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Nanocrystalline gold supported on Fe-, Ti- and Ce-modified hexagonal mesoporous silica as a catalyst for the aerobic oxidative esterification of benzyl alcohol

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ABSTRACT

The materials containing gold nanoparticles supported on pure and Ce, Ti, or Fe-modified hexagonal mesoporous silica were prepared and their structural and electronic properties were studied by XRD, TEM, XPS, and N₂ adsorption techniques. The materials were shown to be effective heterogeneous catalysts for the liquid-phase aerobic oxidation of benzyl alcohol in methanol solutions. It was found that the modifiers significantly improve the catalytic properties of supported gold particles and allow performing the selective one-pot oxidative esterification of benzyl alcohol resulting in methyl benzoate. The modified catalysts exhibited high activity (turnover frequencies of up to ca. $1000 h^{-1}$), selectivity to methyl benzoate (up to 95%), and stability (turnover numbers of up to ca. 4300). Ce and Ti were found to be more effective promoters as compared with Fe in terms of catalyst stability.

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1. Introduction

Recent discoveries have demonstrated the catalytic activity of nanoparticles of gold in various chemical transformations, such as low temperature CO oxidation, hydrogen oxidation, hydrochlorination of acethylene, and some other processes [1–6]. These results are truly remarkable considering that metallic gold is known to be virtually non-reactive in a bulk form. The explosive progress of nanoscience over the past two decades has stimulated a constant growth of publications reporting the catalytic activity of nanosized gold in organic reactions [4–6]. In particular, supported gold catalysts were found to be promising substitutes for platinum group metals in the aerobic oxidations of alcohols [7,8].

The oxidation of alcohols to carbonyl compounds is a vital organic transformation in both laboratory and industrial synthetic chemistry. It is considered as one of the most challenging reactions in green chemistry [8] as many commonly used processes still require stoichiometric amounts of expensive and/or toxic heavy metal oxidants and, therefore, produce large amounts of waste. Several homogeneous [9,10] and heterogeneous [11–14] transition

metal catalysts were reported to promote the oxidation of alcohols with molecular oxygen as the final oxidant. These processes occur with high atom efficiency and give water as the only byproduct, which is especially relevant to a green chemistry concept. Among the catalysts reported for the aerobic oxidation of alcohols, materials containing supported gold nanoparticles are considered as the most promising ones due to their high activity and stability [4–8].

However, the oxidation of alcohols over gold catalysts under mild conditions requires the presence of base (typically NaOH), often in over-stoichiometric amounts [5]. In these reactions, sodium salts of carboxylic acids rather than acids themselves are, therefore, obtained as products. To avoid the use of a base in large amounts it has been recently suggested to perform the reaction in methanol solutions [15–20]. In these systems, methyl esters instead of carboxylic acids are formed as final products. Thus, the base is not consumed stoichiometrically and only catalytic amounts are needed to promote the reaction.

Methyl esters are commercially valuable chemicals used as flavoring agents, solvents, diluents, extractants, etc. Methyl esters are traditionally prepared by two-step procedures, which include the synthesis of carboxylic acids or their derivatives, such as chlorides and anhydrides, and further esterification of these compounds with methanol. Most of the reported examples of the direct transformation of alcohols into methyl esters employ stoichiometric oxidants,

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such as molecular iodine [21] or hypochlorite [22]. Only a few catalysts capable to promote the oxidative esterification of alcohols with molecular oxygen as a final oxidant have been reported, with all of them being based on gold nanoparticles, as far as we know [15–20].

In gold catalysis, the nature of the support is known to be a crucial factor because the catalyst performance strongly depends on the size and morphology of gold particles as well as on their interaction with the support [5]. A wide variety of solids has been tested in an attempt to stabilize gold nanoparticles and to influence their catalytic properties. The aim of the present work is to explore the application of hexagonal mesoporous silica (HMS) as a support for the preparation of gold catalysts for the oxidation of alcohols.

HMS materials have a strong potential in catalysis due to their high surface area and uniform mesoporous structure [23]. A high hydrophobicity of HMS is a particularly advantageous property for gold-catalyzed aerobic oxidations because these reactions produce water and are usually performed in aqueous or alcoholic solutions. HMS materials are prepared by a neutral S⁰I⁰ templating route [24,25], in which primary amines are used as neutral organic surfactants (S⁰). In the course of the material formation, a self-assembly involves hydrogen-bonding interactions between S⁰ and a neutral inorganic precursor (I⁰). Due to the absence of strong electrostatic interactions, the organic phase can be completely removed from HMS materials by solvent extraction preventing the partial degradation of a mesoporous structure at calcination, as it often happens with MCM-41 materials produced with ionic surfactants [26]. HMS materials show a wormhole like pore structure and are less ordered than MCM-41; however, they are more stable thermally and allow faster diffusion of reactants due to shorter mesopores.

