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Oxidation of CO and C_3 hydrocarbons on gold dispersed on oxide supports

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Abstract

Catalysts containing Au nanoparticles (1 wt.% Au) dispersed on oxides of main group elements, MGO (Mg, Si, Sn) and on transition metal oxides, TMO (Fe, Ti, Ce) were obtained by deposition–precipitation method, characterized by TPR, TEM, XPS and tested in oxidation of CO, C_3H_8 and C_3H_6. The catalysts with TMO as supports were considerably more active in the CO oxidation than those with MGO supports. The propane oxidation occurred at temperatures >250 °C, yielding only carbon oxides. In propene oxidation in the presence of H_2, the Au/MGO catalyst were active at temperatures >200 °C, giving mainly selective oxidation products (propanal, ethanal, acrolein), whereas total combustion was the main reaction in these conditions for Au/TMO catalysts. High selectivities to propene oxide (∼70%) were observed only for catalysts containing Ti in the support oxide at temperatures 100–150 °C. No clear correlations have been observed between the activity of the catalysts in the oxidation reactions and reducibility of the catalysts studied by H_2TPR, nor the dominating Au particle size.

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1. Introduction

Reports by Haruta et al. of high activity of Au nanoparticles deposited on oxide supports in low temperature oxidation of CO [1,2], have stimulated in the last decade extensive studies on catalytic properties of gold dispersed on or in oxide matrices in various reactions, reviewed in [3–5]. In addition to low temperature CO oxidation, the supported nanoparticles of Au were also tested in oxidation of hydrocarbons. Gold catalysts in mixture with Co_3O_4, NiO, MnO_x, Fe_2O_3 and CeO_x were active in total combustion of CH_4 at temperatures >250 °C [6]. The activity of Au dispersed on Fe_2O_3, $ZnFe_2O_4$, $NiFe_2O_4$, and Co_3O_4 in total combustion of methane, propene and propane at temperatures 200–400 °C was also reported [7]. Au–V_2O_5 and Au–ZrO_2 catalysts deposited on silica were found active in benzene total combustion at 250 °C [8–10]. Beside total oxidation, the dispersed Au particles, have been found active (though to a smaller extent) in selective oxidation reactions. Haruta and coworkers [11,12] and later Delgass and coworkers [13] have shown that—in the case in which the reaction mixture contains also hydrogen—Au nanoparticles on supports containing titania catalyze selective oxidation of propene to oxygenated products, propene oxide, PO being the main product (selectivity of 80–90%) at temperatures <∼140 °C. Ethanal, propanal and acetone were also observed at higher temperatures [13]. The conversion of propene and yield of PO were, however, very low (usually below 1%).

To date research on the supported nanoparticles of gold has been concentrated on studies of the effect of the preparation method on catalytic behavior of a given system in a selected reaction. The data on the mechanism of the reactions are rather scarce [3,4]. It is not clear, particularly, what is the role of the support in activation of the reactants.

In an attempt to search for the correlations between the nature and properties of the support oxide and catalytic performance of the Au/oxide systems in oxidation reactions, in the present work the catalysts containing Au (1 wt.%) dispersed on oxides of: (a) main group elements (Si, Mg, Sn) (group MGO), (b) transition metals (Fe [Fe_3O_4], Ti, Ce) (TMO), and (c) mixed SiTiO gels, have been prepared, characterized by TEM, TPR and XPS techniques and tested in oxidation of CO, propane, and propene.

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2. Experimental

The list, provenance, symbols and specific surface area of the supports and catalysts used in the studies are given in Table 1. The "home-made" supports were obtained by precipitation (SnO_2) or co-precipitation (mixed Ti–Si–O supports, with $Si(OC_2H_5)_4$ and $Ti(OC_3O_7)_4$ as precursors) and calcination at 550 °C.

