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Catalysis Today 91–92 (2004) 219–223
CATALYSIS TODAY
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Chemoselective oxidation of 2-thiomethyl-4,6-dimethyl-pyrimidine on nanostructured tantalum oxides

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Abstract

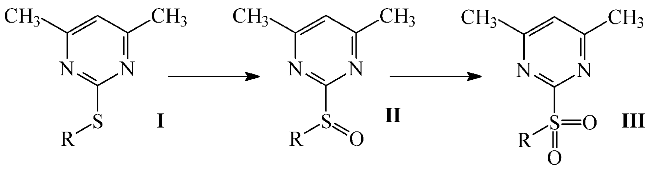
A series of tantala–silica catalysts (15 wt.% Ta_2O_5) were prepared by sol–gel from tantalum and silica ethoxides. These syntheses were carried out using two families of quaternary ammonium salts, $C_nH_{2n+1}(CH_3)_3NBr$ ($n = 14, 16, 18$) and $(C_nH_{2n+1})_4NBr$ ($n = 10, 12, 16, 18$) were used as surfactants. The catalysts were characterized by adsorption–desorption isotherms of N_2 at 77 K, XRD, SAXS, DRUV-Vis, py and $CDCl_3$-FTIR, and XPS. The catalytic tests were carried out in dioxane, methanol or $CHCl_3$, and indicated that both conversion and selectivity depend on the size of tantalum nanoxide. Leaching investigation showed that part of Ta is extracted from the network, but it segregates on the support as Ta_2O_5.

Keywords: Oxidation of 2-thiomethyl-4,6-dimethyl-pyrimidine; Nanostructured tantalum oxides; SAXS; DRUV-Vis; py and $CDCl_3$-FTIR; XPS

1. Introduction

The use of heterogeneous catalysis in the production of fine chemicals received an increased interest lately. Partial oxidation of thiols to produce valuable synthons in pharmaceutical and agrochemistry is one of the most interesting applications [1,2]. Most of the studies were done using titanium containing catalysts, but it is still not clear and under debate if titanium leaches and if the chemoselectivity is related to the presence of homogeneous species. In addition, the oxidation of these substrates require rather mild oxidation conditions and titanium seems to be too strong for such reactions.

An alternative to this system seems to be tantalum. The aim of the present abstract is to show the catalytic activity of a family of tantalo-silicates with different sizes of the incorporated nanoxides in the oxidation of 2-thiomethyl-4,6-dimethyl-pyrimidine (**I**) to the corresponding sulfoxide (**II**). The size of tantalum nanoxides was tuned by modifying the nature of the surfactant:



2. Experimental

Ta_2O_5 (15 wt.%)–SiO_2 catalysts were prepared by sol–gel using as precursor TEOS and tantalum ethoxide. The silica sol was prepared from TEOS under acid hydrolysis (HCl, pH ≈ 1) (TEOS:H_2O:C_2H_5OH = 1:4.5:50). After 2 h of refluxing at 80 °C tantalum ethoxide was added resulting in a transparent gel, and then the surfactant was added. Gelification was carried out at room temperature, and the resulting gel was dried at 80 °C and calcined at 600 °C. Two families of quaternary ammonium salts, $C_nH_{2n+1}(CH_3)_3NBr$ ($n = 14, 16, 18$) and $(C_nH_{2n+1})_4NBr$ ($n = 10, 12, 16, 18$) were used as surfactants. In accordance, the catalysts

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doi:10.1016/j.cattod.2004.03.037