The techniques used for the synthesis of HMS opens the opportunity for the one-pot introduction of transition metal ions into the material via either a direct inclusion into the silica framework or the formation of individual highly dispersed metal oxides embedded in the HMS matrix [26]. Such metal modified HMS materials exhibit different redox and acidic properties and can show higher stability and activity in catalytic processes. For example, it has been reported that the incorporation of Ti into HMS enhances the activity of Co-Mo/HMS catalysts in the hydrodesulfurization of dibenzothiophene [27]. In the case of gold catalysts, it is especially valuable that the modification of the HMS support can help to stabilize gold nanoparticles preventing their aggregation. It has been recently reported that Ce-containing Au/HMS materials are more active in the oxidation of CO than their Ce-free counterpart, probably, due to higher gold dispersion and higher redox ability of the support [28]. In the liquid phase hydrogenation of biphenyl, Au/HMS-Ce and Au/HMS-Fe catalysts have also exhibited higher stability to sintering compared to the unmodified Au/HMS catalyst [29]. The Au/HMS-Fe material has demonstrated, in addition, significantly higher activity, probably, due to higher exposure of $Au^{\delta+}$ species [29].

In the present work, we have prepared the materials containing gold nanoparticles supported on pure and metal modified HMS (HMS-M, where M = Ce, Ti, Fe) and studied their catalytic behavior in the aerobic oxidative esterification of benzyl alcohol. Benzyl alcohol was chosen as a test reactant for this reaction. To our knowledge, the application of gold catalysts supported on HMS to the oxidation of alcohols has not yet been studied.

2. Experimental

2.1. Support preparation

HMS was synthesized by a neutral S^0I^0 templating route (S^0 -neutral primary amine surfactants; I^0 -neutral inorganic

precursor) as described previously [28–30]. Dodecylamine was employed as a surfactant and mesitylene as a swelling organic agent [31]. The Ce-, Fe-, and Ti-modified HMS materials (denoted as HMS-Ce, HMS-Fe, and HMS-Ti, respectively) were prepared by a direct synthesis via co-precipitation using cerium(III) nitrate hexahydrate, iron(III) nitrate nonahydrate, and tetrabuthyl orthotitaniate as Ce, Fe, and Ti precursors, respectively. The Si/M (M = Ce, Fe, Ti) atomic ratio of 40 was used in the preparation of all materials. The reaction products were filtered, washed with distilled water, and dried at room temperature for 24 h and at 100 °C for 2 h. The template was then removed by calcination at 550 °C for 3.5 h in air, at a heating rate of $2.5 °C min^{-1}$.

2.2. Synthesis of Au(en)₂Cl₃

Ethylenediamine (0.45 mL) was slowly added to the solution of HAuCl₄·3H₂O (1.0g) in deionized water (10 mL). The transparent brown solution was magnetically stirred for 30 min. Then, ethanol (70 mL) was added to this solution resulting in the formation of a white precipitate. The suspension was stirred for additional 20 min and filtered. The solid was washed with ethanol and dried at 40 °C in vacuum overnight.

2.3. Catalyst preparation

Au(en)₂Cl₃ (0.05 g) was dissolved in water (50 mL) and the pH of the solution was adjusted to 10.0 by the addition of the aqueous solution of NaOH (5.0 wt%). Then, HMS or HMS-M (1.0 g) was added. The pH of the solution, which dropped after the addition of HMS, was re-adjusted to ca. 10.0. The suspension was stirred at $60-70 \,^{\circ}$ C for 2 h and filtered. The solid was washed with distilled water and dried in vacuum at $70 \,^{\circ}$ C for 5 h. Finally, the catalysts were thermally treated at 300 $^{\circ}$ C in air for 1.5 h to ensure a complete removal of the organic template and then in hydrogen for 1.5 h.

2.4. Catalyst and support characterization

2.4.1. Chemical analysis

Metal contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Perkin Elmer Optima 3300DV instrument. Solid samples were first digested in a mixture of HF, HCl, and HNO₃ in a microwave oven for 2 h. Then, the solutions were diluted with deionized water and analyzed.

2.4.2. High resolution transmission electron microscopy (HRTEM)

HRTEM studies were carried out using a JEM 2100F microscope operating with a 200 kV accelerating voltage. The samples were ground into a fine powder and dispersed ultrasonically in hexane at room temperature. Then, a drop of the suspension was put on a lacey carbon-coated Cu grid. At least ten representative images were taken for each sample. In order to obtain statistically reliable information, the length of ca. 500 particles was measured. A particles size distribution was obtained by counting more than ca. 500 particles for each sample. Particle size diameters were calculated from the following equation: $d_{avg} = \sum (n_i d_i) / \sum n_i$.

2.4.3. X-ray diffractometry (XRD)

The catalysts were characterized by powder XRD according to the step-scanning procedure (step size 0.02° ; 0.5 s) with a computerized Seifert 3000 diffractometer, using Ni-filtered CuK α (λ = 0.15406 nm) radiation and a PW 2200 Bragg-Brentano $\theta/2\theta$ goniometer equipped with a bent graphite monochromator and an automatic slit. The assignment of crystalline phases was based on the JPDS powder diffraction file cards.