The Au/oxide support catalysts were obtained by deposition–precipitation method at room temperature and pH 9.5–10, with the solution of $AuCl_3$ (5.09 wt.% Au) as a precursor of the active gold phase, following the procedure described in [14]. The content of Au was 1 wt.% in all the samples. The samples were calcined for 4 h at 400 °C in a stream of air. The symbols adopted in this table and further in the text are AuX, where X is a symbol of a cation in the oxide support:

- *Specific surface area* was determined with a BET method using AUTOSORB apparatus (QUANTACHROM) with nitrogen as an adsorbate.
- *The size of gold particles* was evaluated with electron microscopy TEM (Philips CM 20 + EDS + EDAX).
- *H_2-TPR measurements* were done using CHEMBET-3000 apparatus. The reduction was realized using H_2 (5 vol.%)/Ar mixture (10 ml/min) in the temperature range 30–550 °C at the heating rate 10 °C/min.
- *The XPS spectra* were recorded with a VG Scientific ESCA-3 spectrometer using Al $K\alpha_{1.2}$ radiation (1486.6 eV) from an X-ray source operating at 12 kV and 20 mA. The working pressure was better than 2×10^{-8} Torr (1 Torr = 133.3 Pa). The binding energies (BEs) were referenced to the C(1s) peak from the carbon surface deposit at 284.8 eV.
- *Catalytic activity* was studied in a fixed bed, flow microreactor (20 mm long, 8 mm i.d.) made of stainless steel, provided with a thermocouple located at the wall. The reactor was coupled on-line by six-way valves with a GC/MS system for analysis of the reaction mixture before, and after passing the reactor. For CO and C_3H_6 oxidation 0.75 ml of a catalyst sample was placed in a reactor, the total flow rate of the reaction mixture being 30 ml/min. The contact time, τ was ~1 s, GHSV ~3600 h^{-1}. For C_3H_8 oxidation τ was 4 s. The composition of the reaction mixture was regulated by mass flow controllers. The volume ratio of the components of the reaction mixtures was: $CO:O_2:He = 2:20:78$ vol.% for the CO oxidation. For C_3H_6 oxidation the reaction mixture contained hydrogen with the ratio of the components: $C_3H_6:O_2:H_2:He = 10:10:10:70$ vol.%. It had a composition used in studies of gas-phase epoxidation of propene [11,12], the presence of hydrogen favoring the formation of hydroxyperoxoradicals. In C_3H_8 oxidation 7.1% of C_3H_8 in air (a mixture used previously in oxidative dehydrogenation [15]) was used. The experiments were performed beginning from 30 °C for fresh (as-received) catalysts and in some cases after pre-activation for 0.5 h at 175 °C in a stream of 20% H_2 in He. The provenance and purity of the gases used was as follows: CO (Linde, 99.97%), C_3H_6 (Fluka, purum), C_3H_8 (Shell Gas >97%), O_2 (BOC 99.7%), He (Linde, 99.999%). The supports were found inactive in the conditions of the studies.

3. Results and discussion

Table 1 summarizes the data of the characterization of the catalysts obtained with various physicochemical techniques. The specific surface area of the catalysts is in most cases lower or comparable to that of a given support, the only exception being AuMg sample for which the increase in the specific surface was observed. The increase in the specific surface area after deposition of an active phase on magnesia was observed earlier for CrO_x/MgO catalysts and ascribed to the formation of magnesium hydroxide during the preparation of the catalysts in aqueous medium [16]. The H_2 TPR technique showed that most of the supports and the catalysts were not reduced by hydrogen up to 550 °C, the TPR signals below this temperatures being observed only for the samples with Fe, Sn and Ce oxides. Columns 3 and 4 of Table 1 give the values of T_{max} and intensities of the TPR signals (in brackets) for pure Sn, Ce and Fe oxide supports and the Au catalysts dispersed on them. For the last three supports, the

