

Effect of the preparation of supported gold particles on the catalytic activity in CO oxidation reaction

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Abstract

Gold catalysts supported on hydrotalcite (HT) with a Mg:Al molar ratio 4:2 were prepared by direct anionic exchange (DAE) or by deposition–precipitation (DP) with NaOH or urea, in order to investigate the influence of the synthesis parameters on the catalytic conversion in CO oxidation. The highest activity was obtained for Au/Mg₄Al₂ prepared by DAE. The influence of various parameters on CO conversion such as the H₂AuCl₄ concentration in the initial solution, the washing procedure, the pre-treatment temperature, the precursor of HT and the gold loadings were investigated. This study confirms the poisoning effect of chloride. The average gold particle size is higher for the catalysts with higher residual chloride content. In order to remove the remaining chloride from the sample, different washing procedures were used, i.e. either with warm water or with ammonia. Changes in activity and particle size were observed according to the washing procedure. Higher calcination temperature increases the surface area of HT, contributing to better dispersion of gold. A smaller particle size, as measured by XRD and TEM, is obtained on HT prepared from sulfate precursor rather than nitrate.

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1. Introduction

In the last few years, it has been pointed out that there is a strong interest in catalysis by gold due to its potential applicability into many reactions of both industrial and environmental importance. It has been shown that gold becomes active in many reactions when it is well dispersed on metal oxides [1,2]. The possibility of using supported gold nanoparticles as efficient catalysts for low temperatures reactions has attracted a lot of interest, since the pioneering work of Haruta which showed high activity towards CO oxidation with gold deposited on various metal oxides [3]. They are also active for a wide variety of reactions, including selective NO_x reduction [4,5], water–gas shift reaction [6,7], selective CO

oxidation [8,9], hydrocarbons oxidation [10], alkene epoxidation [11].

The catalytic activity of supported gold nanoparticles in CO oxidation at low temperature depends upon various factors, including the nature of the support, the Au precursor, the preparation procedure, the pretreatment conditions and the reaction conditions. It is generally accepted that the optimum size of gold nanoparticles should be smaller than 2–3 nm for CO oxidation [12]. Such particle size can be achieved only by a careful control of the conditions during the preparation. The nature of the gold precursor, the method of Au introduction to the support (e.g. coprecipitation, deposition–precipitation) and pH are known to be important variables influencing the resulting dispersion [2,13].

It has been shown that among the key factors for the preparation, the iso-electric point (IEP) of the support is very important. Among, the precursors generally used in the

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preparation of supported gold catalysts, HAuCl_4 is the most common. HAuCl_4 interaction with the support proceeds by anionic exchange and therefore, with oxides with IEP around 7, it is possible to prepare highly active catalysts, while gold supported on acidic oxides such as SiO_2 (IEP 1, 2) [14] or basic MgO (IEP 1, 2) [15] is usually inactive. Al_2O_3 , an amphoteric oxide (IEP 8) was reported as being either very active or even being inactive when as a support of gold was used [16,17]. In a previous paper we have shown that gold catalyst supported on Al_2O_3 prepared by direct anionic exchange provide small gold particle size and high catalytic activity in CO oxidation [18]. It was interesting to apply this method of preparation to other supports, particularly basic ones for which obtaining gold nanoparticles is difficult if not impossible. Thus, hydrotalcite (IEP 10) with Mg:Al molar ratio 4:2 was chosen as a model of basic support.

Hydrotalcite-like compounds, a class of layered double hydroxides, consist of positively charge metal hydroxide layers separated from each other by anions and water molecules. The layers contain metal cations of at least two different oxidation states [19]. Hydrotalcites (HTs) as prepared or after calcination at high temperatures have many applications. They are often used as a catalysts or catalysts precursors, ion exchangers, adsorbents, polymer stabilizers, etc [20]. These catalysts possess a big surface area, basic properties and undergo high metal dispersion [21].

Another effect is the amount of residual chloride in the catalysts, not yet fully understood, but its poisonous effect, e.g. for gold supported on Al_2O_3 or TiO_2 is well established [22,23]. The activity of gold catalysts for CO oxidation depends upon the preparation method, mainly based on precipitation of a gold precursor at a basic pH in order to deposit a gold precursor on different types of metal oxides [2].

