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$M^{II}Cr_2O_4$-spinels as supports for Au nanoparticles in oxidation of CO

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Abstract

Chromium spinels $M^{II}Cr_2O_4$ (M^{II} = Co, Mn, Fe, Mg, Cu) of the same structure but different reducibility, were found new, promising supports for Au nanoparticles in oxidation of CO, including selective (preferential) oxidation in the presence of hydrogen. Oxidation of CO on Au/$M^{II}Cr_2O_4$ occurred already at room temperature, the activity depends on the nature of M^{II} (100% conversion of CO at 50 °C on Au/$CoCr_2O_4$ was observed). The activity in CO oxidation increases with the increasing reducibility of the supports and the catalysts, measured by H_2TPR, and with the increasing potential of the M^{II}/M^{III} redox couple (for Co, Mn, and Fe spinels). This shows the role of the support redox properties in Au-based catalysts. In the presence of hydrogen (selective oxidation of CO), the catalysts are more active and show high (90–100%) selectivity to CO_2.

Keywords: Lean selective catalytic reduction of NO; Propene; Au/Al_2O_3; Catalytic synergy; Mechanism; Mechanical mixtures; Chromium spinels

1. Introduction

Nanoparticles of gold dispersed on oxide supports have been recently a subject of much interest, owing to their high activity in numerous reactions [1–4]. Among these reactions, oxidation of CO, or "selective" or preferential (PROX) oxidation of CO in the presence of hydrogen, occurring at low temperature (even below rt) have been of greatest importance. The latter reaction provides means of purification of industrial hydrogen for application in new energy sources, e.g. fuel cells from traces of noxious CO. Mechanism of the oxidation reactions on Au/oxide supports is under discussion. Beside the role of Au particle size and shape, the importance 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 [5–7]. One can envisage the adsorption and activation of an oxygen molecule on the oxygen vacancies of the support surface localized: (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 [8]. The chemisorption of O_2 on Au particles cannot either be discarded.

In this work, chromium spinels $M^{II}Cr_2O_4$ (M^{II} = Co, Mn, Fe, Cu, Mg) have been used as new supports for Au nanoparticles. The spinels, studied previously by Słoczyński et al. [9] in SCR of NO_x possess the same structure but different reducibility, thus they seemed to us very good models for studying to what extent the properties of the support, in particular its reducibility can affect the catalytic performance of dispersed gold nanoparticles in oxidation reactions. The catalysts Au/$M^{II}Cr_2O_4$ were synthetized, characterized by H_2TPR, TEM, XPS, isopropanol decomposition (probe for acido-basicity), and tested in oxidation of CO, also with H_2 in the reaction mixture ("PROX" oxidation).

2. Experimental

2.1. Preparation

The supports $M^{II}Cr_2O_4$ (M^{II} = Co, Mn, Fe, Cu, Mg) were prepared with citrate method, using stoichiometric quantity of 1 M solutions of metal nitrates and citric acid [10]. After evaporation of water with water pump, at 90 °C, the glasslike, amorphous solids obtained, were heated in a stream of air at a temperature up to 550 °C, with the heating rate of 100 °C/h. The final treatment consisted of annealing the samples in air or hydrogen at 600–900 °C.

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Table 1
Characterization of Au/$M^{II}Cr_2O_4$ catalysts and their supports

Catalyst	Ssp (m^2/g)	H_2TPR data T_{max} (°C)	TEM data Au particle size min (dominating) (nm)	XPS data Au 4f BE (eV)	Isopropanol decomposition (average impulse)	
					C_3H_6 (mol/m^2 s 10^{-7})	C_3H_6O (mol/m^2 s 10^{-7})
AuCoCr	18.0	100	2 (5)	84.3	0.09	54.0
CoCr	19.2	265	–	–	0.02	11.0
AuMnCr	18.0	225	5 (>10)	83.8	0.09	26.0
MnCr	13.0	260	–	–	0.90	16.0
AuFeCr	20.7	450	4 (10)	84.1	340.0	38.3
FeCr	14.8	375		–	320.0	54.8
AuCuCr	12.9	180		84.1	0.21	521.0
CuCr	11.3	208		–	0.21	425.0
AuMgCr	14.7	350		84.0	0.12	50.2
MgCr	15.2	390		–	0.08	48.3

The Au/$M^{II}Cr_2O_4$ catalysts were obtained by deposition-precipitation method at room temperature and pH 9.5–10, with the solution of $AuCl_3$ (5.0 wt %Au) as a precursor of the active gold phase, following the procedure described in [11]. The content of Au was 1 wt.% in all the samples. The samples were calcined for 4 h at 350 °C in a stream of air. The list, symbols and specific surface area of the supports and catalysts used in the studies are given in Table 1. The symbols adopted in Table 1 and further in the text are AuMCr, where M is a symbol of a cation in the chromium spinel.