1	Textural properties of the supports and Au/HMS catalysts. ^a							
	Sample	$S_{BET} (m^2 g^{-1})$	NS _{BET}	Average pore diameter (nm)	$V_{\rm total}~({ m cm^3~g^{-1}})$			
	LINAC	767	4	7.0	1 20			

HMS	/6/	1	7.9	1.20
HMS-Ce	667	1	6.4	0.82
HMS-Fe	847	1	6.7	1.02
HMS-Ti	795	1	8.5	1.46
Au/HMS	687	0.92	7.1	1.14
Au/HMS-Ce	572	0.88	6.0	0.62
Au/HMS-Fe	726	0.88	6.2	0.83
Au/HMS-Ti	714	0.92	8.2	1.25

^a S_{BET} : BET surface area; NS_{BET}: normalized S_{BET} ; V_{total} : total pore volume.

2.4.4. X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed on a VG Escalab 200R electron spectrometer equipped with a hemispherical electron analyzer, using a MgK α ($h\nu$ = 1253.6 eV, 1 eV = 1.603 × 10⁻¹⁹ J) X-ray source. After degassing at 10⁻⁶ mbar, the samples were transferred to an ion-pumped analysis chamber, in which the residual pressure was kept below 4 × 10⁻⁹ mbar during the data acquisition. The binding energy (BE) of the C 1s peak at 284.5 eV was taken as an internal standard. The accuracy of BE values was ±0.1 eV. Peak intensities were estimated by calculating the integral of each peak after subtracting an S-shaped background and fitting the experimental peak to a combination of Lorentzian/Gaussian lines of variable proportions.

2.4.5. N₂ adsorption-desorption isotherms

The textural properties of supports and catalysts were determined from nitrogen adsorption–desorption isotherms ($-196 \,^{\circ}$ C) recorded with a Micromeritics TriStar 3000 apparatus. Prior to experiments, samples were degassed at 270 $\,^{\circ}$ C in vacuum for 5 h. The volume of the adsorbed N₂ was normalized to a standard temperature and pressure. The specific areas of the samples were calculated by applying the BET method to the nitrogen adsorption data within the 0.005–0.25 *P*/*P*⁰ range. An average pore diameter was calculated by applying the Barret–Joyner–Halenda method (BJH) to the adsorption and desorption branches of the N₂ isotherms. A cumulative pore volume was obtained from the isotherms at *P*/*P*⁰ = 0.99.

In order to verify the evolution in the structural parameters of the samples after the introduction of gold, the normalized S_{BET} values were calculated using the following equation:

$$NS_{BET} = \frac{S_{BET of catalyst}}{(1 - y) \times S_{BET of the support}}$$

where NS_{BET} is normalized S_{BET} and y is the weight fraction of the gold phase.

2.5. Catalytic oxidation experiments

The reactions were carried out in a stainless steel reactor equipped with a magnetic stirrer. In a typical run, a mixture of benzyl alcohol (2.5 mmol), methanol (2 mL), K_2CO_3 (if any), and the catalyst (7.5–15.0 mg, ca. 0.4–0.8 wt%) was transferred in the reactor. The reactor was pressurized with oxygen to the total pressure of 10 atm and placed in an oil bath; then, the solution was intensively stirred at 110–130 °C for the reported time. The reactions were followed by gas chromatography (GC) (Shimadzu 17 instrument, Carbowax 20 M capillary column) using anisol as an internal standard. At appropriate time intervals, stirring was stopped and after catalyst settling aliquots were taken and analyzed by GC. To ensure correct GC results, the aliquots were diluted fourfold with methanol before the analysis because of the high initial concentra-



Fig. 1. Nitrogen adsorption–desorption isotherms for the Au/HMS catalysts at $-196\,^\circ\text{C}.$

tion of benzyl alcohol (1.25 M). Products were identified by GC–MS on a Shimadzu QP2010-PLUS instrument operating at 70 eV.

3. Results and discussion

3.1. Characterization of the catalysts

BET surface areas, average pore sizes, and total pore volumes for all prepared catalysts and pure supports are presented in Table 1. The results show that the addition of modifiers only slightly affects the structure of the HMS support. Moreover, in some cases the changes fall within an experimental error and no general correlations can be formulated. The presence of Ce decreases the surface area of HMS; whereas for the HMS-Fe sample the area is higher than for its unmodified counterpart. The influence of Ti on the support characteristics is almost negligible. The introduction of Ce and Fe decreases the average pore size and total pore volume; on the other hand, the introduction of Fe increases these characteristics.