were denoted as Ta-*n* or Ta-4-*n*. They were characterized using several tools. Adsorption–desorption isotherms of N_2 were determined at 77 K using a Micromeritics ASAP 2000 equipment. The XRD patterns were recorded by a SIEMENS D-5000 diffractometer in the range 0–80° min^{-1} 2θ using Cu Kα radiation ($\lambda = 1.54183$ Å). Small-angle X-ray scattering (SAXS) experiments were performed with an evacuated Kratky compact camera mounted on a Siemens rotating copper anode using a take-off angle of 3°. Py- and $CDCl_3$-FTIR spectra were collected in a Bruker IFS88 infrared spectrometer. To investigate the stability of the adsorbed species during temperature elevation, the spectra were recorded at room temperature, 473 and 623 K. The XPS spectra were recorded using a SSI X probe FISONS spectrometer (SSX-100/206) with monochromated Al Kα radiation. The standard oxidation tests were carried out at 333 K in a 10 ml glass flask. The reaction mixture consisting of 80 mg substrate, 10 mg catalyst, and H_2O_2 (12 wt.%) (substrate/H_2O_2 ratios between 1:2 and 2:1) in 5 ml solvent (dioxane, methanol or $CHCl_3$) was mixed under vigorously stirring for maximum 4 h. The analysis of the reactant and products was done by HPLC and ^{1}H and ^{13}C NMR with a Varian Gemini 300BB instrument operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. To control the leaching of tantalum two kinds of experiments were carried out: (i) the filtration of the catalysts at the reaction temperature after 1 h, followed by ICP-AES analysis of the mother liquor (looking for Ta) and (ii) NMR analysis of the evolution of reaction in the absence of catalysts for another 90 min, and re-use of the catalysts in three successive runs. After each run, the catalysts were dried and DRUV-Vis analyzed.

3. Results

3.1. Catalysts characterization

Table 1 compiles the textural properties of the investigated catalysts. Except for Ta-4-16 and Ta-4-18, these correspond to large surface area mesoporous materials with a very sharp pore size distribution. For both kinds of surfactants, the surface area decreased with the increase of *n*. XRD and SAXS confirmed the results of adsorption of N_2 at 77 K, and for large surface area materials, indicated a texture with a 2D-hexagonal symmetry and pores in the range 3.5–3.7 nm (Table 1). No clear XRD evidence of the formation of Ta_2O_5 oxide resulted from these determinations. This was a first evidence of a good dispersion of tantalum in the silica matrix. More details about the dispersion of tantalum were provided by XPS. XPS binding energies and the comparative XPS and chemical Ta/Si ratios are given in the same table. The binding energies corresponding to Ta $4f_{7/2}$ level exhibit typical values for Ta^{5+} [3]. The increase of the XPS Ta/Si ratio with *n* and number of long chains may correspond to a less homogeneous incorporation of tantalum in the silica matrix and, in accordance, with an increase in the size of incorporated XRD silent nano-tantalum oxide.

Py- and $CDCl_3$-FTIR investigation revealed very interesting features of these catalysts. py-FTIR showed only the presence of Lewis acid sites. Only bands assigned to the 8a and 19b vibration modes of adsorbed py forming Lewis-type adducts (1450, 1490, and 1613 cm^{-1}) were detected in the spectra recorded at 373 K [4]. The increase of the temperature to 623 K indicated the same bands, suggesting that these sites are rather strong. The ratio L/L (373/623 K) corresponded to values between 33 and 58%. $CDCl_3$-FTIR indicated for all the samples a band located at 2265 cm^{-1}. This band has been reported for $CDCl_3$ adsorbed on pure silica by Paukshtis et al. [5] and it has been assigned to the stretching vibration ν_{CD} of SiO_2 surface complexes where a chlorine atom of chloroform interacts with a proton of the hydroxyl group of silica and the hydrogen atom is not bonded to the surface, thus suggesting the basic OH sites [5].

3.2. Catalytic behavior

Fig. 1 shows the variation of the conversion of 2-thiomethyl-4,6-dimethyl-pyrimidine on the investigated catalysts in different solvents. These data indicate that the conversion is dependent on both the catalyst and the solvent. Ta-14 exhibited the highest activity, while Ta-4-18 the lowest. For these catalysts the differences in activity

Table 1
Textural properties, XPS binding energies and Ta/Si ratios of the investigated catalysts

