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Effect of Au in V_2O_5/SiO_2 and MoO_3/SiO_2 catalysts on physicochemical and catalytic properties in oxidation of C_3 hydrocarbons and of CO

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This paper is dedicated to Ferruccio Trifiró, in remembrance of our numerous discussions on selective oxidation, and in acknowledgement of nearly 40-years of his friendship and kindness towards his colleagues from the countries once described by the Pope as: "the second lung of Europe".

Abstract

Silica supported vanadia and molybdena catalysts with, and without Au, were prepared, characterized with XRD, TEM, XPS, H_2-TPR and probe reaction of isopropanol decomposition, and tested in the oxidation of propene, propane and CO. The presence of Au: (a) does not affect markedly structural and textural properties, such as specific surface area, size of V_2O_5 or MoO_3 crystallites, or the electronic state of V and Mo ions, (b) increases the reducibility of vanadia and molybdena phase, (c) enhances the dehydrogenation properties in isopropanol decomposition, and (d) modifies catalytic activity in oxidation reactions. The Au particles increase the total activity in CO oxidation. For propane oxidation at high temperatures the increase in total activity is observed, with the decrease in the selectivity to oxidative dehydrogenation product (propene) and increase in the selectivity to CO_2. The catalytic performance in propene oxidation at 200–300 °C depends on the Au presence and the composition of the reaction mixture. The gold-containing catalysts favour allylic oxidation of propene to acrolein and oxyhydration to acetone, and suppress the C_2 products (ethanal, acetic acid) of partial degradation of a propene molecule. In the presence of hydrogen in the reaction mixture, higher selectivities of acetone (product of oxyhydration) were observed for all the catalysts.

Keywords: Gold–molybdena; Gold–vanadia; Oxidation of CO, propene and propane

1. Introduction

The last decade has witnessed a renaissance of interest in catalysis on gold, following reports by Haruta et al. of high activity of Au nanoparticles deposited on oxide supports (TiO_2, Fe_2O_3) in low temperature oxidation of CO (r.t. or even below) [1,2]. The studies of Haruta have stimulated in the last years extensive studies on properties of gold dispersed on or in oxide matrices in variety of reactions, reviewed in [3–6]. Beside CO oxidation, the studied reactions included: hydrogenation, water-gas-shift (WGS), NO_x reduction, N_2O decomposition, hydrochlorination [3–6]. In addition to the low temperature CO oxidation, the supported nanoparticles of Au were also tested in oxidation of hydrocarbons. Gold particles in mixture with Co_3O_4, NiO, MnO_x, Fe_2O_3, CeO_x [7], or dispersed on Al_2O_3 [8] or MgO [9] were found active in total combustion of CH_4 at temperatures >250 °C. 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 [10]. Au-V_2O_5 and Au-ZrO_2 catalysts deposited on silica were found active in benzene total combustion at 250 °C [11]. The total oxidation of methanol, ethanol and *n*-propanol on Au/Fe_2O_3 was reported [12].

Besides total oxidation, the dispersed Au particles have been found active (though to a smaller extent) in selective oxidation reactions. First mention of the activity of gold in selective oxidation is due to Cant and Hall [13]. In 1971 they reported formation of acrolein with the selectivity of ~30% in oxidation of propene on gold deposited on SiO_2 at temperatures about 260 °C. In the last years Haruta [14–16] and later Delgass and co-workers [17] and Moulijn and co-workers [18,19] have shown, that Au nanoparticles (3–5 nm) on supports containing titania or mixed Ti–Si–O systems, catalyse at temperatures <~140 °C oxidation of propene to

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propene oxide, PO with the selectivities of 80–90%. The conversion of propene and yield of PO were, however, very low (usually below 2%). The formation of PO was observed only when hydrogen was added to propene/oxygen mixture, i.e. in the conditions in which hydroperoxide species can be formed [14,20]. Ethanal, propanal and acetone were also observed in propene oxidation (in the hydrogen presence) at higher temperatures on Au/TiSiO [17] and on Au/SiO_2, the latter catalyst producing also some acrolein [21]. Other selective oxidation reaction studied on Au-based catalysts include oxidation of propane to acetone and iso-butane to -butanal [22], and oxidation (in liquid phase) of D-glucose to gluconic acid [23] and ethylene glycol to glycolic acid [24].

Mechanism of the oxidation reactions on Au/oxide supports is under discussion. In particular, the role of the oxide support, not only as a stabilizer of the Au dispersion or modifier of the Au electronic state, but also as a participant in activation of oxygen, has been suggested [25–27]. One can envisage the adsorption and activation of an oxygen molecule on the oxygen vacancies on the support surface situated: (a) at the periphery of the Au particles, or (b) distant from the Au particles, in which case the active oxygen species would migrate by a spill-over towards active Au centres. If this were the case, a correlation between the catalytic performance and reducibility of the oxide support could be expected, but so far the experimental data on this point are ambiguous [21]. The chemisorption of O_2 on Au particles cannot either be discarded. The chemisorption and activation of CO on Au particles is generally recognized [3–5], practically no information, however, is available on activation of hydrocarbons (or generally speaking of a C–H bond) on gold.