In the presence of gold, surface areas of all supports slightly decrease (ca. 10%), which is expected because of partial blocking of the pore volume. The textural properties of the catalysts were evaluated from the nitrogen adsorption–desorption isotherms (Fig. 1). All catalysts exhibit type IV isotherms and H1 hysteresis loops (in the UPAC classification), which indicate the presence of textural mesopores and uniform cylindrical pores with facile pore connectivity. The Au/HMS and Au/HMS-Ti catalysts show two well defined capillary condensation steps: the first one at $P/P^0 \approx 0.45$ indicates the presence of framework mesoporosity, whereas the second one at $P/P^0 \approx 0.85$ is related to the textural interparticle mesoporosity or macroporosity. The adsorption isotherms of the Au/HMS-Ce and Au/HMS-Fe samples show smaller sharpness indicating lower pore uniformity in these materials.

Chemical analysis data (Au, Ce, Fe, and Ti contents) obtained by ICP and the values for the average size of gold particles and their surface density obtained by HRTEM are presented in Table 2. It can be seen that the modification of the HMS support by any of the tested metals significantly improves the efficiency of the gold incorpo-

Table 2
Chemical analysis and HRTEM data for the Au/HMS catalysts.

Catalyst	Au content (wt%)	Ce, Fe, or Ti content ^a (wt%)	Surface density of Au particles (parti- cles/1000 nm ²)	Average Au particle size (nm)
Au/HMS	2.19		4.4 ± 0.3	5.4 ± 0.2
Au/HMS-Ce	2.94	9.6	5.1 ± 0.2	5.9 ± 0.5
Au/HMS-Fe	2.87	4.1	6.5 ± 0.3	4.1 ± 0.4
Au/HMS-Ti	2.96	2.3	5.7 ± 0.2	4.8 ± 0.3

^a Determined for the supports.

ration. In the Au/HMS-M samples, the Au content is higher than in Au/HMS (ca. 2.9 wt% vs. 2.2 wt%). The density of gold particles on the surface of the modified samples is also higher. TEM images show that Au/HMS-Ce contains bigger gold particles as compared with the unmodified Au/HMS sample, while in Au/HMS-Ti and, especially, in Au/HMS-Fe the particles are smaller. However, it should be mentioned that the average size of gold nanoparticles in all samples is within the region of ca. 4–6 nm and these differences between the samples are not substantial.

Thus, we can conclude that the effects of the modifier on the structural properties of the materials do not follow general tendencies. For example, the presence of Ce decreases the surface area of the support and increases the average size of gold particles on the catalyst surface; whereas Fe exerts an opposite influence. The effect of Ti on the textural properties of the support is less pronounced; however, slightly smaller gold particles can be obtained on the HMS modified with Ti.

XRD spectra of the catalysts are presented in Fig. 2. All XRD patterns show the presence of Au(0) microcrystallites, with no defined peaks characteristic of Ce, Fe, and Ti oxides being observed. Thus, the ions of modifiers seem to be essentially incorporated in the silica framework of the HMS material so that the amounts of extraframework metal oxides (if any) are small. The amorphous behavior of all samples observed within the 20–30° 2θ region is due to the amorphous silica matrix.

It should be noted that both TEM and XRD methods do not allow the observation of small gold clusters on the material surface. In our previous studies [32], we have found that the formation of metal nanoparticles on the surface is often accompanied by the formation of small metal clusters with a diameter of less than 1 nm. A study of these small particles is a complicated task due to the difficulty of their detection by standard structural methods, such as XRD and TEM. As a result, the catalytic activity of only TEMand XRD-detectable gold nanoparticles is discussed in the major-



Fig. 2. XRD pattern for the Au/HMS catalysts.



Fig. 3. XP spectra of Au 4f core level for the Au/HMS catalysts before the treatment in H_2 .

ity of published studies, whereas the contribution of small clusters is usually ignored. However, the presence of metal clusters and their relative amounts can exert a significant effect on the catalytic properties of supported metals [33,34].

The surface composition of the catalysts and chemical states of surface gold species were investigated by XPS. The spectra were registered for the catalysts before the treatment in H₂ (after the treatment at 300 °C in air for 1.5 h). These samples are denoted as the oxidized catalysts. The XP spectra of Ce 3d, Fe 2p, and Ti 2p core electron levels for the oxidized catalysts (not shown here) are in agreement with those previously reported for the Au/HMS-M (M = Ce, Fe, Ti) catalysts used in biphenyl hydrogenation [29]. The XP spectra of the Ce 3d core level reveal the presence on the surface of both Ce^{3+} and Ce^{4+} species ($Ce^{3+}/Ce^{4+} = 0.32$). For the Au/HMS-Fe sample, the Fe $2p_{3/2}$ BE at 710.9 eV and satellite line at 717.3 eV indicates the presence of Fe³⁺ ions [35]. The XP spectrum of Ti $2p_{3/2}$ shows two components with BEs at 460 and 458.5 eV. The high intensity component at 460.0 eV is due to the presence of Ti⁴⁺ ions in a tetrahedral coordination, whereas the low intensity Ti $2p_{3/2}$ component at 458.5 eV is characteristic of Ti4+ ions in an octahedral coordination [36].