Catalyst	BET surface area ($m^2\,g^{-1}$)	*t*-Plot surface area ($m^2\,g^{-1}$)	Pore size (nm)		XPS binding energy (eV)		Ta/Si ratio ($\times 10^3$)	
			N_2 adsorption	XRD + SAXS	Ta $4f_{7/2}$	Si $2p_{3/2}$	Chemical	XPS
Ta-14	724	181	3.4[a]	3.7	26.4	103.2	1.15	6.4
Ta-16	692	171	3.4[a]	3.7	26.4	103.2	1.15	6.9
Ta-18	698	178	3.6[a]	3.7	26.5	103.2	1.15	7.5
Ta-4-10	984	179	4.2[a]	3.5	26.4	103.2	1.15	10.2
Ta-4-12	832	297	4.2[a]	3.6	26.5	103.2	1.15	13.4
Ta-4-16	187	25	2.3, 24[b]	–	26.4	103.2	1.15	18.8
Ta-4-18	145	11	2.3, 24[b]	–	26.4	103.2	1.15	19.4

[a] Monomodal pore size distribution.

[b] Multimodal pore size distribution.

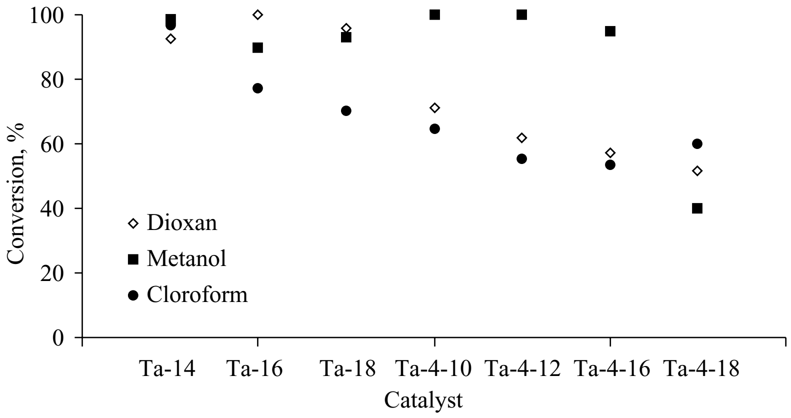


Fig. 1. Variation of the conversion on the investigated catalysts: 10 mg catalyst, 80 mg substrate, 2 ml H_2O_2 (12%) in 5 ml solvent (dioxane, methanol or $CHCl_3$), 333 K, 4 h.

in the investigated solvents were very small. For the other catalysts, the changes in *n* and merely, the replacement of trimethyl long alkylated surfactant with a tetra-long alkylated surfactant led to catalysts which are more sensible to the solvent effect. The conversion was higher in methanol (over 90%) and smaller in chloroform. The hydrogen peroxide efficiency was calculated as the number of H_2O_2 moles transformed in sulfoxide/sulfone per total number of transformed H_2O_2 moles. In all the experiments and on all catalysts the H_2O_2 efficiency was higher than 70% indicating a remarkable behavior of the catalysts.

Fig. 2 shows the variation of selectivity to sulfoxide on the investigated catalysts in different solvents. Ta-14 was the only catalyst on which the highest selectivity to sulfoxide resulted in chloroform. For Ta-16, Ta-18, and Ta-4-10 the differences between methanol and dioxane were rather small, while for Ta-4-12, Ta-4-16 and Ta-4-18 the best selectivity was obtained in dioxane. The highest selectivity was obtained on Ta-4-12, which may correspond to a proper catalytic surface. A high chemoselectivity (98%) using heterogeneous catalyst is indeed remarkable. No major changes in the selectivity were determined after 4 h, namely, at the moment were measured the conversions presented in Fig. 1. Depending on the catalyst, the decrease in the selectivity was maximum, 7%. This decrease was caused by a further oxidation of sulfoxide to sulfone. It is also worth noting that except sulfoxide and sulfone no other reactions products were evidenced by NMR. Higher H_2O_2 concentrations exhibit a negative effect on selectivity.

3.3. Leaching tests

The ICP-AES analyses indicated no tantalum in the filtrate, and the reaction was almost stopped. The re-use of the catalysts in two successive runs showed very similar results, which apparently may be an additional indication of the absence of leaching. But the comparative DRUV-Vis spectra of fresh and tested catalysts (Fig. 3) indicated that the exposure to the reaction conditions caused changes which paralleled the increase in nano-oxide size.