Among numerous oxides used as supports for (or in contact with) Au particles, vanadia and molybdena have not practically been tried so far, except for the works of Andreeva et al. [11] in which Au/V_2O_5 or Au-V_2O_5/SiO_2 were tested in total oxidation of benzene at ~250 °C. These two oxides are the base of numerous catalysts for reactions of selective oxidation (many of them used on an industrial scale) [28–32], operating at temperatures $>\sim$350 °C by a redox Mars and Van Krevelen mechanism.

It seemed then of interest to study the effect of the presence of Au particles in contact with vanadia and molybdena on their catalytic performance in some oxidation reactions. It could be observed that the Au was mentioned as an additive to complex mixed oxide catalysts containing MoVNbW for oxidation of ethane [33] and to BiPbMo for oxidation of hydrocarbons to furan compounds [34].

In the present work the systems based on gold in contact with and V_2O_5 and MoO_3 deposited on SiO_2, have been tested in oxidation of propene, propane and CO. The propene oxidation was studied also in the reaction mixture containing hydrogen, i.e. in the conditions reported previously [14–19] as favourable for the PO formation. The V_2O_5/SiO_2 and MoO_3/SiO_2 catalysts have been shown recently active in oxidative dehydrogenation of propane at temperatures 400–520 °C [35,36]. The gold-containing catalysts were compared with V_2O_5/SiO_2 and MoO_3/SiO_2 catalysts without Au.

2. Experimental

2.1. Preparation

A commercial silica (Aerosil 200, Degussa) was used as a support. The support was pre-treated in water at room temperature and dried at 90 °C for 12 h: its specific surface area after such treatment was 175 m^2/g, the total pore volume 1.2 ml/g with the dominating pore size of 30–40 nm.

The V_2O_5/SiO_2 and MoO_3/SiO_2 catalysts were prepared by impregnation of the treated silica support with aqueous solution containing required amounts, respectively, of ammonium metavanadate (0.11 M) and ammonium heptamolybdate (0.013 M), evaporation of the solute, followed by drying for 12 h at 120 °C and calcination at 450 °C under a flow of air. The content of vanadia corresponded to 1.5 monolayer (mnl), and that of molybdena to 2 mnl, calculated with the assumption that 1 mnl of vanadia contains 10 V atoms/nm^2 [37] and that of molybdena to 6.5 Mo atoms/nm^2 [38].

The catalysts containing Au were prepared by deposition of vanadia or molybdena on Au/SiO_2 precursor. The latter was 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 [18]. After thorough washing till removal of chloride ions, the sample was dried for 12 h at 80 °C and 5 h at 120 °C. Vanadium metavanadate or ammonium heptamolybdate solutions were then introduced onto the Au/SiO_2 samples, evaporated, dried for 12 h at 80 °C and 5 h at 120 °C, and the obtained Au–V–(or Mo)–O/SiO_2 systems were calcined at 400 °C in a stream of air. The content of Au was 1 wt.%. For comparison the Au/SiO_2 sample (AuSi) was obtained by calcination of the Au/SiO_2 precursor at 400 °C in a stream of air. The symbols adopted further in the text are VSi, MoSi and AuVSi, AuMoSi for samples without and with Au, respectively. List of the preparations and their main characteristics are given in Table 1.

2.2. Characterization techniques

Specific surface area was determined with a BET method using AUTOSORB-1 (QUANTACHROME production) with nitrogen as an adsorbate.

The size of gold particles was evaluated with electron microscopy TEM (Philips CM 20). The samples were deposited from a suspension in ethanol on a Cu grid with a carbon film.

H_2-TPR measurements were done using CHEMBET-3000 apparatus. The reduction was realized using H_2

Table 1
Characteristics of Au-V_2O_5/SiO_2 and Au-MoO_3/SiO_2 catalysts.

Symbol	S_{sp} (m^2/g)	XRD data			TEM data Size of Au (nm) min (dominating)
		Phase composition	Size (nm)		
			V_2O_5, MoO_3	Au	
VSi	116.6	V_2O_5	66	–	–
AuVSi	108.9	V_2O_5	52	13	3 (10–20)
MoSi	95.6	MoO_3	36	–	–
AuMoSi	92.4	MoO_3	36	13	3 (12–18)
AuSi	176.0	–	–	–	3 (3–5)

(5 vol.%)/Ar mixture (10 ml/min) in the temperature range 30–550 °C at the heating rate 10°/min. Before the experiments the samples were treated for 2 h at 200 °C in stream of He and then cooled to 30 °C.