Table 1
Characteristics of Au-based catalysts and their supports

Catalyst symbol (specific surface area, m^2/g)	Support, origin (specific surface area, m^2/g)	T_{max} (°C), H_2 TPR data (signal value at T_{max}, a.u.)		BE (eV), XPS data of Au(4f)	TEM data dominating (minimal) size of Au particles (nm)
		Support	Catalyst		
AuTi (57.0)	TiO_2, Tioxide (54.0)	–	–	83.4	3–6 (3)
AuMg (114.0)	MgO, Ubichem (72.0)	–	–		
Au25Ti75Si (246.0)	25%$TiO_2$75%SiO_2, "home-made" (280.0)	–	–	83.6	20–35 (8)
Au75Ti25Si (40.4)	75%$TiO_2$25%SiO_2, "home-made" (58.0)	–	–	83.3	6–10 (3)
AuSn (6.2)	SnO_2, "home-made" (6.8)	311 (9)	273 (6)		
AuCe (2.0)	CeO_2, Fluka (5.4)	384 (4)	240 (4.3)	83.8	10–20 (5)
AuSi (176.0)	SiO_2, Aerosil 200 (175.0)	–	–	83.4	3–10 (3)
AuFe (11.5)	Fe_3O_4, Cerac (12.5)	456 (120)	311 (66), 426 (88)	83.6	10–20 (5)

deposition of Au leads to a decrease in the T_{max}. In the case of the AuFe catalyst, an additional, low temperature peak is observed with $T_{max} = 311\,^{\circ}C$. These facts suggest that the presence of Au particles facilitates activation of a hydrogen molecule, this latter process being usually considered as the r.d.s. of the reduction. The values of the binding energy (BE) for Au(4f) level correspond to that of metallic gold.

3.1. CO oxidation

The activity of the catalysts in the CO oxidation was found to depend on the type of the oxide support. The catalysts with TMO as the supports were active already at low temperatures 30–100 °C with the CO conversions close to 100%, whereas those supported on MGO were less active, showing measurable conversions at temperatures higher than ~200 °C. The pretreatment of the catalysts in hydrogen led to the increase in the activity. The temperature of the 100% conversion, T_{100} for the first group of catalysts, which can be considered for practical applications as a measure of the activity, increased (i.e. the activity decreased) in the sequence:

$$\mathrm{AuTi}\,(50) < \mathrm{AuFe}\,(100) < \mathrm{Au75Ti25Si}\,(150) = \mathrm{AuCe}^{H}\,(150)$$

where the number in brackets after the catalyst symbol is T_{100} in °C and letter H in the superscript here and hereafter denotes reaction after activation in H_2. Fig. 1 gives TOF (calculated per total number of Au moles in the sample) and CO conversions at 50 and 100 °C for this group of catalysts. For the AuTi sample, which at 50 °C and without activation in H_2 gave already 100% CO conversion, the TOF value at 30 °C (corresponding to 90% conversion) is given. For comparison, the data for 30 °C for the AuFe catalyst (the only other catalyst showing measurable conversion at this temperature) are also shown. As seen from the above results, the AuTi catalyst is the most active of this group, even without the hydrogen activation. For the Au MGO catalysts the highest conversions and the temperatures at which these conversions were obtained are given by the following sequence:

$$\mathrm{Au25Ti75Si}^{H}\,(75/350) > \mathrm{AuMg}^{H}\,(60/250) > \mathrm{AuSn}^{H}\,(54/350) > \mathrm{AuSi}^{H}\,(46/350)$$

where numbers in brackets correspond to CO conversion in %/temperature in °C. The TOF values ($\times 10^{-3}\,s^{-1}$, below in brackets) for this group of catalysts at 300 °C decrease in the series:

$$\mathrm{Au25Ti75Si}\,(23) > \mathrm{AuSi}\,(11) > \mathrm{AuMg}\,(8) > \mathrm{AuSb}\,(2.5) > \mathrm{AuSn}\,(2)$$

