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Nano-Au/oxide support catalysts in oxidation reactions: Provenance of active oxygen species

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Abstract

The total and selective oxidation reactions on Au/oxide supports have been reviewed, and the role of the support, in particular its reducibility, in determining catalytic performance and in activation of oxygen has been discussed on the basis of literature and author's own data.

Keywords: Oxidative reaction; Catalytic performance; Activation of oxygen; Au-based catalysts

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 (RT 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 of different nature in variety of reactions, reviewed in Refs. [3–8]. Beside CO oxidation, the studied reactions included: hydrogenation, water–gas-shift WGS, NO_x reduction, N_2O decomposition, hydrochlorination and oxidation of organic compounds.

The present work is an overview of literature and author's laboratory own data on total and selective oxidation reactions on Au/oxide support, an attempt being made to discuss the possible mechanism of the oxygen activation: The special attention will be paid to the role of oxide support and its reducibility in the mechanism of the oxidation reactions.

2. Total and selective oxidation of organic compounds on Au-based catalysts

Representative results of total oxidation of hydrocarbons and alcohols on Au dispersed on different oxide catalysts are collected in Table 1. Hydrocarbons are oxidized at temperatures considerably higher (>200 °C) than CO, the activity roughly depending on the number and strength of C–H bonds. No data are reported for interactions of hydrocarbons with Au nanoparticles, the high temperatures of the oxidation reactions suggest, however, that activation of a hydrocarbon molecule is more difficult on Au nanoparticles than activation of CO. Methanol is readily oxidized to carbon oxides already at 50 °C, higher alcohols (ethanol, isopropanol) yield on the other hand considerable amounts of selective oxidation products.

In Table 2 the data on selective oxidation on Au-based catalysts are summarized. The first mention of the activity of gold in selective oxidation reactions is due to Cant and Hall [16]. In 1971 they reported formation of acrolein with the selectivity of ~30% in oxidation of propene at 260 °C on gold dispersed on SiO_2. The interest in selective oxidation has been renewed in the last decade, following the reports of Haruta and co-workers [3–5] on oxidation of propene to propene oxide, PO on Au/TiO_2 catalyst, when hydrogen is present in the reaction mixture, i.e. in the condition in which hydroperoxy or peroxy radicals are formed. Beside PO, the formation of ethanal, propanal and acetone has been also reported in these conditions [17–19]. The selectivities to PO are high (~90%), but the conversions and yields of PO do not exceed 2–3%. At higher temperatures polymerization of PO on the support poisons the catalyst. More promising are oxidations of more complex molecules, glucose [22] and ethylene glycol [23] in liquid phase, or alcohols to aldehydes and ketones [15], occurring at relatively low temperatures with high yields of products.

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Table 1
Total oxidation of organic compounds on supported nano-Au catalysts

Catalyst	Preparation method	ϕ Au (nm)	Reactant	Reaction temperature (°C)	Remarks	Ref.
Au/Al_2O_3	I, DP	3–5	CH_4	>400	small crystallites active, Au^0	[9,10]
Au/MgO	I	5–10	CH_4	750	Au blocks sites of OMC	[11]
Au/MO_x, M = Co, Ni, Mn, Fe, Ce	I	Not reported	CH_4	250	$Au^{\delta+}$ active	[12]
$Au/MO_x/Al_2O_3$, M = Li, Rb, Mg, Mn, Ce, Zr	DP	2–7	C_3H_6	200–530	CeO_2 improvement (high oxygen storage capacity)	[10]
Au/MO_x, M = Ti, Fe, Ce	DP	5–20	C_3H_6	200–300	Activation by H_2 improves activity	[13]
			C_3H_8	250–300		
$Au/VO_x/TiO_2$	DP	<5	C_6H_6	250		[14]
$Au/ZrO_x/TiO_2$				30 (O_3)		
Au/CeO_2						
Au/Fe_2O_3	CP	Not reported	Methanol	50		[15]
			Ethanol	150–200	150 °C ethanal	
			i-Propanol	150–200	180 °C acetone	
			Acetone	200–300		
			Toluene	250–300		

I, impregnation; CP, coprecipitation; DP, deposition–precipitation; ϕ, particle diameter.

3. Main fundamental problems in catalysis on supported Au catalysts

3.1. Effect of particle size and shape

Like in most metal-based catalysis, the effect of the particle size on catalytic performance has been for Au-based catalysts widely discussed. Several authors argue that the activity of Au is related to the low size (2–5 nm) particles, at which gold looses its metallic character. Lopez et al. [24] have calculated with the DFT the binding energy of CO and O atoms on gold clusters of different size and different coordination number CN of Au atoms, finding practically linear increase in this energy with the decrease in CN from 9 (Au in [1 1 1] plane of bulk gold) to 5 (10 atom cluster): they believe that the higher bonding energy assures higher activity of the small-size Au particles. The shape of Au particles can be also important, hemispherical particles being more active than spherical ones [25].