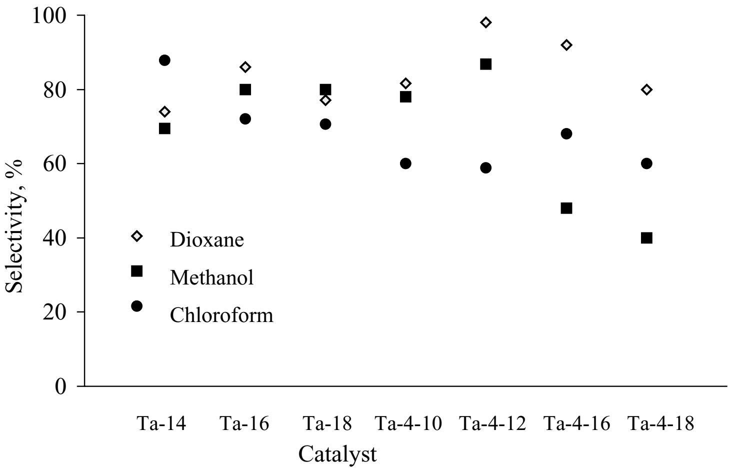


Fig. 2. Variation of the selectivity on the investigated catalysts: 10 mg catalyst, 80 mg substrate, 2 ml H_2O_2 (12%) in 5 ml solvent (dioxane, methanol or $CHCl_3$), 333 K, conversion around 40%.

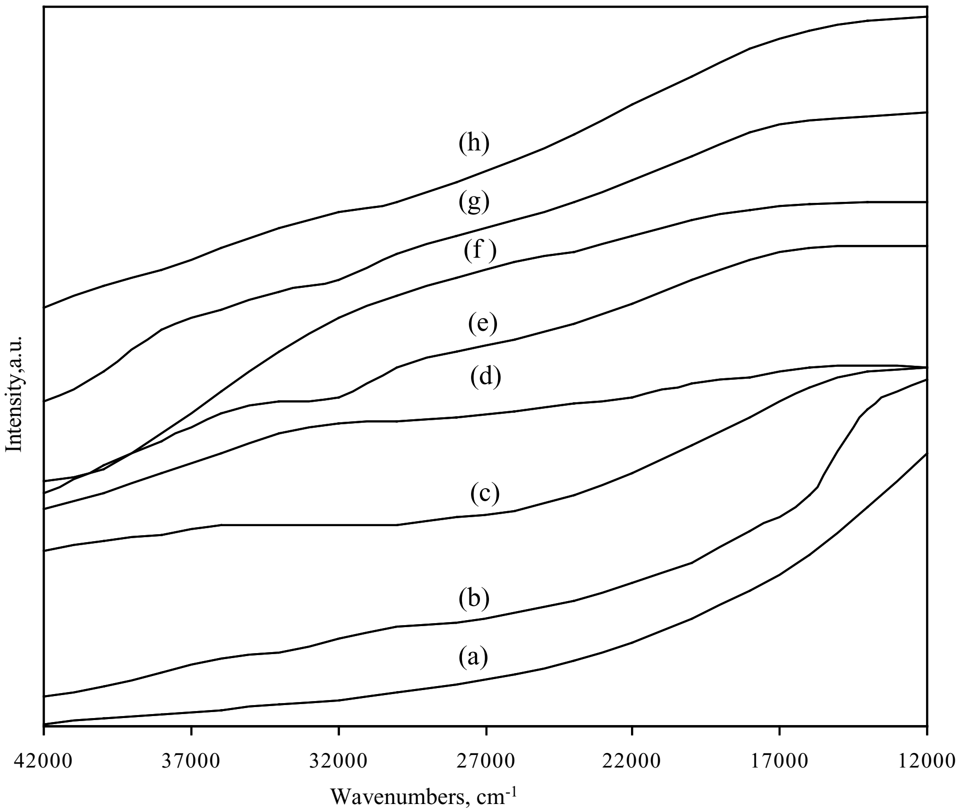


Fig. 3. DRUV-Vis spectra of silica entrapped tantalum nano-oxides: (a) fresh Ta-16; (b) tested Ta-16; (c) fresh Ta-4-10; (d) tested Ta-4-10; (e) tested Ta-4-16; (f) fresh Ta-4-16; (g) tested Ta-4-18; (h) fresh Ta-4-18.

