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# A new way for deNO$_x$ catalyst preparation: Direct incorporation of 12-tungstophosphoric acid $H_3PW_{12}O_{40}$ and platinum into mesoporous molecular sieves material

Hussein Hamad [a,b,*], Michel Soulard [a], Bénédicte Lebeau [a], Joël Patarin [a], Tayssir Hamieh [b], Joumana Toufaily [b], Hakim Mahzoul [c]

[a] *Laboratoire de Matériaux à Porosité Contrôlée, UMR 7016, ENSCMu, UHA, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France*
[b] *Laboratoire de Chimie Analytique, Matériaux, Surfaces et Interfaces, Faculté des Sciences, Université Libanaise, Hadeth, Beyrouth, Lebanon*
[c] *Laboratoire Gestion des Risques et Environnement, EA 2334, UHA, 25 rue de Chemnitz, 68200 Mulhouse, France*

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**Abstract**

Direct incorporation of platinum (Pt) and 12-tungstophosphoric acid $H_3PW_{12}O_{40}$ (HPW) into mesoporous MSU-type silica was achieved by using a mixture of cationic and non-ionic surfactants, such as cetyltrimethylammonium ($C_{16}TMA^+$) and Triton (TX-100). Various amounts of Pt (0.3–7 wt%) and HPW (9–49 wt%) were incorporated and the obtained materials were characterized by X-ray diffraction (XRD), chemical and thermal (TG–DTA) analyses, electron microscopies (SEM, TEM), $N_2$ adsorption–desorption measurements, and solid state $^{31}P$ NMR spectroscopy. The catalytic activity of the calcined silica-based mesoporous molecular sieves containing tungstophosphoric acid (HPW), platinum and platinum–tungstophosphoric acid (Pt/HPW) for $NO_x$ reduction with propene was investigated in the presence of oxygen. Samples which contain small amounts of Pt and moderate loadings of HPW were found the most active (up to 97% at 250 °C and for 1 vol.% $O_2$).


*Keywords:* Mesoporous silica-based material; Direct incorporation; Platinum; Tungstophosphoric acid; $NO_x$ reduction

## 1. Introduction

Since their discovery in the early 1990s, the organized mesoporous molecular sieves of the M41S family [1] have been intensively modified to generate materials with catalytic properties. Thus, the introduction of different elements such as Al, Ti, Zr into organized mesoporous siliceous structures has been reported [2–4]. However, compared to zeolites, the acid properties of aluminum-containing M41S materials are lower and similar to those observed for amorphous silica–alumina [3,5]. Another route was explored such as the preparation of metal supported MCM-41and MCM-48 silica type materials [6–9]. Indeed, the high surface area of these mesoporous materials appears to be very promising for a good dispersion of the active metal component and consequently for an outstanding catalytic activity [9–11]. Junges et al. [12] have reported an interesting approach for the preparation of metal supported mesoporous materials by using different platinum sources introduced directly in the synthesis gel of MCM-41. By this way up to 5 wt% of Pt could be incorporated into the solids without any distortion of the ordered MCM-41 structure.

On the other hand, heteropolyacids (HPAs) with the Keggin structure are widely used as acid catalysts, due to their very strong Brönsted acidity [13–15]. The tungsten addenda atoms present in heteropolyacids exhibit strong acidity, high thermal stability and oxidation properties [13], which allow their use as catalysts in various reactions at moderate temperatures [16]. Moreover, the high solubility of HPAs in water and organic solvents, their quite high thermal stability in the solid state [17] and the possibility of introducing several different elements into the polyanions and counter-cations [18], have opened a new field of research in catalysis. It is well known that HPAs strongly inter-

* Corresponding author at: NanoQam (Laboratoire d'électrochimie avancée) Case postale 8888, succursale Centre-ville Montréal (Québec) H3C 3P8 Canada. Tel.: +1 514 987 3000x1433; fax: +1 514 987 4054.
*E-mail addresses:* hussein29@hotmail.com, hhamad@emt.inrs.ca (H. Hamad).

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act with the support at low loading levels, while bulk properties of heteropolyacids prevail at higher loadings [19].

Furthermore, as mentioned by Nowińska et al., encapsulation of HPAs and transition metal complexes into the channels of mesoporous materials was used to generate stable catalysts with both acid and oxidative catalytic activity [20]. However, the anchoring of HPAs into mesoporous materials walls occurs by means of very weak interactions between the acidic proton and the silanol groups, which might explain, in some cases, the leaching of these species in liquid phase reactions.