3.2. Effect of support, provenance of oxygen species

The support in Au-based catalysts may act not only as a stabilizer of the Au dispersion or a modifier of the Au electronic state, but also as a participant in activation of oxygen.

Three mechanisms of the oxidation reactions involving gaseous oxygen on Au/oxide support systems, suggested in

Table 2
Selective oxidation of organic compounds on supported nano-Au catalysts

Catalyst	Preparation method	ϕ Au (nm)	Reaction	Reaction temperature (°C)	Y (%)	S (%)	C (%)	Ref.
Au/SiO_2	I	Not reported	$C_3H_6 \rightarrow$ acrolein	260	–	33	–	[16]
Au/TiO_2	DP	2.5–5	$C_3H_6 \rightarrow$ PO (H_2 present in r. mixture)	<150	1–2	80–90	1–3	[3–5]
Au/Ti–Si–O								[17,19]
AuMCM-41	DP	2.5	$C_3H_6 \rightarrow$ acetone	120	0.2			[20]
			$i\text{-}C_4H_{10} \rightarrow$ butanol	120	2			
Au/SiO_2	DP	3–5	$C_3H_6 \rightarrow$	250	2.3(a)	80(a)	3	[21]
			CH_3CHO(a)		0.3(c)	10(c)		
$AuMoO_3/SiO_2$		3–18	CH_3COOH(b)		3(a)	90(a)	4	
AuV_2O_5/SiO_2		3–20	Acrolein(c)		1.5(c)	43(c)	4	
					1.1(b)	35(b)	3	
Au/C	Au sol. I	Not reported	D-Glucose → D-gluconic acid (liquid phase)	50–100	95	>95	100	[22]
Au/Al_2O_3	DP, I	1–2 Au^0	Ethylene glycol → glycolic acid (liquid phase)	50–70	40	95	~50	[23]
Au/Fe_2O_3	CP	Not reported	$C_2H_5OH \rightarrow HCHO$	150	60	80	80	[15]
			$i\text{-}C_3H_7OH \rightarrow$ acetone	200	90	90	100	

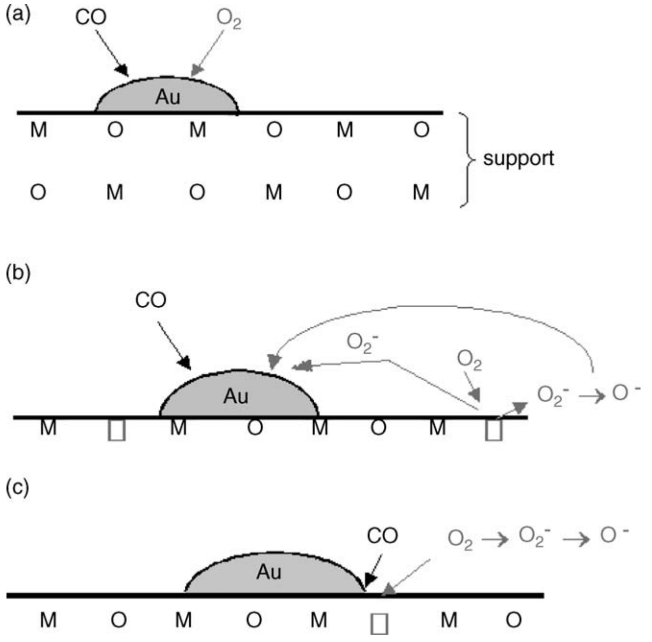

Fig. 1. Mechanism of oxidation on Au/oxide support catalysts. (a) Langmuir-Hinshelwood mechanism: O_2 activation on Au nanoparticles, (b) O_2 activation on oxygen vacancies (□) of support distant form Au particles: reverse spill-over of oxygen species and (c) O_2 activation on oxygen vacancies (□) at interface Au/support/O_2 mixed Au-active centre.

literature [26–29], can be envisaged. Fig. 1 shows them schematically for the CO oxidation. All schemes assume adsorption and activation of CO on metallic Au nanoparticles, which is supported by the FTIR studies of the CO adsorption [30]. On the other hand, adsorption and activation of oxygen may occur on: (1) Au particles, reaction between the adsorbed CO and O species being realized by Langmuir–Hishelwood mechanism (Fig. 1a) or (2) on the oxygen vacancies on the support surface: distant from the Au particles (Fig. 1b), in which case the active oxygen species would migrate by a spill-over towards active Au centres with chemisorbed reactant, or vacancies situated at the periphery of the Au particles (Fig. 1c).