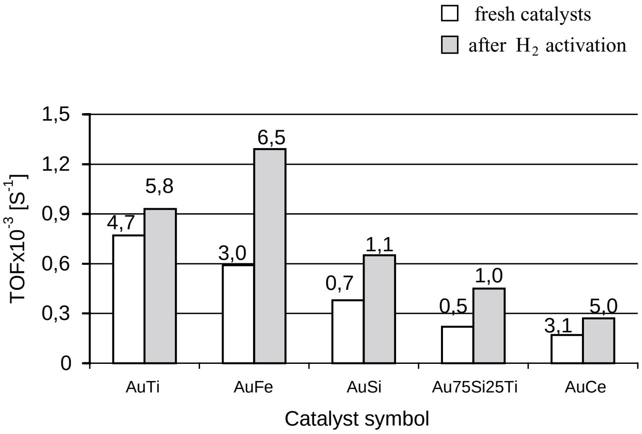

Fig. 2. Oxidation of propane on Au/oxide support catalysts at 300 °C (numbers above the blocks are the conversion values in %).

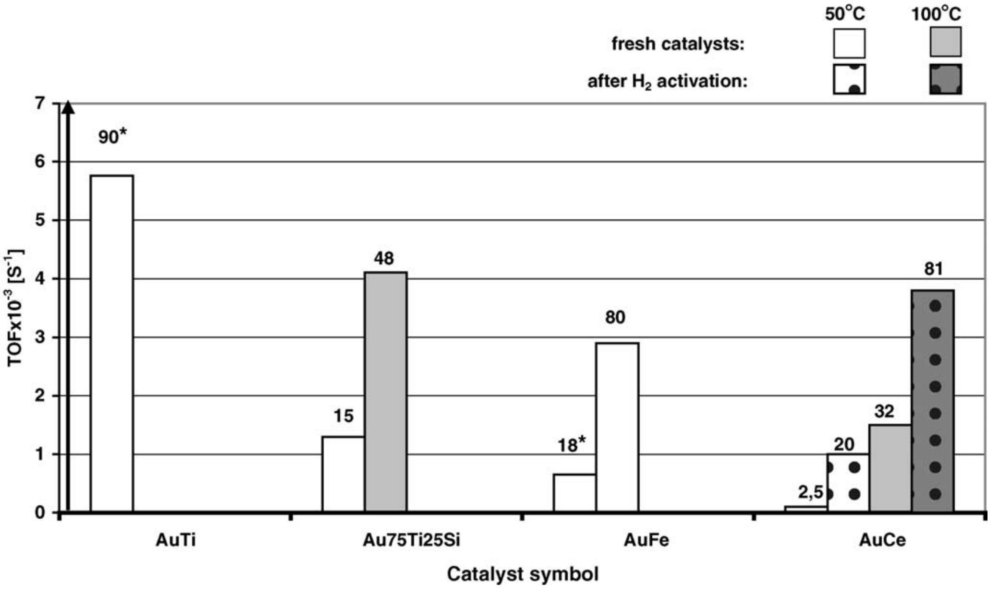

Fig. 1. Oxidation of CO on Au/oxide support catalysts at 50 and 100 °C: (∗) reaction temperature 30 °C (numbers above the blocks are the CO conversion values in %). Symbols of catalysts as in Table 1.