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 (BE's) were referenced to the C (1s) peak from the carbon surface deposit at 284.8 eV, the surface composition was determined using the method described in [39].

XRD was used for determination of the phase composition, the size of MoO_3, V_2O_5 and Au crystals (from Warren–Sherrer equation, Topas program), and the content of the crystalline phases (Rietveld analysis using TOPAS v.2.1 [Bruker-AXS] software. Peak shape was calculated using fundamental parameters. The scale parameters, overall temperature factor, crystallite size parameters [calculated from broadening of Lorentzian component] and lattice parameters were simultaneously refined). XRD patterns were recorded with a Siemens D 5005 diffractometer, with Cu Kα radiation, graphite monochromator.

Isopropanol reactivity was studied with a pulse method at 170 °C. After treatment for 1 h in a stream of He (30 ml/min) at the reaction temperature, doses of 1 μl of isopropanol were injected into a stream of the carrier gas (He), passing over a catalyst bed and directly to chromatograph for analysis of unreacted isopropanol, propene, acetone, and di-isopropyl ether. The activity decreased slightly with the number of pulses, the acetone/propene ratio being, however, preserved. The results are presented in the form of amount of the products for the first pulse in μmol per surface of the catalyst s^{-1}.

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 6-way valves with a GC/MS system for analysis of the reaction mixture before, and after passing the reactor. The composition of the reaction mixture was regulated by mass flow controllers.

The CO oxidation was studied in the temperature range 100–300 °C using 0.5 ml of a catalyst sample (grain size 0.6–1 mm). The volume ratio of the components of the reaction mixtures was: $CO:O_2:He = 2:20:78$ vol.%. The contact time, τ was ~1 s, GHSV ~3600 h^{-1}.

For C_3H_6 oxidation two reaction mixtures with (RMH) and without (RM) hydrogen were used. The composition of RMH was: $C_3H_6:O_2:H_2:He = 10:10:10:70$ vol.%, and RM:$C_3H_6:O_2:He = 10:10:80$ vol.%, RMH mixture had a composition used in studies of gas-phase epoxidation of propene [14,17]. The reaction was studied in the temperature range 200–300 °C using 0.5 ml of the sample with the contact time, $\tau = 1$ s. For some experiments in propene oxidation, to obtain the selectivity versus propene conversion curves, the contact time was varied from 0.5 to 1.5 s by changing the total flow rate of the reaction mixture.

The propane oxidation was studied at higher temperatures (420 °C for AuVSi and 500 °C for AuMoSi catalysts), and with the 7.1% of C_3H_8 in air, and contact time $\tau = 4$ s, i.e. in the conditions which were used previously in studies of VSi and MoSi samples without Au [35,36]. The provenance and purity of the gases were 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 SiO_2 was found inactive for all the studied reactions in the conditions of the experiments with conversion below ~0.2–0.3%.

3. Results and discussion

3.1. Characterization of the catalysts

Main characteristics of the catalysts are given in Table 1. Specific surface area of the samples with Mo and V is lower that that of pure support (175 m^2/g) and is not affected markedly by the presence of Au. Since the specific surface area of AuSi is the same as that of the pure support, the decrease observed in V- and Mo-containing samples is due to vanadia and molybdena phase, which may block the pores in silica.

XRD data revealed the presence of crystalline vanadia or molybdena, and Au (in AuVSi and AuMoSi). The SiO_2 used was found amorphous. Raman spectra did not show the presence of dispersed VO_x and MoO_x monolayer species, the only bands observed corresponding to vanadia or molybdena phases. The size of V_2O_5 grains determined from the

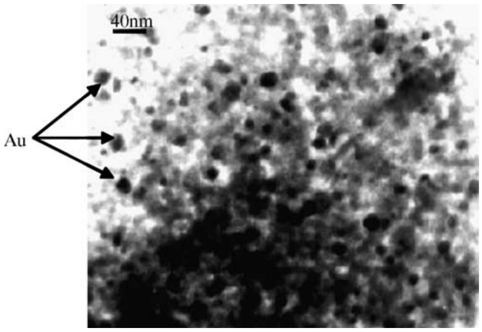


Fig. 1. TEM micrograph of AuMoSi catalyst.

Warren–Sherrer equation was 60 and 50 nm for VSi and AuVSi, respectively, and 36 nm for MoSi and AuMoSi. The presence of Au does not affect then markedly the dispersion of vanadia and molybdena. The average size of the Au crystallites was estimated as 13 nm for both AuVSi and AuMoSi samples. The Rietveld analysis allowed to determine the content of crystalline Au in both catalysts as ~5.7 wt.% of all the crystalline phases (vanadia or molybdena).

TEM pictures show the presence of small Au particles of different size. Last column in Table 1 gives their minimal and dominating size. Fig. 1 presents a TEM picture of the AuMoSi catalyst.