DRUV-Vis spectra of fresh Ta catalysts indicated no band assigned to Ta_2O_5, which is in very good concordance with XRD and XPS data, that indicated a rather good dispersion of Ta in these catalysts. The exposure of these catalysts to the reaction conditions led to the occurrence of two bands one located around 36,000 cm^{-1}, and another at ca. 29,300 cm^{-1}. Catalysts Ta-4-10 and Ta-4-12 make an exception. According to literature data the band located at 36,000 cm^{-1} can be assigned to Ta_2O_5 [6]. However, the size of these embedded nano-oxides should still be small since XRD not indicate reflection lines due to Ta_2O_5. The band at ca. 29,300 cm^{-1} could be assigned to the increase of tantalum coordination as a consequence of exposure to H_2O_2. This band disappeared when the catalysts were heated. Successive exposures of the catalysts in several runs did not change these spectra.

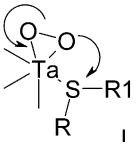
In conclusion these studies show that even if no tantalum was found by ICP-AES analysis in the mother liquor, H_2O_2 extracts tantalum, which agglomerates as XRD silent nano-Ta_2O_5 oxides, that are in fact the real catalyst. This process occurs in the presence of substrate.

4. Discussion

The characterization of the catalysts revealed a strong influence of the surfactant on the homogeneity of the mixed oxide. The increase of *n* and merely the presence of four large chains led to larger Ta_2O_5 nanoxides. The agglomeration of tantalum is enhanced by the exposure of the catalysts to H_2O_2 in the catalytic conditions. However, the size of Ta_2O_5 is still small since it is XRD silent.

The size of Ta_2O_5 nano-clusters and the solvent controlled the catalytic performances. Hence, small as well as very large particles of Ta_2O_5 generated overoxidation to sulfone. However, the solvent is very important in this process.

The oxidation of thioether to sulfoxide led to a change in the sulfur properties; in the first case the electron pairs imposing a basic character, while the presence of the oxygen transforms the sulfur in a Lewis acid. The acidity of the catalysts plays an important contribution in this process and Lewis acids sites control the selectivity to sulfoxide. In addition, it is already known that Brønsted acids cause a non-selective decomposition of hydrogen peroxide [7]. The hydrogen efficiency measured with these catalysts confirmed FTIR results indicating the almost total absence of Brønsted acidity. The way in which Ta catalyses the selective sulfoxidation can only be speculated by comparison with Ti [8]. Since Ta may exhibit more coordinations than Ti [9], the thioether can be activated either by coordination at tantalum atom (**I**) (in this way the electron density at sulfur is lowered, and the reactivity towards nucleophilic oxygen enhanced), or directly by the peroxo group (**II**). The existence of peroxo species could be supposed from the DRUV-Vis spectra indicating an increased coordination of Ta:



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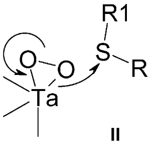

II

The 2-thiopyrimidine substrate is less reactive than other derivatives, such as phenyl, for example. The electron density on the sulfur atom is lowered by the −E effect of pyrimidine ring making these thioethers very reactive towards nucleophiles [10]. The solvent competes with thioether to chemisorb on peroxo species and both the variations in conversion and selectivity indicated that this competition is strongly related to the size of embedded nano-oxides. The experimental data indicated that Ta-4-10 and Ta-4-12 are very active in methanol, and Ta-4-12 and Ta-4-16 are very selective in dioxane. This means that from the point of view of the size of tantalum nano-oxides, these catalysts provide the better acidic properties of the exposed peroxo species.

In conclusion, oxidation of 2-thiomethyl-4,6-dimethylpyrimidine on nano-tantalum oxides occurred with very high conversion and chemoselectively. Both activity and selectivity were controlled by the size of Ta nanoxides.

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