The XP spectra of the Au 4f core electron levels for the oxidized Au/HMS catalysts are presented in Fig. 3. A spectra analysis shows that in all samples gold exists on the surface in at least two forms: as Au^0 or $Au^{\delta+}$ (BE = 84.3 eV) and as Au^+ (BE = 85.7 eV). In addition, a low BE signal at 83.0 eV can be observed in the spectra of all samples. The latter signal could be assigned to small clusters of metallic gold formed on the surface which bear some negative charge due to the electron transfer from the support (Au^{δ -} species). The formation of such negative states of gold was previously suggested in [37–39]. On the surface of Au/HMS, the relative amount of the cationic states of gold is much higher than that in the modified samples, whereas the contribution of the low BE signal is negligible (Fig. 3 and Table 3). On the other hand, in the spectra of all modified samples, the relative intensity of the signal at 85.7 eV is low, whereas the signal at 83.0 eV, assigned to small gold clusters, is much more pronounced than in the unmodified sample (Fig. 3 and Table 3). Thus, it seems that gold supported on the pure HMS is more susceptible to oxidation as compared to the modified HMS.

Table 3

Relative signal contributions in the XP spectra for the oxidized Au/HMS catalysts (Fig. 3).

BE (eV)	Au/HMS	Au/HMS-Ti	Au/HMS-Ce	Au/HMS-Fe
83.0	5%	29%	25%	33%
84.3	33%	67%	57%	55%
85.7	62%	4%	18%	12%



Fig. 4. XP spectra of Au 4f core level for the Au/HMS catalysts after the treatment in H₂.

The reduction of the catalysts by the treatment in H_2 resulted in the significant shifts of the signals in their XP spectra toward the low BE region. The signals attributed to gold now appear at 82.7, 83.9, and 85.0 eV instead of 83.0, 84.3 and 85.7 eV (Fig. 4 and Table 4). Although the XP spectra of all reduced samples are rather similar (Fig. 4), it can be noted a significant increase in the contribution of the low-energy signal (82.7 eV) in the spectrum of Au/HMS after the reduction (Table 3 vs. Table 4).

Although the XPS technique did not detect the presence of Au³⁺ ions in the samples, since a peak at BEs of about 86.7 eV was not detected, we cannot discard their existence on the catalyst surface, especially, in the oxidized catalysts considering that during the XPS measurements the ions can be reduced by the X-ray beam.

Thus, the XPS study showed that the introduction of the modifier in the HMS support changes significantly the redox properties of supported gold as well as its electronic state. These differences can influence the catalytic behavior of the sample, especially, under oxidative conditions. In our work, the reduced samples, in which the electronic state of supported gold seems to be similar, have been used for the catalytic tests. However, under the reaction conditions, gold species should be oxidized, at least partially, due to the

Table 4	
Relative signal contributions in the XP spectra for the Au/HMS catalysts (Fig	. 4).

BE (eV)	Au/HMS	Au/HMS-Ti	Au/HMS-Ce	Au/HMS-Fe
82.7	25%	35%	25%	30%
83.9	50%	49%	59%	53%
85.0	25%	16%	16%	17%

Ph-CH₂OH
$$\xrightarrow{Au/HMScatalyst}_{O_2,methanol}$$
 PhCHO + PhCO(OCH₃)
1 2 3

Scheme 1. Oxidation of benzyl alcohol 1 into benzaldehyde 2 and methyl benzoate 3.

adsorption of molecular oxygen. Thus, the difference in the oxidative ability of gold could become of a crucial importance for the performance of the catalyst in the oxidation of alcohols.

3.2. Catalytic studies

The catalytic activity of the Au/HMS and Au/HMS-M (M = Ce, Ti, Fe) samples in the oxidation of benzyl alcohol (1) was examined in methanol solutions. In all experiments, these materials were applied together with potassium carbonate as the base co-catalyst, used in sub-stoichiometric amounts (usually 0.16 equiv.), under the atmosphere of molecular oxygen. The results are presented in Tables 5 and 6.

All gold containing samples effectively catalyzed the oxidation of benzyl alcohol showing high activities, whereas in the presence of the supports (HMS, HMS-Ce, HMS-Fe, or HMS-Ti) or without any catalyst added the conversion of benzyl alcohol was negligible. The reaction gave two major products, benzaldehyde **2** and methyl benzoate **3** (Scheme 1), with a combined selectivity of 97–100% at nearly complete conversions. Only trace amounts of benzaldehyde dimethyl acetal and benzoic acid were detected in reaction solutions. The distribution of the products depended strongly on the nature of the doping metal in the HMS support and, for a given catalyst, on the reaction time. However, in most of the runs methyl ester **3** was a predominant product accounting for 60–90% of the products at the end of the reaction.