XPS data for the studied catalysts are collected in Table 2. The binding energy (BE) values, referenced to C 1s at 284.8 eV, indicate a metallic state of Au in the Au-containing samples [40]. The BE values for molybdenum and vanadium are not affected by the presence of Au and in all samples correspond to Mo^{6+} and V^{5+} species [41,42]. The BE value of the main O 1s peak (O_I) corresponds to that characteristic of oxygen in SiO_2 (532.5 ± 0.5 eV) [43], a peak of small intensity (about 10× smaller) at ~530–531 eV (O_{II}) can be attributed to the oxygen in VO_x or MoO_x phases [43]. The presence of Au in both catalysts leads to the slight decrease in the amount of O_{II}, which could suggest lower dispersion of vanadia and molybdena. This is confirmed by the lower V/Si and Mo/Si ratios for the Au-containing samples, in particular for AuVSi. The XRD data did not show, however, the marked change in the size of vanadia and molybdena crystallites in the presence of Au. The BE of O_{II} is not affected by Au in the case of VSi catalyst and is shifted to the lower by ~1 eV value for MoSi sample. The latter fact implies the higher basicity (nucleophilicity) of lattice oxygen in molybdena in the presence of Au. Similarly, the BE of Mo lower by 0.7 eV for AuMoSi sample, as compared with MoSi, suggests the effect of Au on the electronic state of ions in MoO_x phase. The surface atomic ratios of Au/Si are similar for AuVSi and AuMoSi and lower than that for the AuSi sample. This suggests a screening of a part of the Au particles by V and Mo oxide phases, which can be understood since the precursors of these latter phases were introduced after that of Au.

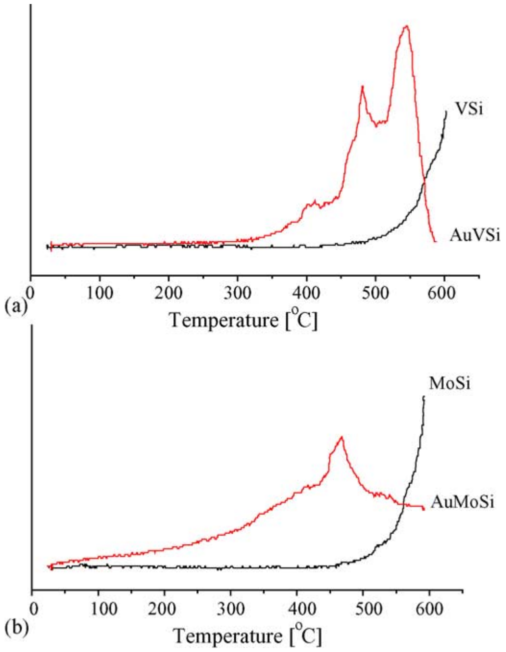


Fig. 2. Effect of Au on H_2-TPR of V_2O_5 (a) and MoO_3 (b) on SiO_2 catalysts.

H_2-TPR curves (Fig. 2) show a marked effect of the Au particles on reducibility of vanadia and molybdena phases on SiO_2. Pure SiO_2 support is not reduced up to 600 °C. The reduction of vanadia and molybdena (samples VSi and MoSi) begins at temperatures >~550 °C, whereas for AuVSi and AuMoSi distinct peaks at lower temperatures are observed with T_{max} = 400, 480 and 500 °C (AuVSi) and 470 °C for AuMoSi. For the later catalyst the onset of the reduction can be already seen at low temperatures, the distinct peak at 470 °C being marked on a large hump starting at (~200 °C). Since the rate determining step in reduction with hydrogen is dissociation of a hydrogen

Table 2
XPS data for Au-V_2O_5/SiO_2 and Au-MoO_3/SiO_2 catalysts

Symbol	BE (eV)				Au/Si	Au/V(Mo)	V(Mo)/Si
	Au 4f	V 2p (Mo 3d)	O 1s				
			O_I	O_{II}			
AuVSi	84.0	516.9	532.7	530.5 (3.0%)	0.004	0.11	0.033
VSi	–	516.8	533.0	530.3 (6.4%)	–	–	0.070
AuMoSi	83.9	232.2	532.8	530.1 (2.6%)	0.004	0.14	0.031
MoSi	–	232.9	532.9	531.1 (7.0%)	–	–	0.036
AuSi	83.4	–	532.1	–	0.009	–	–

Table 3
Isopropanol decomposition at 170 °C on Au-V_2O_5/SiO_2 and Au-MoO_3/SiO_2 catalysts

Catalyst	µmol/m^2 s			Ac/Pr
	C_3H_6	C_3H_6O	Di-isopropyl ether	
VSi	31.7	1.2	0.2	0.04
AuVSi	31.7	2.1	0.2	0.07
MoSi	14.2	0.4	0.9	0.03
AuMoSi	21.9	0.7	1.1	0.03
AuSi	0.005	0.08	0.0	17.9
Si	0.03	0.05	0.0	2.1

molecule, these results indicate that Au particles can activate hydrogen; the formed hydrogen atoms migrate onto the molybdena or vanadia surface reducing it. Such effect of the Au particles was observed earlier for other transition metal oxides (e.g., Fe_2O_3, Co_3O_4, etc.) [4].