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_2TPR measurements were done using CHEMBET-3000 apparatus. The reduction was realized using H_2 (5 vol.%)/Ar mixture (50 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 (BEs) were referenced to the C(1 s) peak from the carbon surface deposit at 284.8 eV.

Isopropanol decomposition was studied with a pulse method at 200 °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 average pulse in mol 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. The reactor was coupled on-line by 6-way valves with a gas chromatograph 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 35–300 °C using 0.75 ml of a catalyst sample (grain size 0.2–0.5 mm). The volume ratio of the components of the reaction mixtures was—CO:O_2:He = 2.3:23.3:74.4 vol.%, and for selective oxidation—CO:O_2:H_2:He = 2.3:10:10:74.7. The contact time, τ was ~1.5 s, GHSV ~2400 h^{-1}. The samples were studied as received and after pre-treatment in the H_2 (33 vol%)/He mixture at 150 and 250 °C. The provenance and purity of the gases were as follows: CO (Linde, 99.97%), O_2 (BOC 99.7%), H_2 (BOC, 99.97%), He (Linde, 99.999%).

Small conversion of CO on pure supports $M^{II}Cr_2O_4$ was observed, much lower however than that of the AuMCr catalysts: the highest conversion values for the supports did not exceed 6–8% at the highest reaction temperature.

3. Results and discussion

3.1. Characterization of the catalysts

Table 1 summarizes the data of the characterization of the catalysts obtained with various physicochemical techniques.

BET data show that the specific surface area of the catalysts is in most cases lower or comparable to that of a given support, with except for AuMnCr and AuFeCr samples for which the slight increase in the specific surface was observed.

H_2TPR measurements show a marked effect of the Au particles on reducibilty of $M^{II}Cr_2O_4$ supports. It was found that the deposition of Au nanoparticles leads to a decrease in the T_{max} in all the samples, with exception of AuFeCr for which the reverse effect was observed (cf. column 3 of Table 1). Moreover, the addition of Au causes a considerable increase in TPR signal intensity for most of the samples. To illustrate these effects Fig. 1 gives TPR curves for selected

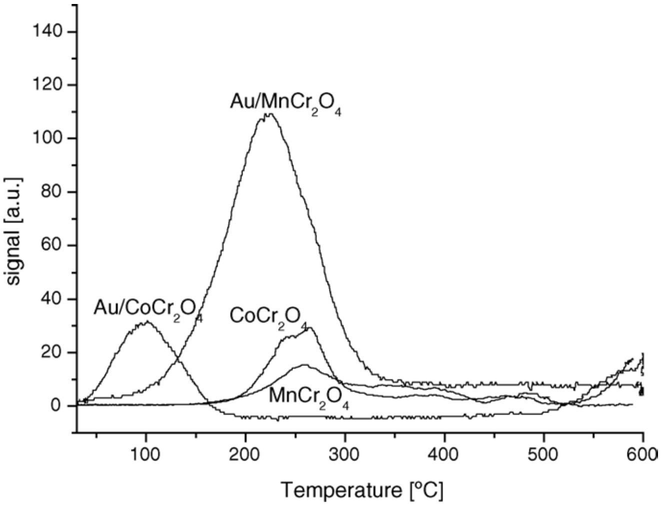

Fig. 1. H_2TPR curves for Au/$M^{II}Cr_2O_4$ catalysts and their supports.

supports and catalysts. The decrease in the temperature of reduction of the Au/MCr catalysts as compared with pure supports, suggests, that the presence of Au particles facilitates activation (dissociation) of a hydrogen molecule, this latter process being usually considered as the r.d.s. of the reduction. The dissociated hydrogen species migrate by a spill-over process from the surface of the Au particles to the support. The amounts of H_2 consumed by different samples vary, the highest consumption of H_2 being observed for the samples containing Cu and Fe. Different consumption of hydrogen, observed by Słoczyński et al. [9] for different Cr spinels was ascribed by them to different extent of the reduction: for the Cu and Fe spinels the reduction involves decomposition in the bulk, whereas the other spinels are reduced only on the surface, with transformation of surface Cr^{6+} ions to Cr^{3+}.