The reactions occurred with very low catalyst loadings (0.4–0.8 wt%) in highly concentrated solutions of the substrate in methanol, which allowed to achieve high concentrations of the products in final mixtures (up to 20 wt%). Turnover numbers (TONs) also reached high values (up to ca. 4300) reflecting the high stability of the catalysts. It should be mentioned that in the oxidation of alcohols over palladium systems, TONs rarely exceed a few hundred units [40]. These features represent the important technological advantages of the process. It is also important that the catalysts are solid materials which are insoluble in the reaction mixture and can be separated from the products by simple centrifugation or filtration and re-used (see below).

The oxidation of benzyl alcohol in the presence of Au/HMS occurred smoothly at 130 °C resulting in a 68% conversion for 2 h to give almost exclusively aldehyde **2** and methyl ester **3** in comparable amounts (Table 5, run 1). Keeping the mixture under stirring for more than 2 h resulted in a further substrate conversion up to nearly 80%; however, then the reaction became stagnated. The selectivity for the methyl ester increased to 60%, indicating that benzaldehyde was partially oxidized further to give the ester. On the other hand, over the Au/HMS-Fe, Au/HMS-Ce, and Au/HMS-Ti catalysts prepared from the modified supports, nearly complete conversions were obtained for 4 h under the same conditions (Table 5, runs 2–4).

The results of these runs correspond to the TONs of nearly 2000 with respect to the total amounts of gold in the material. However, the real efficiency of the surface gold atoms is much higher, because the dispersion of gold is obviously much less than 100%. Although all three catalysts on the modified silica have shown similar rates of the alcohol conversion under the conditions used in runs 2–4 (Table 5), there is a significant difference in the product distribution. The Au/HMS-Ce and Au/HMS-Ti materials promoted the almost complete oxidation of not only the alcohol but also the

Table 5
Au-catalyzed oxidation of benzyl alcohol (1) in methanol solutions.

Run	Catalyst	Time (h)	Conversion (%)	Product selectivity (%)		TON ^b
				Aldehyde 2	Ester 3	
1	Au/HMS	2	68	48	51	
		4	76	38	60	1790
2	Au/HMS-Fe	2	88	48	50	
		4	94	40	57	1640
3	Au/HMS-Ce	2	87	14	86	
		4	96	12	88	2040
4 ^c	Au/HMS-Ti	2	89	20	79	
		4	98	10	90	2110
5 ^d	Au/HMS-Ti	2	80	31	68	
		4	95	18	82	1960

^a Conditions: Substrate (2.5 mmol); catalyst (15.0 mg; ca. 0.8 wt%; Au: ca. 0.08 mol%); K₂CO₃ (0.4 mmol); methanol (2.0 mL); 130 °C; 10 atm (O₂). Conversion and selectivity were determined by GC.

^b TON is calculated as a ratio between the amounts of **2** and **3** formed and the total amount of Au, considering that **3** is formed from **1** via **2** and both steps are catalyzed by Au: TON = [n(2) + 2n(3)]/n (Au), where *n* represents the amount of the indicated compound or Au in moles.

^c After reaction, the catalyst was separated by centrifugation, the supernatant was added with a fresh portion of substrate and allowed to react on for 3 h, with no conversion observed thereupon. The separated catalyst was reused without loss of activity and selectivity.

^d 110 °C.

primarily formed aldehyde giving the ester. After the 4-h reactions in runs 3 and 4, selectivities for ester **3** were nearly 90%. On the other hand, the Au/HMS-Fe and Au/HMS samples produced the aldehyde and the ester in comparable amounts (runs 2 and 1, Table 5). Thus, gold nanoparticles supported on the unmodified or Fe-modified silica are less effective catalysts for the oxidative esterification of benzyl alcohol compared to the Ti- and Ce-modified counterparts. Namely, Au/HMS-Fe and Au/HMS seem to be less effective in the second step of this process: the oxidation of the primarily formed aldehyde to ester, at least under the conditions used in these runs.

Although it is unlikely that metallic gold could be soluble in methanol, we have tested leaching of the active component from the catalyst. To prove the absence of any contribution of homogeneous catalysis, the Au/HMS-Ti catalyst was removed from the reaction system after the completion of the reaction in run 4 (Table 5), fresh substrate was added to the supernatant and the reaction was allowed to proceed further. No activity was observed in this experiment, which indicates that Au did not leach from silica into the reaction medium under the conditions used. The catalyst can be recycled. After run 4 (Table 5), the catalyst was re-used after washing with hexane without any loss in its activity and selectivity.

The reactions in runs 1–4 (Table 5) were relatively fast showing nearly 90% conversions for 2 h, when the first aliquots were taken for the GC analysis. To compare the catalytic performance of different catalysts we decreased the reaction rate by decreasing the temperature and then the catalyst amounts. At 110 °C, the reaction was still too fast giving 80% conversion for 2 h (Table 5, run 5). In this run, it can be clearly seen the increase in ester selectivity with the reaction time. The result is consistent with a two-step mechanism involving the oxidation of alcohol to aldehyde and further oxidation of aldehyde to ester (see below). The individual selectivities to ester **2** and aldehyde **3** were different at 110 and 130 °C at almost the same conversions. It probably reflects a different effect of temperature on the rates of two steps of the whole process. However, the combined selectivity for the aldehyde and ester in both runs was ca. 100%.