Three reduction peaks observed for AuVSi catalyst and the big hump for AuMoSi suggest moreover the presence of bonds of different M–O bond energy in the vanadia and molybdena phase. In view of the fact that vanadia and molybdena are the main phases in the catalysts, these peaks could be ascribed tentatively to different M–O bonds in these oxides (terminal M=O and bridging oxygens doubly or triply coordinated), which possess different electronic properties and different bond order [44,45].

Isopropanol reactivity data (Table 3) show practically no activity of the silica support and of the AuSi catalyst in this reaction. Au particles on silica do not seem then to activate the isopropanol molecule. The catalysts containing vanadia or molybdena phase show high activity (three orders of magnitude higher than the support or Au/Si system). Propene (a product of the isopropanol dehydration) is the main reaction product, similarly like in the case of other systems containing vanadia and molybdena [46–48], which indicates high acidity of the catalysts. Small amounts of acetone (higher for VSi catalysts as compared with MoSi), and di-isopropylether DIPE (higher for MoSi samples) were also observed. The presence of Au did not influence markedly the amount of propene on VSi catalyst and increased it for MoSi. No explanation can be given at present for this fact. The amount of acetone for both VSi and MoSi catalysts increased in the presence of Au, suggesting some synergy effect between Au and vanadia or molybdena phase, leading to enhanced dehydrogenation of isopropanol.

3.2. Catalytic activity

3.2.1. Propene oxidation

The measurable conversions of propene in the presence of hydrogen in the reaction mixture were observed at temperatures >200 °C. The results obtained in the temperature range 200–300 °C are given in Table 4 and Fig. 3. The conversions for VSi and MoSi are low, thus the selectivity data are burdened with an error. Still we may say, that the main selective oxidation products in this temperature range are ethanal and acetone: their amounts decrease with the increase in the reaction temperature with the simultaneous increase in the amount of CO_2. The formation of these products could be explained in terms of the oxyhydration mechanism proposed for low temperature oxidation of olefins [49,50], followed by oxidative scission of acetone (formed in oxyhydration of propene and dehydrogenation of the alcohol formed) to acetaldehyde and acetic acid [51].

For catalysts containing Au a considerable increase in the conversion and a marked change in the distribution of products is observed as compared with the catalysts without Au. The selectivities to partial degradation oxygenated products C_2 (ethanal and acetic acid) decrease considerably,

Table 4
Oxidation of propene on Au-V_2O_5/SiO_2 and Au-MoO_3/SiO_2 catalysts in the presence of H_2 in reaction mixture

Catalyst symbol	Reaction temp. (°C)	Conversion (%)	Selectivity to CO_x (%)		Selectivity to products of partial oxidation (%)			
			CO	CO_2	C_2		C_3	
					Ethanal	Acetic acid	Acetone	Acrolein
AuVSi	200	1.0	0.8	53.7	0.0	0.0	2.0	43.5
	250	6.7	0.2	58.2	11.3	0.0	4.3	26.0
	300	14.2	0.1	77.5	3.6	7.2	1.4	10.3
VSi	200	1.3	0.8	8.0	91.2	0.0	0.0	0.0
	250	1.7	1.1	31.8	51.6	10.1	5.2	0.0
	300	2.1	1.9	43.8	32.7	17.4	4.7	0.0
AuMoSi	200	3.4	0.07	2.12	8.4	0.0	39.8	49.5
	250	10.5	0.02	1.68	5.5	18.3	36.7	37.7
	300	11.6	0.02	7.75	4.6	21.2	35.6	30.1
MoSi	200	0.1	0.8	-	49.6	0.0	22.6	0.0
	250	0.2	1.4	1.2	78.1	0.0	19.5	0.0
	300	0.4	1.7	–	19.9	0.0	10.9	0.0
aussi	200	2.8	0.0	0.0	76.1	0.0	0.4	10.6; 13.2*
	250	4.4	4.4	3.1	65.3	0.0	0.5	11.2; 15.3*
	300	7.1	5.0	3.8	59.3	0.0	0.3	18.1; 13.1*

* Propanal.