The chemisorption of O_2 does not occur on massive gold, few reports indicate, however, the dissociative chemisorption for Au nanoparticles (1.5–22 nm) dispersed on SiO_2, MgO [31] and Al_2O_3 [23,31], with the stoichiometry Au_s:O = 2 at 200 °C [23,31] and Au_s:O = 1 at 300 °C [31]. The adsorption maximum has been found between 200 and 350 °C, depending on the system. In model, surface science studies, oxygen atoms generated from ozone or from ionization source have been found adsorbed on [1 1 1] Au [32], with the desorption energy E_d of 30 kcal mol^{-1}, or on Au islands two to six atoms thick dispersed on [1 1 0] TiO_2 film [33]. In the latter case a monolayer of oxygen atoms was estimated as 1.5×10^{15} at O cm^{-2}, and the E_d value varied between 26 and 21 kcal mol^{-1} when the Au film thickness increased from 2 to 6 atoms. Out of numerous oxygen species possible on the oxide surfaces O_2^- has been detected on Au/TiO_2 catalysts by ESR [34,35]. These species were localized on Ti^{3+} ions of the support or at the interface Au/support. Monoatomic oxygen species have not been evidenced, and the problem which of the oxygen forms: molecular, or atomic, interacts with CO, is open.

Beside Au particles, oxygen adsorption could involve oxygen vacancy on the supports. On one hand the Schottky junction, existing at Au/oxide interface and leading to equalization of the Fermi levels of the metal and oxide, may induce spontaneous formation of the vacancy close to Au atoms. On the other hand, some reduction of the catalyst (i.e. formation of oxygen vacancies) may occur in the reaction mixture. It is generally recognized that in the oxidation reactions the catalyst surface may be partially reduced, adapting itself to the redox potential of the reducing agent/oxygen mixture. In the formalism of Mars and Van Krevelen or steady state adsorption model (SSAM) of the oxidation, the degree of the catalyst reduction (corresponding to the concentration of the vacancies $[V_o]$ depends on the rates of the catalyst reduction, k_r and reoxidation (chemisorption) with gaseous oxygen, k_o, and is given by the formula: $[V_o] = 1 - [1/(k_r p_r/k_o p_{O_2}) + 1]$. If an oxygen vacancy is involved in the reaction mechanism, one would expect then a correlation between the catalytic performance and reducibility of the oxide support.

It is not clear how the properties of the oxide support decide about the mechanism. Schubert et al. [29] have proposed an interesting classification of oxides into ‘‘active’’ (Fe_2O_3, NiO_x, CoO_x) and ‘‘inert’’ (SiO_2, MgO, Al_2O_3) supports. The Au particles supported on ‘‘active’’ supports: (a) are highly active in CO oxidation, (b) oxygen is adsorbed on support vacancies, dissociating at the Au/support interface, (c) CO oxidation is less structure- (particle size-) sensitive. The ‘‘inert’’ supports give: (a) less active Au catalysts, (b) oxygen is adsorbed and dissociates on defects (steps, kinks) of Au particles, (c) CO oxidation is structure- (particle size-) sensitive. This classification roughly corresponds to easily (‘‘active’’) and hardly (‘‘inert’’) reducible oxides. Our studies on oxidation of CO and C_3 hydrocarbons have shown [13] that Au nanoparticles on transition metal oxides TMO (TiO_2, mixed Ti–Si–O gels, Fe_3O_4, CeO_2), reducible at temperatures χ500 °C (on the surface or in the bulk of the catalyst), are more active in CO (at temperatures close to RT) and in propane (at 250–300 °C) total oxidation, than Au deposited on non-reducible oxides of main group elements MGO, (SiO_2, MgO). The catalysts containing Au in contact with hardly reducible vanadium and molybdenum oxides, deposited on SiO_2 [21] show also small activity in CO and propane oxidation. Quite clear correlation between the reducibility of the support (estimated from T_{max} in H_2TPR studies) and the activity was found, using as supports chromites of transition metal oxides, $M^{II}Cr_2O_4$, MR where M^{II} = Co, Mn, Fe [36]. The compounds possess the same, spinel structure and similar specific surface area, but exhibit different reducibility. The sequence of increasing activity: Au/CoCr(80) > Au/MnCr(26) > Au/FeCr(1), where values in brackets are conversions of CO at 35 °C), follows the sequence of decreasing reducibility: Au/CoCr(100) > AuMn(225) > AuFeCr(410), where values in brackets are T_{max} (in °C) in H_2TPR.

