu on the external surface while the exchange method promotes the penetration into the pores. The natural samples have a lower pore volume than synthetic samples due to the impurities originally present in the pores of the material. As expected from the calculable cation exchange capacity, the copper content in the exchanged samples is lower than in the impregnated ones.

The powder diffraction analysis (Fig. 1) of the samples reveals the characteristic peaks of clinoptilolite [29] at 2Θ values of 9.87, 11.20, 17.35, 22.38, and 22.76 (PDF-70-1859 and 79-1460). The zeolites remain crystalline in the natural materials after loading of copper. The NC samples contain quartz as main impurity. No crystalline CuO was observed in the impregnated samples.

3.2. Characterization of Cu species by FTIR spectroscopy using CO and NO

CO is a small molecule that forms a donor bond to the metal centers. FTIR spectroscopy is used to study the carbonyl complex formed with transition metal cations by their carbonyl stretching frequency which responds very sensitively to coordination onto cationic sites, shifting the frequency of gaseous CO at 2143 cm^{-1}. The frequency shifts give information about the oxidation and coordination state of the cation. In the case of copper, CO is preferentially adsorbed over Cu(I) ions since the formed carbonyl complex is stabilized by π-back donation while no stable carbonyls are formed with the participation of Cu(II) ions at room temperature [30].

The Cu(I) species in the clinoptilolite samples were studied by the CO adsorption at room temperature. The obtained CO adsorbate spectra in different spectral areas are displayed in Fig. 2. During CO adsorption the formation of CO_2 could be observed to a different extent which is caused by the partial oxidation of CO with

Table 1
Chemical composition (wt.%) of the raw zeolites used as catalysts in this study.

Zeolite	Al_2O_3	SiO_2	Na_2O	MgO	K_2O	CaO	Fe_2O_3	Si/Al
SC	11.69	64.70	0.46	0.17	10.80	0.32	0.06	4.9
NC	12.45	64.73	0.27	0.60	4.62	2.58	1.84	4.6

Table 2
Copper content, surface area, and pore volume of Cu-clinoptilolite catalysts.

Catalyst	Cu content (wt.%)	S_{BET} ($m^2\,g^{-1}$)	Total pore volume ($cm^3\,g^{-1}$)
SC_{ex}	1.2	21	0.158
SC_{im}	3.3	35	0.252
NC_{ex}	0.9	–	–
NC_{im}	4.0	22	0.134