

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

J. Wisniewska^a, M. Ziolek^a, N. Artioli^b, M. Daturi^b

^a Adam Mickiewicz University in Poznan, Department of Chemistry, Poznan 61-614, Poland

^b Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, Caen F-14050, France

* asia890@vp.pl

1. Introduction

Total oxidation of methanol 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. Taking into account the oxidizing properties of silver and platinum we may expect new, unique properties resulting from the interactions between metals in the bimetallic system supported on mesoporous foams. The aim of this contribution is to prepare new Pt-Ag catalysts based on mesoporous cellular foams MCF, NbMCF, TaMCF, characterise them and test their application in the oxidation of methanol. Strong metal (Ag, Pt) - support (NbMCF, TaMCF) interactions, leading to changes in metallic and bimetallic phases on the support surfaces and in the activity and selectivity in methanol oxidation, are discussed.

2. Experimental

MCF supports were prepared according to a published procedure [1]. Supports were functionalized with 3-aminopropyltrimethoxysilane (APTMS) or 3-mercaptopropyltrimethoxysilane (MPTMS) before anchoring metals. The method for modification was selected on the basis of our previous studies with amorphous silica [2]. After incorporation of both metals (1 wt.% Pt, 1wt.% Ag) all materials were reduced with NaBH₄ at room temperature and calcined at 773 K. Before methanol oxidation, the materials were activated at 673 K in Ar flow.

The catalysts prepared were thoroughly characterized by the standard and sophisticated techniques: N₂ adsorption/desorption, ICP, XPS, XRF, XRD, UV-Vis, FT-IR in-situ spectroscopy after adsorption of probe molecule (CO, methanol). Catalytic activity of the prepared materials was studied in methanol oxidation carried out in two different systems, by the use of FTIR-MS *operando* device and in a traditional fixed-bed flow reactor.

3. Results and discussion

Silver and platinum loading in the bulk of the materials is almost the same as the assumed values, i.e. ca. 1 wt. % of each metal. Platinum concentration is higher in the bulk than on the surface of materials. For silver this dependence is the reverse - it is deposited selectively on the surface, especially on metalosilicates (NbMCF, TaMCF). The functionalization agent (APTMS or MPTMS) influences the Nb/Ta interaction with Pt/Ag. Within both series of catalysts (APTMS and MPTMS functionalized) the presence of Nb or Ta in the MCF structure increases platinum dispersion because the Nb/Ta-Pt interaction inhibits platinum agglomeration during the calcination process. In bimetallic catalysts, the formation of Pt-Ag clusters was detected. Activation in inert gas at 673 K led to the reduction of cationic silver to metallic one. The strong Ag - Nb interaction induced the reduction of Nb(V) to Nb(IV) and oxidation of metallic silver.

The catalysts based on the supports functionalized with MPTMS were more active in methanol oxidation than those based on the supports modified with APTMS. In bimetallic samples it was proved that MPTMS interacted at first with Pt to form Pt-Ag clusters highly active in CH₃OH oxidation. The activity of all monometallic platinum containing samples was the highest, but the catalysts were not selective, whereas monometallic silver catalysts were not active in methanol oxidation at low temperatures. At higher

temperatures they were more active and selective mainly to formaldehyde (FA) and methyl formate (MF). If silver was loaded together with platinum, the activity was enhanced and selectivity was turned towards the products characteristic of the silver catalyzed reaction.

Niobium and tantalum in MCF supports modify the platinum and silver species in the way allowing increased activity of the catalysts in methanol oxidation and are responsible for changes in selectivity. Niobium species provide much higher effects than tantalum species. All these features are illustrated by Figure 1.

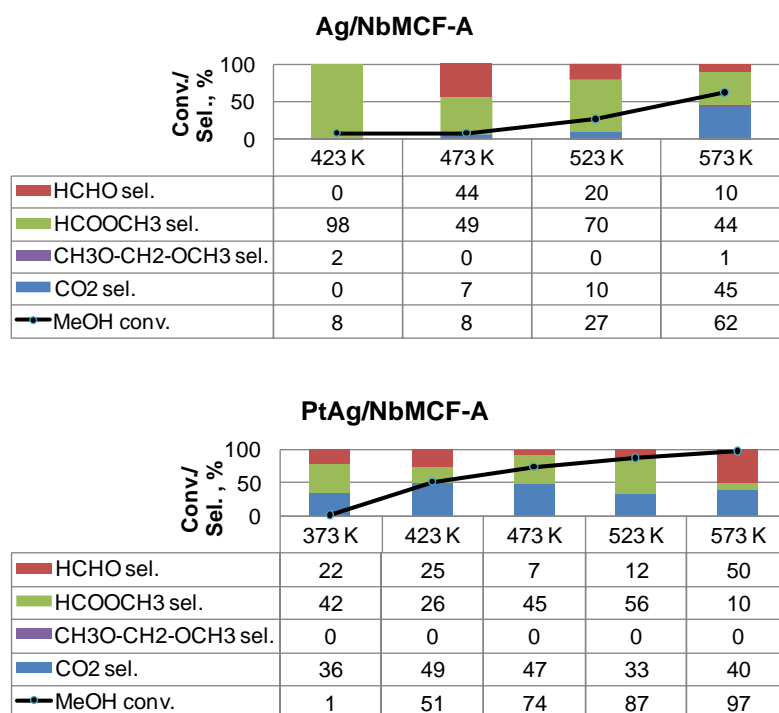


Figure 1. Results of methanol oxidation in the fixed-bed flow reactor ($O_2 : CH_3OH = 2$) - activity and selectivity at different temperatures for selected catalysts.

4. Conclusions

The nature of the functionalizing agent strongly influenced the metals dispersion and the type of active species formed on the surface of bimetallic catalysts containing platinum and silver. The most important for high activity in methanol oxidation is the synergistic interaction between platinum and silver and high dispersion of the active phase. In bimetallic Pt-Ag system, platinum is responsible for the activity and silver for the selectivity in the low-temperature oxidation of methanol. It seems that niobium and tantalum incorporated into MCF structure act as promoters. By selecting the support chemical composition and the amount of platinum and silver, the selectivity of methanol oxidation reaction can be controlled.

References

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