Therefore, the aim of this work is the preparation of gold particles on hydrotalcite and the attempt of understanding of the effect of preparation procedure on the catalytic total oxidation of CO.

2. Experimental

2.1. Au/Mg₄Al catalysts preparation

The different samples of hydrotalcite, like compounds with Mg:Al molar ratio 4:2 were used as supports. Mg_4Al_2 samples were obtained by the standard co-precipitation method in Institute of Chemical Process Fundamentals CAS (Prague, Czech Republic) [21]. Two of them were prepared with a sulfate precursors of magnesium and aluminum and pretreated at either 60 °C or 450 °C, the third one was obtained with the nitrate precursors and calcined at 450 °C.

The gold precursor was HAuCl_4 (Alfa Aesar). The Au/ Mg_4Al_2 catalysts were obtained by the direct anionic exchange (DAE) method as previously described by Pitchon et al. [18] and their activities were compared with the catalysts prepared by the deposition–precipitation (DP) method

with either NaOH or urea, as a precipitant agent, according to Zanella et al. [12].

The first method of preparation is based on the direct anionic exchange of the gold species with the hydroxyl groups of the support. Aqueous solution of HAuCl_4 with the concentration either 2.37×10^{-4} , 1.4×10^{-3} or 1.05×10^{-2} M were prepared and added to 1g of support Mg_4Al_2 . The obtained suspension was heated up to 70 °C, thermostated and vigorously stirred for 1 h, and then centrifuged and washed, in order to remove the remaining chloride. Depending on the washing procedure, the solids were suspended in either 4 M ammonia solution, warm water (50 °C) or concentrated ammonia without filtration before washing step—this method of washing was called in situ washing and stirred for 1 h and centrifuged again. After drying in an oven at 120 °C overnight, the catalysts were calcined under air at 300 °C for 4 h.

In the DP method with NaOH, 75 ml of an aqueous solution of HAuCl_4 (1.4×10^{-3} M) was heated up to 80 °C. The pH was adjusted to 8 by dropwise addition of 1 M NaOH and then 1 g of Mg_4Al_2 (dried at 60 °C) was dispersed in the solution, the pH was readjusted to 8 with NaOH. The suspension was thermostated at 80 °C, vigorously stirred for 1 h and then centrifuged. The solid was washed by suspension in water (100 ml/g), stirred for 10 min at room temperature and centrifuged again. The washing procedure was repeated four times. After drying in an oven at 120 °C overnight, the catalysts were calcined in air at 300 °C for 4 h.

In the DP method with urea, 1 g of Mg_4Al_2 was added to 75 ml of an aqueous solution of HAuCl_4 (1.4×10^{-3} M) and of urea (0.42 M). The initial pH was ~ 2 . The suspension thermostated at 80 °C was vigorously stirred for 4 h and then centrifuged, washed, dried and calcined following previously reported procedure.

2.2. Methods of characterization

Chemical analysis of Au and Cl in the samples was performed by inductively coupled plasma atom emission spectroscopy (ICP-AES) at the CNRS Center of Chemical Analysis (Vernaison, France). The detection limit for Cl was 200 ppm. Chemical analysis was performed for calcined samples.

X-ray diffraction (XRD) measurements were carried out on a Siemens D-5000 diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation, with a continuous acquisition between 15° and 80° and a position sensitive detector using a step size of 0.02° and a step time of 2 s.

The gold particle size (D_{hkl}) was estimated from the width of principal diffraction peak (1 1 1) using the Scherrer equation as presented in formula (1.1):

$$D_{hkl} = \frac{k\lambda}{\beta \cos \theta} \quad (2.1)$$

where θ is the incidence angle for hkl reflection (rad), β is the angular line width at medium height (rad) and k corresponds to the Scherrer constant (0.9). The average particle size ($\overline{D_{hkl}}$)

were calculated taking into account the intensities of each diffraction peak as follow:

$$\overline{D_{hkl}} = \frac{\sum D_{hkl} I}{\sum I} \quad (2.2)$$

where I corresponds to the intensity of each peak relative to the highest intensity peak.

