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Nb-containing mesoporous materials of MCF type—Acidic and oxidative properties

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ABSTRACT

The new niobium-containing mesoporous catalysts based on MCF structure were prepared by niobium introduction *via* grafting and co-precipitation. The materials were characterised by N_2 adsorption, XRD, UV–vis, pyridine adsorption followed by FTIR and test reactions. Three various Nb precursors were applied: ammonium oxalate complex, ethoxide and chloride. It is documented by UV–vis that the best isolation of Nb species is reached when $NbO(C_2O_4)_2(NH_4)\cdot H_2O$ is applied for grafting and the same sample reveals the highest acidity determined by the test reaction—2-propanol conversion and pyridine adsorption combined with FTIR study. Niobium-containing MCF materials reveal both acidic and oxidative properties. The redox centres are active in the presence of oxygen and lead to very high selectivity in formaldehyde production from methanol. For liquid phase oxidation of cyclohexene with hydrogen peroxide both kinds of centres are active. Oxidative one causes the formation of epoxide, and acidic sites lead to the ring opening and diol production.

1. Introduction

Siliceous mesostructured cellular foams (MCF) are a relatively new class of porous materials with well-defined uniform ultralarge mesopores [1,2]. Their structure is templated by oil in water microemulsions. The catalytic activity of these materials were examined in different processes, e.g. esterification [3], selective oxidation of α-pinene [4]. Due to the presence of a well-defined large mesopore system this kind of materials can be attractive for processes in which the diffusion within the pores plays an important role, e.g. for the oxidation carried out in the liquid phase [5,6]. Since the discovery of mesoporous silicates in 1992 [7], designated as MCM-41, many works have been devoted to the synthesis of metallosilicates (TMCM-41) containing various transition metals and their application in liquid phase oxidations.

Mesoporous molecular sieves of M41S family (MCM-41 and MCM-48) have been modified by transition metals *via* post synthesis grafting or tethering, or *via* inclusion of metal during the synthesis (co-precipitation). The nature of metal active species depends on metal location (extra-framework or framework positions). Location of metal and sizes of metal clusters can affect the diffusion effect (e.g. the accessibility of reactant molecules to metal active sites) [5,6].

There is no doubt that TS-1 is still the best heterogeneous catalyst for many oxidation processes carried out in the liquid phase. However, due to the diffusion limitation there is still a need to look for the materials containing larger pores. Therefore, the focus of many researchers was on the preparation of Ti-containing mesoporous materials [8–13]. However, the disadvantage in using such materials in the liquid phase oxidation is their low hydrophobicity, which is important when diluted hydrogen peroxide is used as an oxidant. Corma et al. [14] proposed two strategies to improve the catalytic activity of TiMCM-41 in the epoxidation of olefins. The first involves the increase of the hydrophobicity of the material *via* silylation of the catalyst surface, and the second is based on the removal of water from the reaction media.

Instead of TiMCM-41 modification *via* silylation necessary for the improvement of epoxidation activity one can look for mesoporous materials containing other active metal species, giving rise to a different reaction pathway or to increase of hydrophobicity. NbMCM-41 and NbSBA-15 seem to be very useful catalysts for epoxidation of olefins [15–18]. The increase of Nb content caused the enhancement of selectivity to epoxide on NbMCM-41 samples [16]. However, in the case of NbMCM-41 mesoporous molecular sieves the growth of niobium content led

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also to the increase of Nb species in the extra-framework location. This kind of species can be easier leached into the solution and can increase undesired selectivity to diols. Therefore, still there is room for looking for the other mesoporous catalysts.

The idea of this work was to prepare mesoporous materials which posses different structural properties compared to samples examined before. The MCFs materials composed of uniformly sized, large spherical cells that are interconnected by uniform windows to create a continuous 3D pore system [1]. This interconnected nature can be very attractive and makes the MCFs materials promising candidates for supports of catalysts. This structure differs from parallel mesopores in MCM-41 and SBA-15 type materials. Moreover, the new structure of host material can generate a different surrounding for niobium species and therefore create new properties of active species. In this work three different sources of niobium were used for the modification of MCF siliceous foams. Metal precursors were introduced into the solid *via* grafting method. Additionally, for the stabilization of active species in liquid phase reactions, the catalysts were also prepared *via* co-precipitation technique. We have expected that this method will enhance the isolation of niobium species, which is an important factor in the cyclohexene epoxidation process [5]. The characterisation of prepared materials and their catalytic activity in gas and liquid phase reactions are presented and discussed in this paper.

2. Experimental

2.1. Catalyst preparation

For the preparation of siliceous MCFs a typical procedure have been used [2]. Surfactant, Pluronic P123 (0.4 mmol), was dissolved in 1.6 M HCl (75 cm^3) at room temperature. 1,3,5-Trimethylbenzene (17 mmol) and NH_4F (0.6 mmol) were added under vigorous stirring. Then the mixture was heated to 333 K. Following 1 h of stirring TEOS was added (4.4 g) to obtain solution A. Then A was stirred for 2 h and stored at 333 K for 20 h and subsequently at 373 K for 24 h. After cooling to room temperature, the precipitate was isolated by filtration, dried at room temperature for 4 days and calcined in air at 773 K for 8 h.