The above results suggest that, indeed, the support may provide centres for oxygen activation in form of the oxygen vacancies, although it cannot be decided which of the mechanisms (Fig. 1b or c) does operate.

Oxidation of propene also depends on the nature and properties of the support oxide [13,21]. Gold dispersed on easily reducible supports, e.g. MCr spinels, Fe_3O_4, shows low activity in propene oxidation, the only product being CO_2. On the other hand, Au in contact with hardly reducible oxides, e.g SiO_2, MgO, V_2O_5, MoO_3 gave in propene oxidation oxygenated products C_3 (propanal, acetone, acrolein) and C_2 (ethanal, acetic acid), the latter being formed with partial degradation of the propene molecule. It is interesting to note that Au in contact with MoO_3 and V_2O_5, the oxides which themselves were active mainly in oxidation with the partial degradation of the C_3 chain, changed their selectivity towards the formation of acrolein. The origin of oxygen species in this type of the reactions is not clear. The formation of the oxygenated products case may also involve oxyhydration mechanism in which water of OH groups may be the source of oxygen.

Fig. 2 summarizes the results of oxidation of CO and C_3 hydrocarbons on Au dispersed on different oxides [13,21,36], showing trends in both activity and selectivity of the reactions with the changes in the support reducibility.

Beside gaseous oxygen, some authors point out to the possibility of water or OH groups being the source of oxygen species in oxidation on gold-based catalysts. Kung and co-workers [37] proposes a mechanism in which CO is added to OH groups on a cationic form of Au in contact with Au^0. Haruta and co-workers [38] reports the 10-fold increase in CO oxidation when the reaction mixture contains 200 ppm of water, though does not provide explanation of this effect. Kiely and co-workers [39] point out to high activity of gold oxyhydroxide AuOOH, which could imply participation of other than gaseous oxygen species. Further studies seem necessary to prove these mechanisms and to decide in which way the properties of the support and the type of Au species influence the source and nature of active oxygen.

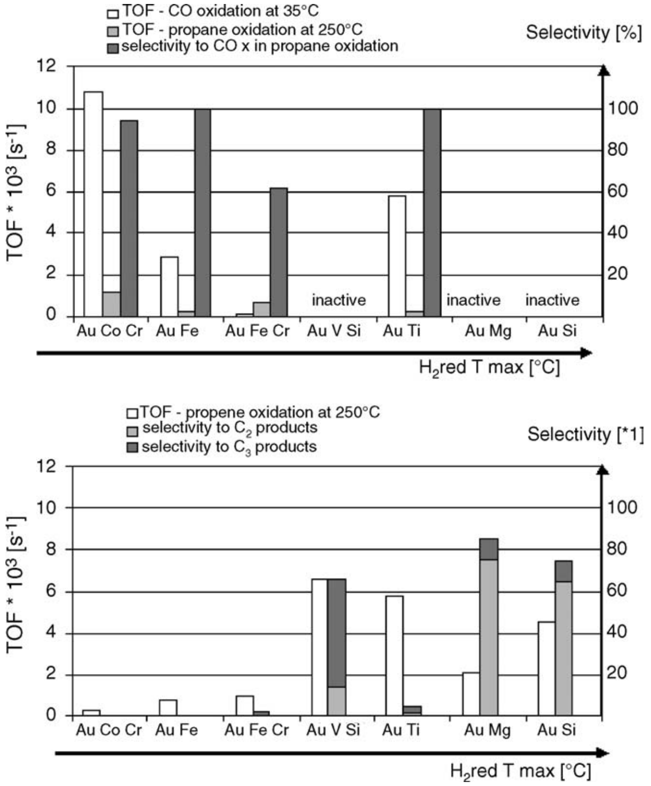

Fig. 2. Oxidation of CO and C_3 hydrocarbons on Au dispersed on oxide of different reducibility.

4. Conclusions

Activity and selectivity of Au nanoparticles dispersed on oxide supports in oxidation of CO and hydrocarbons depend on the nature and properties of the support, in particular on its reducibility:

(a) Catalysts containing Au dispersed on easily reducible (in bulk or on the surface) transition metal oxides are more active in CO oxidation and in total oxidation of hydrocarbons.
(b) Catalysts containing Au dispersed on hardly reducible oxides of main group elements are less active in CO oxidation and total oxidation of hydrocarbons, but catalyse selective oxidation of hydrocarbons (e.g. propene) to oxygenated products.

Correlation, observed between the total activity in CO oxidation and reducibility confirms the suggestion about oxygen vacancies on the support surface being centres for oxygen molecule activation in the oxidation reactions.

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