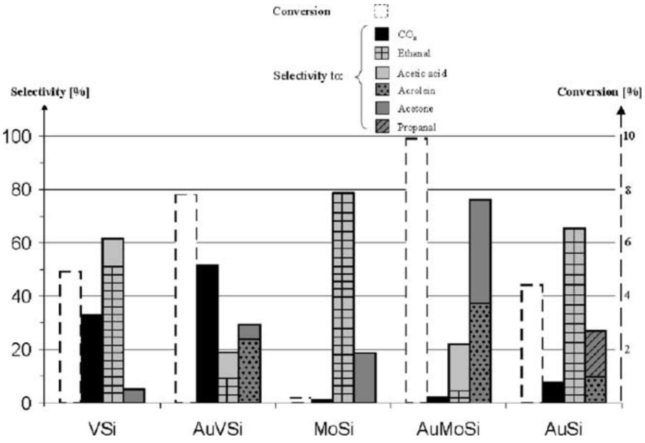


Fig. 3. Oxidation of propene in the presence of H_2 in the reaction mixture on Au-V_2O_5/SiO_2 and Au-MoO_3/SiO_2 catalysts at 250 °C.

and acrolein – a product of allylic oxidation – appears. The selectivity to acrolein decreases with the temperature, which is accompanied by the increase in the CO_2 selectivity. The Au/SiO_2 catalyst yields ethanal as a main product, some propanal and acrolein are also observed, with no carbon oxides. The results indicate that the gold particles are capable of the propene oxidation with formation of allylic species at relatively low temperatures, in agreement with the early work by Cant and Hall [13]. The different distribution of products observed for Au/Si and AuV(Mo)Si catalysts (preference of allylic oxidation for Mo and V containing catalysts), suggests, however, different fate of the allylic species on these catalysts. It cannot be excluded that vanadia or molybdena phase participates to higher extent in activation of oxygen than the SiO_2 phase. The differences in the acidity between AuSi and AuV(Mo)Si catalysts, observed in the isopropanol decomposition, can also be responsible for the observed differences in catalytic performance. The change of the selectivity to various products with conversion of propene at 250 °C for AuVSi and AuMoSi catalysts are shown in Fig. 4. For both systems selectivity to acrolein decreases considerably with the increase in conversion with the simultaneous increase in the selectivity to CO_2, which indicates the possibility of consecutive reaction of the acrolein combustion. The selectivities to acetone and products C_2 do not change markedly with the conversion, which suggests that the mechanism of the oxidative scission cannot be responsible for formation of the C_2 products. It can be also observed that the selectivities to acetone are much higher for AuMo catalyst as compared with AuVSi: this can be related to the higher amounts of water observed on AuMoSi catalyst (c.f. Fig. 5), which would favour the oxyhydration path of the reaction.

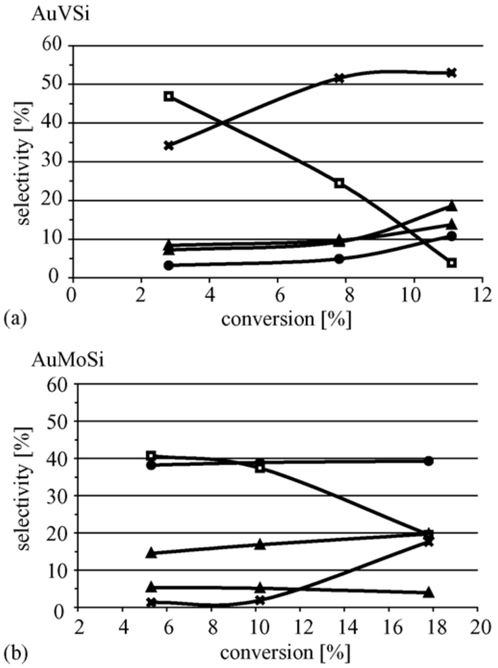


Fig. 4. Selectivity to different products as a function of conversion in oxidation of propene at 250 °C in the presence of H_2 in the reaction mixture on AuVSi (a) and AuMoSi (b): ×, CO_x; ▲, ethanal; ●, acetone; □, acrolein; △, acetic acid.

The conversion and distribution of products in propene oxidation depend also on the composition of the reaction mixture. In Fig. 5 comparison is given for this reaction at 250 °C on AuVSi and AuMoSi catalysts, in the reaction mixture propene/oxygen with and without hydrogen, denoted RMH and RM, respectively. For both catalysts the propene conversion is higher for the RMH as compared with the RM mixture, the changes in the distribution of products are, however, markedly different for catalysts containing vanadia and molybdena. For AuVSi higher selectivities to acrolein and acetic acid and lower to ethanal, acetone and CO_x are observed in the absence of hydrogen in the reaction mixture. On the other hand, for AuMoSi catalyst, the only reaction products in the absence of hydrogen are ethanal (selectivity of 90%) and small amounts of CO_x. Higher amounts of water are observed for the reaction in the presence of hydrogen, particularly for the Mo catalyst, whereas the selectivity to CO_2 is higher in the presence of hydrogen for V catalyst and lower for the Mo sample.