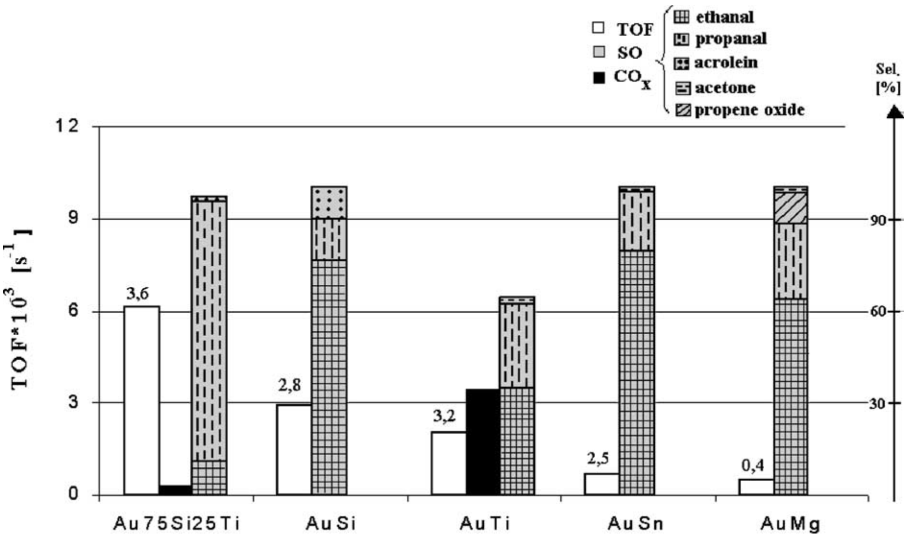

Fig. 3. Oxidation of propene on Au/oxide support catalysts at 200 °C (numbers above the blocks are the conversion values in %).

3.2. Propane oxidation

The reaction occurred at higher temperatures, the measurable conversions of propane for the catalysts of both the groups being obtained above ∼250 °C. Fig. 2 shows TOF and propane conversion values (the numbers above the blocks in %) at 300 °C for selected catalysts of the two groups, obtained for fresh catalysts and after activation in H_2. The only reaction products observed were carbon oxides, with the exception of the AuCe sample for which propene (a product of oxidative dehydrogenation) was also observed with the selectivity of ∼25%. The latter product was due to the reaction on the ceria support, confirming the earlier findings about the activity of CeO_2 in this reaction [17]. For all the catalysts pre-activation in hydrogen led to the increase in the activity. The highest propane conversions were obtained for the AuTi, AuFe and AuCe catalysts. The highest TOF values were observed for AuTi and AuFe samples, still the TOF values for the catalysts with silica as a component of the support were of the same order of magnitude and even higher than that of the AuCe sample.

3.3. Propene oxidation

For most of the catalysts the measurable conversions (>∼1%) were observed at temperatures higher than ∼150–200 °C. For AuFe, and AuCe samples carbon oxides were the main reaction products at these temperatures (selectivities >95%): high selectivity to CO_x was also found in these conditions for the AuTi catalysts. On the other hand, for the catalysts containing MGO as supports, the selective oxidation to oxygenated compounds was the main reaction in this case, the small amounts of carbon oxides being observed above 250 °C. The main products of the selective oxidation at these temperatures comprised propanal and ethanal, small amounts of acrolein, acetone and propene oxide were also found. Fig. 3 gives the TOF values and selectivities to different products at 200 °C for some of the catalysts of this group, and compares them with the data for the AuTi sample. Propene oxide was observed at low temperatures <150 °C only for Ti-containing supports; selectivities of 67% at conversion of 1.2% were found for AuTi sample at 100 °C, and 66% at 0.16% conversion for AuSiTi catalysts at 150 °C. It should be observed that this compound was found only in the first 60 min of the reaction, after longer time the formation of propanal was observed. Small amounts of this compound (selectivity of 9%) were also found for AuMg catalysts at higher temperatures.

Analysis of the data of Table 1 shows that no general correlations can be found between the catalytic activity of the studied catalysts and the dominating size of the Au particles, or reducibility of the supports and the catalysts.

4. Conclusions

Catalytic behavior of Au/oxide support catalysts in oxidation of CO, propane and propene depends mainly on the nature of the support: no clear correlations have been observed between catalytic properties and the dominating size of the Au particles, or catalyst reducibility determined by H_2 TPR:

(a) Activity in CO oxidation is higher for Au-based catalysts with transition metal oxides as the supports as compared with those supported on oxides of main groups' elements.
(b) Oxidation of propane gives carbon oxides as only reaction products: no clear correlation between the nature of the supporting oxide and the activity is found.
(c) Propene oxidation (in the presence of H_2) gives at temperatures higher than ∼150 °C oxygenated products

(mainly propanal and ethanal) on Au supported on oxides of main group elements, whereas catalysts with transition metal oxides perform in these conditions mainly total combustion. Propene oxide, as the main reaction product was observed only at low temperatures (<150 °C) for catalysts containing Ti in the support, with the yield of ∼1%.

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