The kinetic curve for the reaction at 110 °C with a half amount of Au/HMS-Ti (Table 6, run 6) is shown in Fig. 5. The reaction was almost completed in 6 h giving benzaldehyde and methyl benzoate in a nearly quantitative combined yield. The ester was a predominant product at the end of the reaction (95% selectivity), whereas at 42% conversion, it accounted only for ca. 50% of the mass bal-

Table 6

Au-catalyzed oxidation of benzyl alcohol (1) in methanol solutions.^a

Run	Catalyst	Time (h)	Conversion (%) Pro	Product selectivity	Product selectivity (%)		$TOF^{c}(h^{-1})$
				Aldehyde 2	Ester 3		
6	Au/HMS-Ti	1	43	47	50		
		4	91	10	90		
		6	96	4	95	4260	950
7	Au/HMS-Ce	1	43	60	40		
		4	94	12	88		
		6	98	5	94	4280	995
8	Au/HMS-Fe	1	42	54	46		
		4	69	40	60		
		6	70	39	60	2520	905
9	Au/HMS	1	23	66	33		
		4	58	50	49		
		6	60	51	48	2625	744
10 ^d	Au/HMS	6	58	54	45	2490	760
11 ^e	Au/HMS-Ti	6	<1	_	-	-	-

^a Conditions: Substrate (2.5 mmol); catalyst (7.5 mg; ca. 0.4 wt%; Au: ca. 0.04 mol%); K₂CO₃ (0.4 mmol); methanol (2.0 mL); 110 °C; 10 atm (O₂). Conversion and selectivity were determined by GC.

^b TON is calculated as a ratio between the amounts of **2** and **3** formed and the total amount of Au, considering that **3** is formed from **1** via **2** and both steps are catalyzed by Au: TON = [n(2) + 2n(3)]/n (Au), where *n* represents the amount of the indicated compound or Au in moles.

^c Initial rate of the substrate conversion per mol of Au (initial TOF).

^d K₂CO₃-0.6 mmol.

^e In the absence of K₂CO₃.



Fig. 5. Oxidation of benzyl alcohol over the gold catalysts. Conditions: substrate (2.5 mmol), catalyst (0.4 wt%), K₂CO₃ (0.4 mmol), methanol (2.0 mL), 110 °C, 10 atm (O₂).

ance. A behavior of other materials under the conditions used in run 6 (Table 6) has confirmed a remarkable effect of the doping metal on both catalytic activity and stability of supported gold in the oxidation of benzyl alcohol. The Au/HMS-Ce material has promoted the oxidative esterification of alcohol with efficiency similar to that of Au/HMS-Ti (Table 6, run 7 and Fig. 5). The data obtained with Au/HMS-Ce and Au/HMS-Ti correspond to the TONs of more than 4200 and to the turnover frequency (TOF) of ca. 1000 h⁻¹ in the 0–90% conversion range. These results compare well with most of the reported catalysts and put the prepared materials among the best gold catalysts developed for the oxidative methoxylation of benzyl alcohol [16,18–20]. It should be mentioned that reaction rates were not affected by changes in the intensity of stirring.

The reaction with the Au/HMS-Fe catalyst begins at almost the same rate as with Au/HMS-Ti and Au/HMS-Ce (TOF = 905 h⁻¹) and shows a similar performance until ca. 50% conversion (Table 6, run 8 and Fig. 5). Thus, the initial activity of gold nanoparticles is similar for all three catalysts regardless on the doping metal. However, the reaction with Au/HMS-Fe becomes stagnated at ca. 70% conversion after 3 h. Moreover, a product distribution is different from that for Au/HMS-Ti and Au/HMS-Ce. Benzaldehyde accounts for ca. 40% of the products after the 4-h reaction over Au/HMS-Fe and is not being converted further to the ester at longer reaction times. This result implies that the catalyst is losing its activity under the reaction conditions. In other words, despite Au/HMS-Fe is also a highly efficient catalyst for the oxidation of benzyl alcohol promoting more than 2500 catalytic cycles, it is not stable to the same extent as Au/HMS-Ce and Au/HMS-Ti and does not complete the reaction under the conditions used in this run. It should be noted that in this run the Au/HMS-Fe catalyst lost the activity in the oxidation of both the alcohol and primarily formed aldehyde as the conversion of both the substrate and the aldehyde became stagnated. Such a behavior could be related to less stability of gold nanoparticles in Au/HMS-Fe to aggregation under the reaction conditions due to the weaker support-catalyst interaction as compared to Au/HMS-Ti and Au/HMS-Ce.