The picture obtained is then rather complex. Some explanation of the observed differences in catalytic behaviour of the samples in different reaction mixtures, and the differences between the catalysts containing vanadia and molybdena phase, could be sought for in different state of the catalysts during the reaction and different physicochemical properties of the catalysts. One can argue, that in the presence of hydrogen (which, as shown by TPR data described above, can be activated on the Au particles), the surface of vanadia and molybdena phase in contact with the Au particles can be slightly reduced. The reduced species can provide the centres for the oxygen sorption and total combustion of propene and/or acrolein. As the molybdena catalysts are as a rule more easily reoxidized than vanadia [28,30], the sorbed oxygen on the

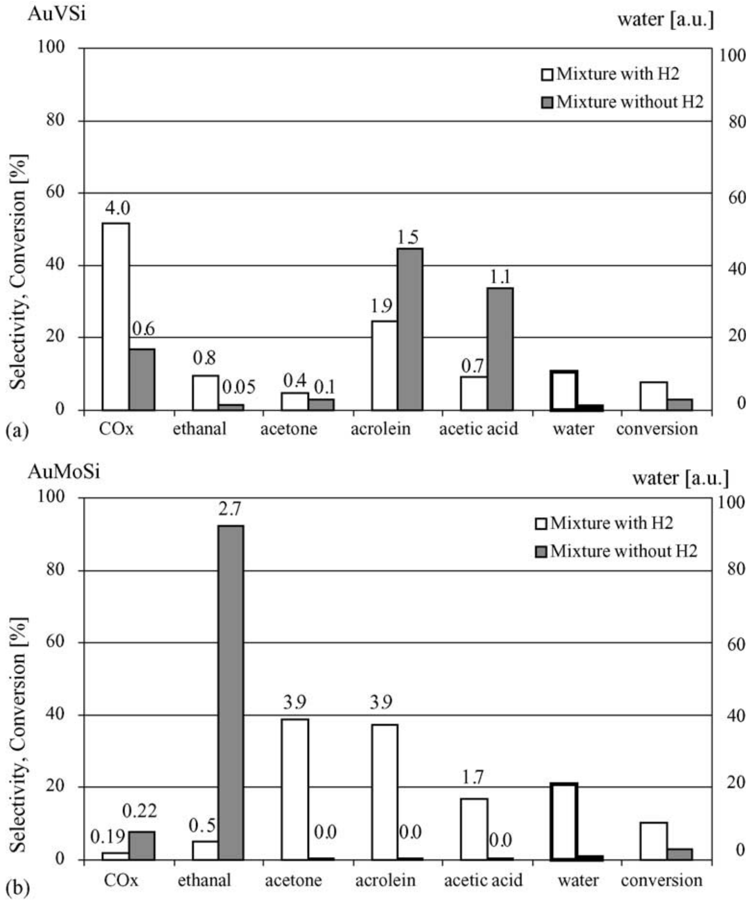
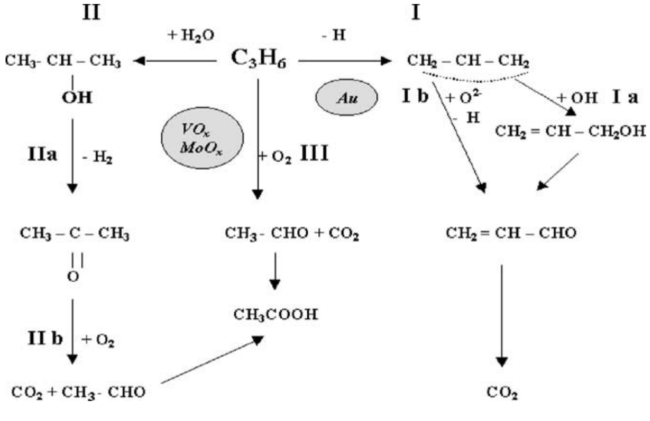


Fig. 5. Effect of H_2 addition to C_3H_6/O_2 mixture on oxidation of propene at 250 °C on AuVSi (a) and AuMoSi (b) catalysts. Numbers above the blocks are yields of particular products (in %).

Mo catalyst is transformed quickly into nucleophilic, selective form, whereas on the V catalyst it may stay in the form of the electrophilic, unselective forms, leading to total combustion. This could tentatively explain higher amounts of CO_x on the vanadia catalyst. It could be recalled that oxidation of propene of bulk vanadia at higher temperatures yields mainly carbon oxides and some acrolein [52], whereas on pure molybdena, selectivities to carbon oxides are relatively smaller [53,54].

On the other hand oxidation of hydrogen, which can take place parallel to the oxidation of propene, would lead to the covering of the catalyst surface in the stationary state with water. Indeed, higher amounts of water were observed in the reaction products in the RMH mixture as compared with the RM mixture. It is perhaps worth observing that the amounts of water were considerably higher for AuMoSi as compared with AuVSi catalyst. This could account for higher amounts of acetone – a product of oxyhydration – on Mo-containing catalysts. The formation of acrolein on AuMoSi in the presence of hydrogen can be also explained by a mechanism involving OH groups as water as source of oxygen, similarly as it was proposed for oxidation of propene on Pd in liquid phase [55].