There are many papers describing the use of mesoporous molecular sieves, such as MCM-41, as a catalyst support and the role played by their textural properties in the degree of metal dispersion and metal reduction and the corresponding effect on catalytic behavior [21]. Thus, MCM-41 materials containing metals or metallic ions, have showed outstanding activity for $NO_x$ reduction [6,10,11], especially Pt-supported MCM-41 obtained by impregnation. Recently, Jang et al. [22] reported that the catalytic performances in $NO_x$ reduction by Pt-impregnated MCM-41 and MCM-48 depended on the characteristics of the supports used. In addition, Jentys et al. [11] have studied the catalytic properties of MCM-41 impregnated with platinum and tungstophosphoric acid. Such an impregnation generates strong Brønsted acid sites on the solids and improves their activity. Toufaily [23] showed that the preparation of MSU-type materials under acidic medium using two types of surfactants, cetyltrimethylammonium ($C_{16}TMA^+$) and Triton (TX-100), enhance the incorporation of tungstophosphoric acid (HPW) into the pores of MSU-type materials. The addition of a cationic surfactant such as $C_{16}TMA^+$ during the synthesis might be an advantage for the incorporation of negatively charged species such as chloroplatinic and tungstophosphoric species.

In the present paper, the direct synthesis of organized mesoporous MSU-type silica modified with platinum (Pt), tungstophosphoric acid (HPW) or Pt + HPW at various loadings is described. The effect of the incorporation of Pt and HPW on the structure of the mesoporous solid was investigated. A detailed physico-chemical characterization of the obtained materials was carried out by using different techniques: namely, X-ray diffraction (XRD), elemental, SEM, TEM and TGA/DTA analyses, $N_2$ adsorption–desorption measurements, and solid state $^{31}P$ NMR spectroscopy.

The three types of prepared catalysts named HPW/MSU, Pt/MSU and Pt/HPW/MSU with various loadings in Pt and HPW were tested in catalytic de$NO_x$ reactions with propene in the presence of variable amounts of oxygen at different temperatures.

## 2. Experimental

### 2.1. Materials

The synthesis of MSU-type silica was carried out according to the procedure developed by Toufaily [23] in which tetraethoxysilane (TEOS, purchased from Aldrich 98%) was used as silica source, cetyltrimethylammonium bromide ($C_{16}TMABr$, 96%, Fluka), polyethylene glycol-*tert*-octylphenyl-ether (TX-100, Fluka) as surfactants and sodium fluoride (NaF, Fluka) as nucleophilic catalyst for the condensation of the silica network [24]. For the Pt- and HPW-containing samples, hexahydrate chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, Strem Chemicals) and 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, Fluka) were used as reactants. Pure silica, Pt-, HPW- and Pt/HPW-containing samples are named MSU, Pt/MSU, HPW/MSU and Pt/HPW/MSU, respectively.

### 2.2. Synthesis procedures

#### 2.2.1. Synthesis of Pt/HPW/MSU samples

The synthesis of the Pt and HPW-containing MSU-type samples was performed with the following molar composition: $1SiO_2$:0.22TX-100:0.02–0.04$C_{16}TMABr$:($0 \le m \le 0.035$) HPW:($0 \le n \le 0.04$)Pt:0.02NaF:300$H_2O$ (see Table 1).

In a first step, 7.4 g of TX-100 and 0.41–0.82 g of $C_{16}TMABr$ were dissolved in 210 mL distilled $H_2O$ containing 10 mL of

Table 1
Synthesis of MSU, Pt/MSU, HPW/MSU and Pt/HPW/MSU samples

| Sample | Type | Composition of the starting mixture | | | | Composition of the MSU-type samples[a] | |
|---|---|---|---|---|---|---|---|
| | | HPW, $x$ (g) | HPW/$SiO_2$ molar ratio, $m$ ($\times10^{-3}$) | $H_2PtCl_6$, $y$ (g) | Pt/$SiO_2$ molar ratio, $n$ ($\times10^{-3}$) | wt% of HPW and (HPW/$SiO_2$ molar ratio, $\times10^{-3}$) | wt% of Pt and (Pt/$SiO_2$ molar ratio, $\times10^{-3}$) |
| A | MSU | 0 | 0 | 0 | 0 | 0 | 0 |
| B | Pt/MSU | 0 | 0 | 0.20 | 7.3 | 0 | 1 (3) |
| C | Pt/MSU | 0 | 0 | 1.04 | 38 | 0 | 7 (26) |
| D | HPW/MSU | 1.65 | 9.4 | 0 | 0 | 9 (2.2) | 0 |
| E | HPW/MSU | 3.30 | 20 | 0 | 0 | 29 (9.8) | 0 |
| F | HPW/MSU | 4.00 | 24 | 0 | 0 | 38 (14.2) | 0 |
| G | Pt/HPW/MSU | 1.61 | 9 | 0.19 | 7 | 13 (3) | 0.5 (1.6) |
| H | Pt/HPW/MSU | 1.50 | 8.5 | 0.19 | 7 | 20 (5) | 0.4 (1.5) |
| I | Pt/HPW/MSU | 3.00 | 17 | 0.19 | 7 | 22 (9) | 0.3 (1.1) |
| J | Pt/HPW/MSU | 5.90 | 34 | 0.36 | 13 | 49 (23) | 0.8 (2) |

Starting molar composition: $1SiO_2$:0.22TX-100:0.02–0.04$C_{16}TMABr$:$m$HPW:$n$HPt:0.02NaF:300$H_2O$.
[a] Determined by X-ray fluorescence spectroscopy.