TEM pictures show the presence of small Au particles of different size. Column 4 in Table 1 gives their minimal (2–5 nm depending on the catalyst) and dominating size.

The BE values from *XPS data* for Au 4 f level of 84 ± 0.3 eV, in the studied catalysts (column 5), indicate a metallic state of Au in the AuMCr catalysts. The XPS data indicate moreover the presence of Cr^{3+}, Co^{2+}, Mn^{2+}, Cu^{2+}, $Fe^{3+} + Fe^{2+}$ (BE = 710.4 ± 0.2 eV) as dominating cationic species on the support surface. Some amounts of cations of other valencies (Cr^{6+}, Co^{3+}, Mn^{4+}, Cu^{1+}) were also observed.

Isopropanol decomposition gives acetone as the main reaction product for all the samples, with the exception of systems containing Fe, for which the main product was propene. This indicates high acidity of the Fe-containing samples, and high dehydrogenating properties (basicity) of the other samples. The presence of Au nanoparticles leads to an increase of amount of acetone for all the samples, except of AuFeCr, and did not influence markedly the amount of propene.

3.2. Catalytic activity

3.2.1. CO oxidation

The catalysts were active at low temperatures (already at rt), with the CO conversion close to 100% for AuCoCr sample at 50 °C. The activity increased with the reaction temperature. Fig. 2 gives the results of CO oxidation on Au/$M^{II}Cr_2O_4$ catalysts at 35 °C for fresh catalysts and after activation in the H_2, in the form of the TOF values (calculated per total amount of Au), and CO conversion (numbers above the blocks). The H_2TPR data (T_{max}) are also presented. The activity depends on the type of the cation M^{II} in chromium spinel, increasing in the order:

$$\text{AuFeCr} < \text{Au MgCr} < \text{AuMnCr} < \text{AuCuCr} < \text{AuCoCr}, \qquad (1)$$

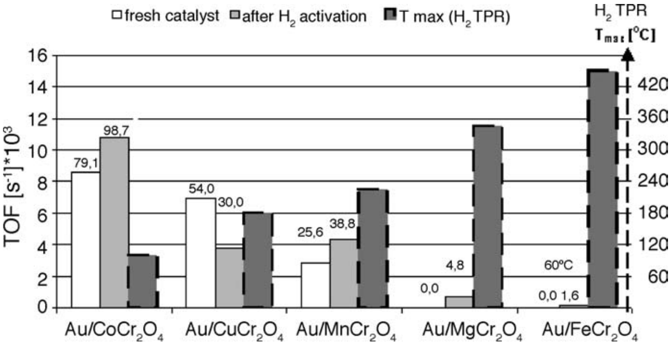

Fig. 2. Oxidation of CO on Au/$M^{II}Cr_2O_4$ catalysts at 35 °C and their reducibility (T_{max}) form H_2TPR measurements.

It is seen that the sequence of the increasing activity clearly follows the sequence of the increasing reducibility of the catalysts (decreasing T_{max}). It can be also observed, that for the catalysts in which a redox couple M^{2+}/M^{3+} may be present in the stationary conditions of the reaction, the activity increases with the increasing redox potential: Fe^{2+}/Fe^{3+} (0.77 V) < Mn^{2+}/Mn^{3+} (1.51 V) < Co^{2+}/Co^{3+} (1.84 V). Such a couple may be involved in activation of an oxygen molecule during the reaction. In the two other systems (CuCr, MgCr), in which such a couple cannot be envisaged, the redox processes may involve Cr ions.

