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The effect of niobium and tantalum on physicochemical and catalytic properties of silver and platinum catalysts based on MCF mesoporous cellular foams

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ABSTRACT

MCF, NbMCF and TaMCF Mesostructured Cellular Foams were used as supports for platinum and silver (1 wt%). Metallic and bimetallic catalysts were prepared by grafting of metal species on APTMS (3-amino propyltrimethoxysilane) and MPTMS (2-mercaptopropyltrimethoxysilane) functionalized supports. Characterizations by X-ray diffraction (XRD), ultraviolet–visible (UV–Vis) spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF) spectroscopy, and in situ Fourier Transform Infrared (FTIR) spectroscopy allowed to monitor the oxidation state of metals and surface properties of the catalysts, in particular the formation of bimetallic phases and the strong metal–support interactions. It was evidenced that the functionalization agent (APTMS or MPTMS) influenced the metals dispersion, the type of bimetallic species and Nb/Ta interaction with Pt/Ag. Strong Nb–Ag interaction led to the reduction of niobium in the support and oxidation of silver. MPTMS interacted at first with Pt to form Pt–Ag ensembles highly active in CH_3OH oxidation. The effect of Pt particle size and platinum–silver interaction on methanol oxidation was also considered. The nature of the functionalization agent strongly influenced the species formed on the surface during reaction with methanol and determined the catalytic activity and selectivity.

1. Introduction

Siliceous Mesostructured Cellular Foams (MCF) are porous materials with well-defined uniform ultra-large mesopores [1,2] especially attractive for processes in which the diffusion within the pores plays an important role. The preparation procedure of MCF materials is very simple. Moreover, the incorporation of niobium and tantalum into the silica structure in MCF materials is effective [3,4]. Therefore, mesoporous cellular foams were chosen as supports for platinum and silver in this study.

Recently, NbMCF materials were applied as supports for gold and the obtained catalysts were used for methanol oxidation [5]. The interaction between gold and niobium led to high activity and selectivity to formaldehyde in the oxidation of methanol in the 523–623 K range.

The oxidation of alcohols using gaseous oxygen as clean oxidant, in the presence of heterogeneous catalysts is an important process in chemical syntheses and elimination of volatile organic compounds (VOCs) emitted from industrial processes. Total oxidation of alcohols to carbon dioxide is attractive for direct alcohol fuel cells and for control of VOCs emissions, whereas partial oxidation to e.g. aldehydes or esters is useful for production of various fine chemicals. The oxidation of methanol is also a valuable probe reaction in the metal supported catalysts to investigate the influence of the metal, the support and the metal–support interaction as it was shown for gold loaded on titanium and zinc oxides [6].

It is well known that silver is commercially used in selective methanol oxidation to formaldehyde [7–9]. The interaction between oxygen and silver species plays a crucial role in the first step of methanol oxidation, which is the formation of methoxy species [10,11]. The temperature and O_2/CH_3OH ratio are known to influence the formation of different products of methanol oxidation over silver-based catalyst, e.g. a low concentration of oxygen and temperatures of 500–650 K favor the formation of methyl formate, which is considered as an important product in C1 chemistry [12].

Catalysts containing platinum in total [13–15] and selective oxidation reactions [16–19] have been widely studied. Wang and

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coworkers have reported catalytic oxidation of methanol [20,21]. The activity of platinum nanoparticles supported on mesoporous SiO_2, Co_3O_4, MnO_2, Fe_2O_3, NiO and CeO_2 changed with the increase in Pt particle size in the range of 2–8 nm but not monotonically. The activity increased with the growth of Pt particle size from 2 to 6 nm, and decreased for 8 nm Pt particle size. The authors indicated that the use of mesoporous silica support affected the product selectivity in the methanol oxidation reaction in the gas phase, as it impacted the adsorption/desorption pathways of the reactants, intermediates and products. The role of the size of Pt nanoparticles loaded on silica on the methanol oxidation rate was also considered by Tu and Chin [22]. Study of methanol ODH performed on platinum clusters encapsulated within LTA and SiO_2 also shows size effects. Smaller clusters of platinum in LTA zeolites are less reactive than larger clusters on silica. These size effects reflect the higher binding of chemisorbed oxygen, the most abundant intermediate, on sites of lower coordination, which prevail on smaller clusters [23]. Not only the size of Pt particles is an important feature in the oxidation of methanol but also the nature of the support and the additives added to the catalysts. If transition metals were applied as the supports the reaction rates were significantly affected by the strong interaction between the platinum nanoparticles and transition metal oxide supports [21].

There are only a few reports in the literature about Pt–Ag bimetallic systems and their catalytic activity. Different Ag–Pt nanostructures (alloy, core–shell) exhibited the enhanced catalytic activity for methanol electrooxidation [24,25] and hydrogenation of 3,4-epoxy-1-butene [26]. The activity of Pt, Ag, and Pt–Ag nanoparticles in methanol conversion to syngas (with and without oxygen added) has been reported by Qayyum et al. [27]. The properties of bimetallic Pt–Ag were intermediate between those of the parent catalysts, but with different respects to those of their physical mixture, which indicated Pt–Ag bimetallic formation. The catalytic activity for partial methanol oxidation was greater than for methanol decomposition, for all catalysts.