Nb-MCFs were prepared by the direct incorporation of the niobium precursor during the synthesis of MCFs (co-precipitation method) or by the post synthesis procedure to obtain samples with Si/Nb molar ratio of about 30. In both methods three niobium precursors were used: $NbO(C_2O_4)_2(NH_4)\cdot H_2O$ (I), $NbCl_5$ (II) and $Nb(OC_2H_5)_5$ (III). All compounds were from Aldrich.

In the co-precipitation procedure a suitable amount of the niobium precursor, dissolved in 5 cm^3 of solvent, was added dropwise to solution A after addition of TEOS and then the procedure was the same as for the siliceous MCFs. To obtain NbMCF-1 sample 0.307 g of (I) was dissolved in 5 cm^3 of methanol. In the case of NbMCF-2 and NbMCF-3, 0.187 g of (II) and 0.175 cm^3 of (III), respectively, were dissolved in 5 cm^3 of ethanol.

Before grafting of niobium, pristine MCFs were contacted overnight with water vapour at room temperature followed by calcination at 473 K for 2 h. The silanols concentration, determined by the thermogravimetric method [19], was ca. 3 OH/nm^2. Niobium precursor was dissolved in 30 cm^3 of solvent, 1 g of siliceous MCF was dispersed therein and the mixture was reflux for 24 h prior to the removal of solvent by evaporation at 323 K. Finally the samples were calcined at 773 K for 8 h under air flow. Three samples NbMCF-4, NbMCF-5 and NbMCF-6 were obtained using 0.247 g of (I) dissolved in methanol, 0.15 g of (II) dissolved in ethanol and 0.14 cm^3 of (III) dissolved in hexane.

2.2. Catalyst characterisation

N_2 adsorption/desorption isotherms were obtained in a Micromeritics ASAP equipment, model 2010. The samples (200 mg) were pre-treated *in situ* under vacuum at 573 K for 3 h. The surface area was calculated using the BET method. The pore size distributions (PSDs), the pore sizes (the maximum of the PSD), and the mesopore volumes were determined from the adsorption branch of isotherms.

UV–vis spectra were registered using a Varian-Cary 300 Scan UV–vis spectrophotometer. Catalyst powders were placed into the cell equipped with a quartz window. The Kubelka–Munk function ($F(R)$) was used to convert reflectance measurements into equivalent absorption spectra using the reflectance of SPECTRALON as a reference.

The surface properties were characterised by pyridine adsorption followed by FTIR spectroscopy and by 2-propanol conversion.

Infrared spectra were recorded with a Bruker Vector 22 FTIR spectrometer using an *in situ* cell. Samples were pressed under low pressure into a thin wafer of ca. 6 mg cm^{-2} and placed inside the cell. Catalysts were evacuated at 673 K during 2 h and pyridine (PY) was then admitted at 373 K. After saturation with PY the samples were degassed at 373, 423, 473, and 523 K in vacuum for 30 min. Spectra were recorded at room temperature in the range from 4000 to 400 cm^{-1}. The spectrum without any sample (“background spectrum”) was subtracted from all recorded spectra. The IR spectra of the activated samples (after evacuation at 673 K) were subtracted from those recorded after the adsorption of PY followed by various treatments. The reported spectra are the results of this subtraction.

The 2-propanol conversion (dehydration and dehydrogenation) was performed, using a microcatalytic pulse reactor inserted between the sample inlet and the column of a CHROM-5 chromatograph. The catalyst bed (0.02 g with a size fraction of $0.5 < Ø < 1$ mm) was first activated at 673 K for 2 h under helium flow (40 cm^3 min^{-1}). The 2-propanol (Aldrich) conversion was studied at 423, 473 and 523 K using 3 μl pulses of alcohol under helium flow (40 cm^3 min^{-1}). The reactant and reaction products: propene, 2-propanone (acetone) and diisopropyl ether were analysed using CHROM-5 gas chromatograph on line with microreactor. The reaction mixture was separated on 2 m column filled with Carbowax 400 (80–100 mesh) at 338 K in helium flow (40 cm^3 min^{-1}) and detected by TCD.

2.3. Methanol oxidation

Reactions were performed in a fixed-bed flow reactor. The pressed materials were granulated to $0.5 < Ø < 1$ mm size fraction. 0.02 g of the catalysts (calculated for the dehydrated materials) were placed into the reactor. The samples were activated in helium flow (40 cm^3 min^{-1}) at 723 K for 2 h. Next the temperature was decreased to 573 K. The gas mixture of CH_3OH and O_2, diluted by He, was used for the oxidation process with a total flow rate of 40 cm^3 min^{-1}. The reactor effluent was analysed using an online gas chromatograph (SRI 8610 GAS) with FID and TCD detectors. Hydrogen was used as a carrier gas. Substrates and products were separated on a 30 m column filled with GS-Q. The column was heated as follows: at 308 K for 40 min, then 10 K min^{-1} up to 508 K. Following products were analysed: formaldehyde, dimethyl ether, methyl formate and methylal.

2.4. Oxidation of cyclohexene with hydrogen peroxide

The reaction was performed at 313 K in the liquid phase using acetonitrile as a solvent. The catalytic reaction between cyclohex-