Transmission electron microscopy (TEM) was performed in a high resolution microscope EM-002B (TOPCON 200 kV) at 10^{-5} Pa. For analysis, samples were placed on a Cu-mesh. The mean particle diameters d_m were calculated from prepared size histograms with the following formula:

$$d_m = \frac{\sum_i (x_i d_i)}{\sum_i x_i} \quad (2.3)$$

where x_i is the number of particles with diameter d_i . To determine the mean diameter of gold particles at least 300 particles were chosen. The corresponding standard deviation σ was calculated using the following equation:

$$\sigma = \sqrt{\frac{\sum_i (x_i (d_m - d_i)^2)}{\sum_i x_i - 1}} \quad (2.4)$$

CO oxidation reaction was conducted at atmospheric pressure in a quartz flow microreactor containing 50 mg of catalyst and 150 mg of inert cordierite in a fixed bed, using a series of mass flow controllers with diluted gases. The catalytic tests were made using a gas mixture containing 2% CO and 5% O₂ (He as an eluant gas) with a flow of 50 cm³/min, in the temperature range 20–300 °C with a ramp rate 2 °C/min. The temperature was monitored and controlled by an Eurotherm system. Rosemount infrared analyzers were used to perform the analysis both CO and CO₂. Before the reaction, a pre-treatment in air at 300 °C for 4 h with a ramp rate of 5 °C/min was carried out.

The test procedure comprised a stabilization period, at first for He, of 10 min in the bypass, and after for the complete gas mixture, of 15 min in the bypass. The gas was then allowed to flow through the reactor, following a second period of stabilization for 60 min at room temperature. The furnace was heated from 25 to 300 °C, with a ramp rate 2 °C/min. This procedure was repeated in order to verify the reproducibility of the experiments.

The catalysts performance was assessed in terms of both T_{10} temperature, defined as the temperature, when 10% conversion was obtained (no diffusion effects) and T_{50} temperature, defined as the temperature, when 50% conversion was obtained.

3. Results and discussion

The study of Au supported on Mg₄Al₂ in CO oxidation was undertaken. The reaction is structure-sensitive, therefore, a difference in the activity reflects a change of the particle size. The size of gold particles can not be deduced from the

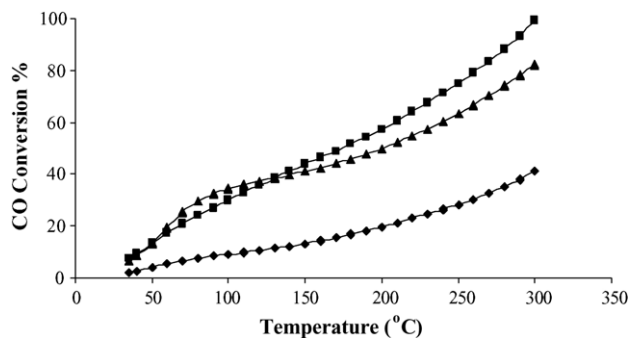


Fig. 1. Influence of the preparation method on CO oxidation activity for Au/Mg₄Al₂: DP urea (▲); DP NaOH (◆); direct anionic exchange (■).

activity because of many factors like, e.g. gold-support interaction, chemical state of gold, that can influence activity. In general the activity increases as the particle size decreases [2,18]. Gold species must be in the nanosize diameter range on the support to be active. The synthesis of highly dispersed small gold particles is highly sensitive toward the preparation procedure. Haruta and Date [13] showed that incipient wetness impregnation is unsuitable to produce highly dispersed gold catalysts and that in order to obtain high activity, the catalysts have to be prepared via coprecipitation or deposition–precipitation. The preparation method which could be applied to the widest range of the different supports is the deposition–precipitation which consist of the precipitation of a gold precursor on a support by increasing the pH in order to deposit gold precursor on different metal oxides [13].

Therefore, in this work we have presented the preparation method based on direct anionic exchange of a gold precursor with hydrotalcite and the influence of preparation procedure on CO conversion.

3.1. Effect of the preparation method on CO oxidation activity

The activity of the catalysts prepared by direct anionic exchange method has been compared with the activity of those catalysts obtained by deposition–precipitation with either NaOH or urea as a precipitant agent. The results are presented in Fig. 1 and in Table 1.