The idea of this work was the construction of platinum–silver bimetallic catalysts based on mesoporous cellular foams, also modified with niobium or tantalum, potentially active in low temperature selective oxidation of methanol to formaldehyde. In our previous study [28] commercial silica (Ultrasil–BET surface area 158 $m^2\,g^{-1}$) was modified with platinum and/or silver. Before metal loading, the silica was functionalized with 3-aminopropyltrimethoxysilane (APTMS) or 2-mercaptopropyltrime thoxysilane (MPTMS). It was proved that the nature of organosilane (MPTMS or APTMS) used for functionalization of silica before silver and platinum loading, played an important role in anchoring Pt and Ag species and affected the kinds of bimetallic particles formed. The reported results proved that selectivity of bimetallic catalysts in methanol oxidation depends on metals loading and dispersion, whereas their activity is influenced by the interaction between platinum and silver in bimetallic particles. In this study we applied the mesoporous silica as the support according to the notification that Pt loaded on mesoporous silica showed considerably higher catalytic activity for methanol oxidation than those without mesoporous silica support [20]. Moreover, we added additional elements to the supports, namely niobium and tantalum, both belonging to the same group Vb in the periodic table. We expected strong metal (Ag, Pt) support (NbMCF, TaMCF) interactions which would lead to changes in metallic and bimetallic phases on the support surfaces and result in changing the activity and selectivity in methanol oxidation. Silica mesoporous cellular foams of MCF type and metalosilicates NbMCF and TaMCF were used as supports functionalized with organosilanes (APTMS or MPTMS) before silver and platinum loading. The prepared materials were thoroughly characterized by the standard and sophisticated techniques: N_2 adsorption/desorption, inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF) spectroscopy, X-ray diffraction (XRD), ultraviolet–visible (UV–Vis) spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy combined with CO adsorption, in situ FTIR with methanol adsorption, *operando* technique (FTIR + MS) for methanol oxidation.

2. Experimental

2.1. Synthesis of MCF materials

MCF support was prepared in polypropylene bottle, according to procedure described in [1]. Pluronic 123 (poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)-block) (16 g, 2.8 mmol) was dissolved in 600 g of 0.7 M HCl solution at 308–313 K. Then 1,3,5-trimethylbenzene (Aldrich) (16 g, 133.12 mmol) and NH_4F (Aldrich) (0.1868 g, 5.04 mmol) were added under vigorous stirring. After 1 h of stirring, TEOS (Fluka) (34,108 g, 163.98 mmol) was added. The final mixture was stirred at 308–313 K for 24 h and then transferred into a polypropylene bottle and heated at 373 K under static conditions for 24 h. The solid product was recovered by filtration, washed with distilled water and dried at room temperature. The template was removed by calcination at 773 K for 8 h.

For the preparation of NbMCF and TaMCF materials, niobium(V) ethoxide or tantalum(V) ethoxide, respectively, were added to the synthesis gel 5 min after TEOS addition. The nominal Si/Nb or Si/Ta molar ratio was 64. In order to establish niobium and tantalum content in MCF samples, XRF and ICP techniques were applied. The catalysts obtained were labeled as MCF, NbMCF, TaMCF.

2.2. Functionalization of MCF materials with organosilanes

MCF was grafted with 3-aminopropyltrimethoxysilane (APTMS) (97%, Sigma–Aldrich) or 2-mercaptopropyltrimethoxysilane (MPTMS) (95%, Sigma–Aldrich) to functionalize the support before modification with metals. 7 g of the support powder was refluxed in a dry toluene solution (200 mL) containing 18 mL of APTMS or 18.7 mL of MPTMS at 373 K for 18 h. The reagents were not purified before use. The materials were recovered by filtration followed by washing in: dry toluene (200 mL), water (100 mL), and acetonitrile (20 mL) (in the case of APTMS); and dry toluene (200 mL), ethanol (200 mL) and distilled water (100 mL) (in the case of MPTMS). The powders were dried in an oven at 353 K.

2.3. Modification of MCF-NH_2 and MCF-SH with platinum and/or silver

Modification of functionalized MCF, NbMCF and TaMCF supports was performed according to the procedure described in our previous work [28]. The difference is that in this work water solutions of precursors were used. To obtain monometallic catalysts, the functionalized support (MCF-NH_2, NbMCF-NH_2, TaMCF-NH_2) was stirred for 4 h in 50 mL of water solution of silver nitrate ($AgNO_3$, $\geqslant$99.8% – Sigma–Aldrich) (1 wt% of Ag as assumed) or hexachloroplatinate(IV) hydrate (H_2PtCl_6, 38.84%, Johnson Matthey) (1 wt% of Pt as assumed) at room temperature (RT). The solid was recovered by filtration and washed with 80 mL of distilled water. The recovered material was stirred at room temperature with 60 mL of 0.1 M ($NaBH_4$ > 99.8%, Sigma–Aldrich) solution. After 40 min, the solid was recovered by filtration and washed with 80 mL of distilled water. The materials were dried at 333 K for 12 h and calcined in air at 773 K for 4 h.

The preparation procedure of the bimetallic Pt–Ag system was as follows: 25 mL of water solution of silver nitrate (1 wt% of Ag as assumed) and 25 mL of water solution of hexachloroplatinate