Scheme 1 shows tentative paths of the propene conversion, which could account for formation of different products. On supported vanadia and molybdena the main reaction is path III with partial degradation of a propene molecule. The detailed mechanism of this reaction, particularly the type of the oxygen species participating in it, is not known. It may be only recalled, that this type of



Scheme 1.

Table 5
Oxidation of propane on Au-V_2O_5/SiO_2 and Au-MoO_3/SiO_2

Catalyst	Reaction temp. (°C)	Conv. (%)	Selectivity (%) C_3H_6	CO_2	CO
VSi	420	7.0	25.8	14.6	59.7
AuVSi	420	9.6	13.4	82.5	4.2
MoSi	500	1.5	87.0	13.0	0.0
AuMoSi	500	3.6	0.0	100.0	0.0
AuSi	400	5.3	25.7	65.2	7.3

the reaction is considered as electrophilic oxidation [30], in which electrophilic oxygen species O_2^- or O^- add to a double bond with formation of peroxo or oxo intermediates.

The latter can then decompose with breaking of a C–C bond. Still, formation of such species would require the presence of reduced V or Mo centres, which has not been evidenced (though cannot be excluded) in the vanadia or molybdena catalysts in the stationary state of the reaction at low temperatures. In the presence of Au allylic species are formed. Their transformation into acrolein can be realized by path Ia and Ib. Path Ia suggests the participation of lattice oxygen, again not obvious in the reaction conditions: it is proposed hypothetically to explain formation of acrolein on AuVSi catalyst in the absence of hydrogen, for which the amounts of water necessary for path Ib are very small. Path II explains formation of acetone (IIa) and accounts for the experimental facts observed. IIb route (oxidative scission), on the other hand, is not confirmed by the selectivity versus conversion experiments described above.

3.2.2. *Oxidation of propane*

Table 5 compares the activity and selectivity in oxidative dehydrogenation of propane for V(Mo)Si and Au V(Mo)Si samples. For both VSi and MoSi samples the presence of Au increases the conversion and changes considerably the selectivity. The decrease in the selectivity to propene and CO and increase in the selectivity to CO_2 is observed. For AuMoSi catalyst the effect is spectacular, the presence of Au completely suppressing ODH reaction, the only reaction product being CO_2. The behaviour in this reaction is completely different from that observed for propene oxidation at lower temperatures at which the Mo samples produce much less CO_x than the V one. This can imply that at high temperature gold can activate an oxygen molecule and the formed oxygen species lead to total combustion.

3.2.3. *Oxidation of CO*

The data for the reaction temperatures in the range 100–300 °C are given in Table 6. VSi and MoSi catalysts are little active in this reaction. The presence of Au leads to the considerable increase in the conversion, particularly for the VSi catalyst. Still the values of conversions for the studied catalysts are relatively small as compared with 100% observed for Au/TiO_2 or Au/Fe_2O_3 [1–4], which renders vanadia and molybdena a non-attractive partner for Au particles in oxidation of CO.

Table 6
Oxidation of CO on Au-V_2O_5/SiO_2 and Au-MoO_3/SiO_2

Catalyst symbol	Reaction temp. (°C)	Conversion (%)
VSi	100	0.0
	200	0.4
	300	10.5
AuVSi	100	6.7
	200	8.6
	300	1.6
MoSi	100	0.0
	200	0.5
	300	5.2
AuMoSi	100	0.4
	200	0.9
	300	7.0
AuSi	100	0.0
	200	3.5
	300	8.0

4. Conclusions

Au particles in contact with molybdena and vanadia phases deposited on SiO_2 modify their physicochemical and catalytic properties.

In the presence of Au particles:

1. The reduction of vanadia and molybdena with hydrogen is facilitated, which indicate the activation of a hydrogen molecule on Au centres.
2. The dehydrogenation of isopropanol to acetone is enhanced.
3. The activity of vanadia and molybdena in oxidation of CO increases.
4. The activity in oxidation of propane at high temperatures increases with the simultaneous decrease in the selectivity to propene and increase in the selectivity to CO_2, suggesting possible activation of an oxygen molecule on Au particles.
5. Distribution of products in oxidation of propene at 200–300 °C is modified: the Au containing catalysts favour allylic oxidation to acrolein and suppress partial degradation of propene to ethanal and acetic acid.
6. The presence of hydrogen in propene/oxygen reaction mixture increases the selectivity to products of oxyhydration of propene (acetone).

The dispersion, texture and electronic state of V and Mo are not affected by the presence of Au particles.

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