It can be seen that there are major differences in the activity when gold has been precipitated with either NaOH or urea. First of all, it is related to the amount of gold deposited on Mg₄Al₂ by precipitation with NaOH which is much lower than urea. The significant difference

Method of preparation	T_{10} (°C)	T_{50} (°C)	Au (%)	Cl (ppm)
DP urea	42	200	1.87	500
DP NaOH	140	–	0.55	≤200
DAE	48	175	1.48	≤200

comes from the conditions of precipitation. According to Zanella et al., in the comparison with DP NaOH, DP urea method permits the gradual and homogenous addition of hydroxide ions throughout the whole solution, $\text{CO}(\text{NH}_2)_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{CO}_2 + 2\text{OH}^-$ and avoids local increase of pH and the precipitation of metal hydroxide in the solution [12].

The increase of the activity was observed when the catalyst prepared by DAE method was investigated. The T_{50} is equal to more than 300 and 200 °C for DP NaOH and DP urea, respectively, and decreases to 175 °C for the catalyst prepared by DAE method. In addition, the elemental analysis confirmed that the DP urea catalyst contains bigger amount of chlorides, which are commonly known to be poisoning for many reactions, than the DAE catalyst.

Direct anionic exchange method of Au/Mg₄Al₂ preparation seems to be promising and further investigations during different steps of preparation have been undertaken. The effect of HAuCl₄ concentration in the initial solution, washing procedures, the pre-treatment temperature, precursor of HT and gold loading on CO conversion was investigated.

3.2. Effect of the HAuCl₄ concentration in the solution on the catalytic activity

The study of the influence of HAuCl₄ concentration in the initial solution on the CO oxidation activity was undertaken. It was investigated for Au/Mg₄Al₂ catalysts prepared by direct anionic exchange method. The hydrotalcite used as a support was obtained by coprecipitation method using sulfate precursor and pre-treated at 60 °C.

The different concentrations of the gold solution lead to the different initial pH. Belevantsev et al. [24] showed that HAuCl₄ may hydrolyze with obtaining different gold complexes depending on the temperature and pH. According to Peck et al. [25], at pH 1.5 only the complex of AuCl₄⁻ exists in the solution. According to Nechayev and Zvonareva [26], with the increase of pH up to 3–4, the concentration of those species decreases and different less chlorinated gold species are obtained. In fact, for a value of pH smaller than 5, all those species coexist in the solution [18]. It was confirmed by Chang et al., that at pH ≥ 7 a precipitation of Au(OH)₃ is observed, the reason of a noticeable loss of gold during different step of preparation, e.g. filtration and washing step [27].

Aqueous solution of HAuCl₄ with the concentration either 2.37×10^{-4} , 1.4×10^{-3} or 1.05×10^{-2} M were prepared us-

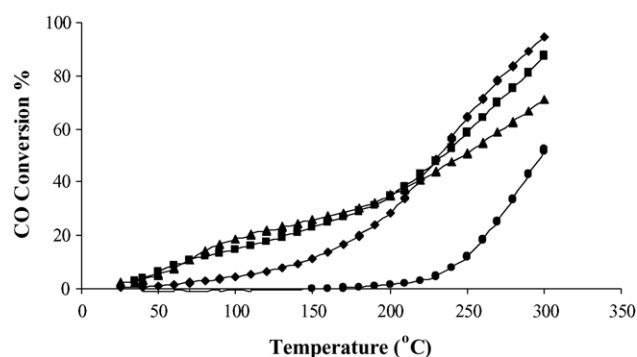


Fig. 2. Effect of the HAuCl₄ concentration in the initial solution on CO conversion: Mg₄Al₂ (●); 1.05×10^{-2} M (▲); 1.4×10^{-3} M (■); 2.37×10^{-4} M (◆).

ing 450, 75, 10 ml of distilled water, respectively. Depending on the initial gold concentration, the initial pH of the solution, and the pH after stirring and thermostating at 70 °C for 1 h in the presence of Mg₄Al₂ was monitored. The pH values are summarized in Table 2.

The addition of Mg₄Al₂ to the gold solution causes a continuous increase of pH with time. If the concentration of the gold solution and the temperature are constant, the change of pH comes from modifications of the surface of the support and from the gold-support interactions [18]. During the preparation, increases of pH from 3.3 to 8.1 and from 1.8 to 6.0, for a gold concentrations 2.37×10^{-4} and 1.05×10^{-2} M, respectively, were observed. The rapid increase of pH, after the support addition, is related to the high value of the IEP of Mg₄Al₂ (IEP = 9.3) and to its basic character. The influence of the initial gold concentration on CO conversion is presented in Fig. 2 and Table 2.

