

## Catalytic Properties of Au/HMS-Ti towards the oxidation of 1-hexene

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### Introduction

Catalytic oxidation in liquid phase is widely used in the manufacture of bulk chemicals [1,2], and it has become an important process in the synthesis of fine chemicals where traditionally, it has been employed inorganic oxidants. The use of heterogeneous catalysts in these reactions has the very well known advantage, compared to their homogeneous counterparts, of facile recovering and recycling.

Zeolites and other molecular sieves containing isolated framework Ti atoms have shown that they can be used as oxidation catalyst. However their catalytic performance depends strongly on several factors such as molecular sieve structure, temperature of the oxidation reaction, or the solvent used, but diffusion of substrate molecules as well as its acidic properties are the main concern. It makes catalysts prepared over a mesoporous material, a good choice to face up, in first instance, diffusion limitations. Besides, there are mesoporous silicas that possess surface hydroxyls (terminal) which are not strong acids. For example, the hexagonal mesoporous silica materials (HMS), exhibit high surface area (ca 1000 m<sup>2</sup>/g), with tunable pore size in the range 2-20 nm (pore diameter).

The selective oxidation of ethylene to ethylene oxide is an important catalytic process, and it has been examined for a series of metallic catalysts supported on low or relatively high surface area oxides (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, etc.). It has been found that Ag catalysts were active with all of the supports in the isomerization/oxidation of ethylene oxide. The activity of these catalysts was related to the surface acidity of the supports. Additionally, an effect of the type of oxygen species bonded on silver atoms has been proposed [3].

In order to explore other metallic systems able to run out the oxidation of olefins, in this work we report preliminary results of the catalytic properties of gold catalysts supported on hexagonal molecular silica modified by titanium (TiHMS), towards the oxidation of 1-hexene in liquid phase using H<sub>2</sub>O<sub>2</sub> as oxidizing agent. A gold catalyst supported on a commercial TiO<sub>2</sub> was used for comparison.

### Materials and Methods

HMS as well as Ti-HMS with a molar 8% Ti content were synthesized by sol-gel method by using dodecylamine (DDA), as a template; tetraethyl orthosilicate (TEOS) dissolved in ethanol and tetra-isopropyl-orthotitanate (TIPO) in isopropanol were the Si and Ti sources, respectively. The resulting gel was aged at room temperature for 20 h, filtered, washed with distilled water, dried at room temperature, and calcined at 723 K for 6 h. TiO<sub>2</sub> P25 from Degussa was used for the catalyst for comparison. HMS-Ti and HMS supports were characterized by XRD, UV-Vis diffuse reflectance and N<sub>2</sub> physisorption.

The supported Au catalysts were prepared by a deposition-precipitation (DP) method as described in [4]. An aqueous solution of HAuCl<sub>4</sub>·4H<sub>2</sub>O was used to obtain 1 wt% of

Au. The catalysts were analyzed by temperature-programmed reduction (TPR) with H<sub>2</sub> and transmission electron microscopy (TEM).

The oxidation reactions were carried out in a 50 mL thermostated glass reactor, mechanically stirred. In a standard procedure, 20 mg of catalyst, 0.0162 mol of 1-hexene, 0.014 mol of mesitylene (internal standard) and 0.371 mol of CH<sub>3</sub>OH as solvent were added. The mixture was heated to 333 K, 0.0161 mol of H<sub>2</sub>O<sub>2</sub> 30 % was added, and the reaction started with constant stirring. The total reaction volume was 19.5 mL. The reaction mixture was analyzed using a Shimadzu 8A gas chromatograph (GC) equipped with an Alltech 20% SE-30 column and FID. The reaction products were identified by using standard compounds injected to the GC. Reaction conversion (mol%) was determined at 360 min of reaction.

### Results and Discussion

The XRD patterns of the HMS-Ti support confirm that this material presented the expected HMS structure. A higher S<sub>BET</sub> and a unimodal distribution diameter pore centered at ca. 3.0 nm was obtained.

TEM showed large-sized metallic particles (ca. 6 nm) on both supported catalysts.

Catalytic activity experiments for the oxidation of 1-hexene were carried out at 333 K. The results are shown in Table 1. Only, Au/HMS-Ti and Au/TiO<sub>2</sub> were active catalysts in the 1-hexene oxidation reaction. However, in both catalysts 1,2-hexanediol was observed as the only product. 1,2-epoxy-hexane was not detected. Au-HMS-Ti supported catalyst showed higher activity than the one prepared on commercial titania. The change in activity may be related with the dispersion of TiO<sub>2</sub>, which in turn is related with the mesoporous structure of the first one.

The superior performance of Au/HMS-Ti in terms of activity over Au/TiO<sub>2</sub> can also be attributed to its three dimensional pore system, which should be more resistant to blockage than the pore system of TiO<sub>2</sub>.

**Table 1. Textural properties and reaction conversion (%mol) on oxidation of 1-hexene**  
(T<sub>R</sub> = 333 K, t<sub>R</sub> = 360 min; m<sub>c</sub> = 20 mg; atmospheric pressure).

Catalyst	S <sub>BET</sub> (m <sup>2</sup> /g)	d <sub>pore</sub> (nm)	Conversion (mol%)
Au/SiO <sub>2</sub>	70	n. d.	0
Au/HMS	359	6.9	0
Au/TiO <sub>2</sub>	54	3.0	17
Au/HMS-Ti	384	9.7	36

### Significance

This work is a preliminary study of gold catalysts for epoxidation reactions. Characterization and catalytic activity will be correlated to the HMS-Ti composition and gold dispersion.

### References

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