The observed correlations indicate the importance of the support redox properties in controlling the performance of the Au nanoparticles/oxide support catalysts. The higher reducibility suggests the higher concentration of the surface oxygen vacancies in the stationary state of the reaction, which can be the centres of the oxygen activation as suggested in [5–7]. Such vacancies may be formed even in the reaction mixture $CO + O_2$, which exhibits lower redox potential as compared with the oxygen atmosphere [12]. It cannot be decided whether these vacancies are formed on the support and oxygen adsorbed on them migrates by spill-over to the Au particles, or whether they are formed on the support centres at the periphery of Au particles.

The pretreatment of catalysts in H_2 stream leads generally to an increase in the activity with the exception of AuCuCr catalyst. In the latter case the reduction with hydrogen leads to decomposition of spinel support to Cu^0 [9]. The effect of the increasing activity after the H_2 treatment is relatively stable in time (practically, no deactivation after 5 h of CO oxidation was observed for AuCoCr, AuMnCr, and AuFeCr catalysts), which suggests that the effect may be due to reduction (''cleaning'') of the oxidic (less active) species on the surface of the Au particles, rather than to the reduction of the support.

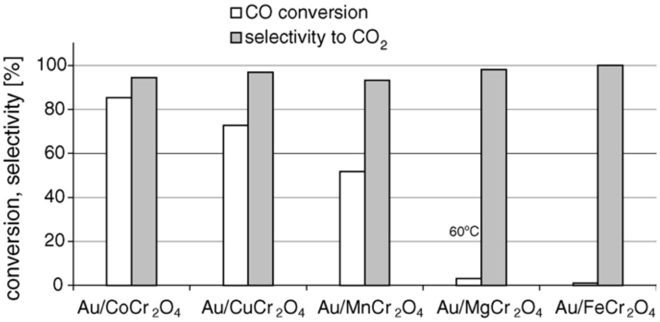

Fig. 3. Selective oxidation of CO on Au/$M^{II}Cr_2O_4$ catalysts at 35 °C.

3.2.2. *Selective (preferential) CO oxidation*

The results of oxidation of CO on Au/$M^{II}Cr_2O_4$ catalysts in the presence of hydrogen in the reaction mixture are presented in Fig. 3. The selectivity to CO_2 indicates the percent of the oxygen which was consumed for CO oxidation (the rest being used for hydrogen oxidation). The catalysts are active in selective oxidation of CO already at 35 °C, moreover, the presence of hydrogen in the reaction mixture leads to higher conversion of CO for all catalysts, in comparison to results in mixture without H_2. This confirms the hypothesis that higher reduction degree of the catalyst surface (expected in the presence of hydrogen) leads to the increase in the activity. The apparent discrepancy between the results for AuCuCr spinel in selective oxidation (increase in the CO conversion) and after pretreatment in H_2 (decrease in conversion), can be due to the fact that the pretreatment was performed at higher temperatures (150 °C) at which deactivating reduction may take place, whereas the selective oxidation at 35 °C. The sequence of the activity is the same as that without the hydrogen (1). Selectivity to CO_2 depends very little on type of the cation in chromium spinels and amounts to >90% at 35° for all the catalysts. When increasing the reaction temperature, the selectivity to CO_2 decreases: such an effect was the strongest for Fe–containing sample (100% at 35 °C and 40% at 250 °C).

4. Conclusions

Chromium spinels $M^{II}Cr_2O_4$ are promising supports for Au nanoparticles in oxidation of CO, both for practice and fundamental studies:

(1) The activity depends on the type of the cation increasing in the order:

$$\text{AuFeCr} < \text{AuMgCr} < \text{AuMnCr} < \text{AuCuCr} < \text{AuCoCr}$$

(2) The sequence of the increasing activity is followed by the sequence of increasing reducibility of the catalysts. This indicates the importance of the support redox properties in controlling the performance of the Au nanoparticles/oxide support catalysts.

(3) The catalysts are selective in CO oxidation in the hydrogen presence (selective oxidation) at low temperatures, with the selectivity to CO_2 of 90–100%.

(4) The activity in CO oxidation increases after activation in H_2 or in the presence of H_2 in the reaction mixture: the effect is relatively stable in time.

(5) Presence of Au particles facilitates the reduction of the supports as indicated by the decrease in the T_{max} in the H_2TPR. This implies activation of the H_2 on Au nanoparticles.

(6) No clear correlations is observed between catalytic and the acido-basic properties of the catalysts, nor the size of the Au particles.

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