The initial activity of the Au/HMS catalyst calculated per mol of Au (initial TOF = 744 h^{-1}) is significantly lower than that of the mod-

ified samples (TOF>900 h⁻¹). In addition, the reaction becomes stagnated at ca. 60% conversion (TON=2625) giving the equal amounts of the aldehyde and the ester (Table 6, run 9 and Fig. 5). In attempts to complete the reaction and to clarify the origin of the deactivation, we increased one-and-a-half times the amount of base (Table 6, run 10 vs. run 9). However, the reaction stagnation has been observed again at 60% conversion, indicating that the supported gold particles are no more able to activate molecular oxygen not because of the lack of base. It should be emphasized that a small amount of base is really necessary for the reaction to proceed since in the absence of base no conversion of the alcohol has been observed over Au/HMS-Ti (Table 6, run 11 vs. run 6). The base co-catalyst is considered to be necessary for the first abstraction of hydrogen from the substrate [5].

Thus, the results obtained reveal that the catalysts prepared from the HMS modified by any of tested metals are more active in the oxidative esterification of benzyl alcohol. The presence of the doping metal ions in the HMS framework influences the catalytic properties of the supported gold. The modifiers have changed the morphological properties of the HMS supports as well as those of the gold catalysts (Table 1). However, these changes are not significant and no direct correlations with the catalyst behavior have been observed. The differences in the average size of the gold particles are also not significant (Table 2). Thus, the activation effect of the doping metal should be associated with other factors, such as doping metal influence on the electronic state of gold, redox properties of gold nanoparticles, and/or their aggregation tendency.

According to the XPS data, the oxidized Au/HMS-M materials contain larger amounts of small gold clusters (signals at 83.0 eV, Fig. 3) than the unmodified Au/HMS sample. The modifiers seem to favor the formation of small gold clusters under oxidative conditions, at the expense of bigger gold nanoparticles. Gold atoms in these clusters probably bear some negative effective charge due to a strong interaction with the oxygen atoms of the modified surface acting as Lewis basic sites. It is reasonable to expect that small gold clusters are also active in the oxidation of alcohol and their relative amounts should influence the catalytic behavior of the material. In addition, higher susceptibility of gold on the unmodified surface to oxidation could also affect the catalytic activity of the Au/HMS sample.

Among the studied modifiers, Ce and Ti were found to be more effective promoters as compared to Fe in terms of catalyst stability (Table 6 and Fig. 5). The Au/HMS-Ce and Au/HMS-Ti materials perform a deeper oxidation of benzyl alcohol resulting in methyl benzoate as a virtually exclusive final product. On the other hand, the reactions over Au/HMS-Fe and Au/HMS give benzaldehyde and methyl benzoate in comparable amounts.

The mechanism proposed for the oxidative esterification of primary alcohols involves the formation of hemiacetal as a key intermediate as illustrated in Scheme 2 [16,19]. The alcohol is first oxidized to give the aldehyde as an intermediate product. The base co-catalyst seems to facilitate the abstraction of the first hydrogen from the substrate [5]. A condensation reaction between the aldehyde and alcohol results in a hemiacetal, whose further dehydrogenation gives the ester. Small amounts of benzaldehyde dimethyl acetal detected in the reaction solutions could be formed from the hemiacetal due to its interaction with a second molecule of methanol. Another minor product, benzoic acid, could be the result



Scheme 2. A proposed pathway for the oxidation of benzyl alcohol.

of the dehydrogenation of a hydrate formed by the interaction of the aldehyde with trace water instead of methanol. The oxidation of primary alcohols to carboxylic acids over gold catalysts is usually presented by a similar mechanism which involves the intermediate formation of an aldehyde followed by the formation of a hydrate and subsequent oxidation of the latter to a carboxylic acid [16].

4. Conclusions

Nanosized gold supported on HMS is an effective catalyst for the liquid-phase aerobic oxidation of benzyl alcohol. The modification of the support with Ce, Ti, or Fe ions improves significantly the catalytic performance of the materials. Ce and Ti are more effective promoters as compared to Fe in terms of catalyst stability. Although the modifier changes the morphological properties of the materials, no direct correlations with the catalyst behavior have been observed. The Au/HMS-Ce and Au/HMS-Ti materials efficiently perform the one-pot aerobic oxidative esterification of benzyl alcohol exhibiting high activity, selectivity to methyl benzoate and stability. The significant practical advantages of the process are the use of easily recoverable heterogeneous catalysts in very low loadings and molecular oxygen as a final oxidant as well as the possibility to obtain the desired product in high final concentrations. Large pore HMS catalysts could be especially important for the conversion of bulky molecules in the fine chemicals industry. Therefore, our further studies will be targeted toward the application of the Au/HMS catalysts for the oxidation of bulky biomass-based alcohols within our ongoing project aimed at adding value to the natural ingredients of renewable essential oils.

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