The decrease of the initial concentration of the gold solution from 1.05×10^{-2} to 1.4×10^{-3} M and finally to 2.37×10^{-4} M leads to a higher activity with T_{50} of 250, 235, 233 °C, respectively. Simultaneously, the decrease of the concentration leads to an increase of the loss of gold during the filtration step. As a result, the gold loading does not correspond exactly to the amount of gold introduced to the solution. It is related to the changes of pH during preparation. At the pH more than 8, obtained after 1 h of impregnation for 2.37×10^{-4} M initial gold concentration, the precipitation of Au(OH)₃ is observed which led to a loss of gold during the filtration step. However, at the pH c.a. 6, the main species is [AuCl(OH)₃]⁻, which is more appropriate for the formation of stronger anchored gold species on the support. This

Table 2

Effect of the HAuCl₄ concentration on pH solution before and during the preparation, activity and gold loading Au/Mg₄Al₂

HAuCl ₄ concentration (M)	pH solution	pH after 1 h of stirring at 70 °C (solution + HT)	T_{10} (°C)	T_{50} (°C)	Au (%)	Cl (ppm)
2.37×10^{-4}	3.3	8.1	145	233	1.34	≤200
1.4×10^{-3}	2.3	7.1	70	235	2.22	≤200
1.05×10^{-2}	1.8	6.0	70	250	2.63	0.15%
HT (dried at 60 °C)	–	–	248	300	–	–

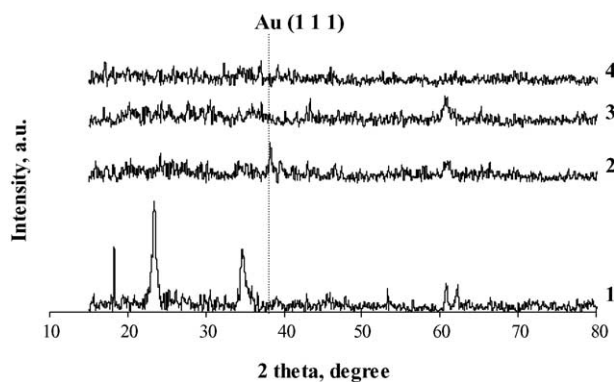


Fig. 3. Diffractograms of Au/Mg₄Al₂ depending on the initial gold concentration: (1) Mg₄Al₂; (2) 1.05×10^{-2} M; (3) 1.4×10^{-3} M; and (4) 2.37×10^{-4} M.

value of pH was observed for an HAuCl₄ concentration of 1.05×10^{-2} M.

The pH of the synthesis solution is important not only to determine the speciation of $[\text{AuCl}_x(\text{OH})_{4-x}]^-$ and the amount of adsorbed gold, but it also influences the amount of chloride adsorbed on the support, as can be seen from Table 2. With the increase of pH, less chlorinated gold complexes formation is observed. For that reason, catalysts prepared using less concentrated gold solution (higher pH value) contain less chloride. The significant quantity of chloride, shown by elemental analysis, could be the reason why an increase of the activity was not detected. It confirmed its role in the sintering of gold particles during calcination is important [18].

The XRD patterns of the catalyst prepared using different gold concentration in the comparison with Mg₄Al₂ are presented in Fig. 3. The XRD pattern of the catalyst prepared using the most diluted gold solution (2.37×10^{-4} M) does not contain Au(111) reflection at $2\theta \sim 38^\circ$. According to Wolf and Schüth [14], if the catalysts contain less than 1.5 wt.% of gold, the determination of gold particle size from X-ray diffraction line broadening becomes difficult. With the decrease of the initial gold concentration, the broadening of the Au(111) reflection was observed. The XRD pattern of the catalyst prepared using the most concentrated solution (1.05×10^{-2} M) exhibits the Au(111) reflection at $2\theta \sim 38^\circ$, corresponding to an average particle size of crystallites 22 nm, calculated by the Scherrer equation using peak (111).

Table 3

Effect of washing procedure on CO oxidation activity and gold loading for Au/Mg₄Al₂

Washing procedure	T_{10} (°C)	T_{50} (°C)	Au (%)	Cl (ppm)
Without washing	70	250	2.63	0.15%
Washed with NH ₄ OH	48	198	1.5	≤200
Washed with warm water	48	175	1.48	≤200
Washed with ammonia 'in situ'	48	218	1.33	≤200

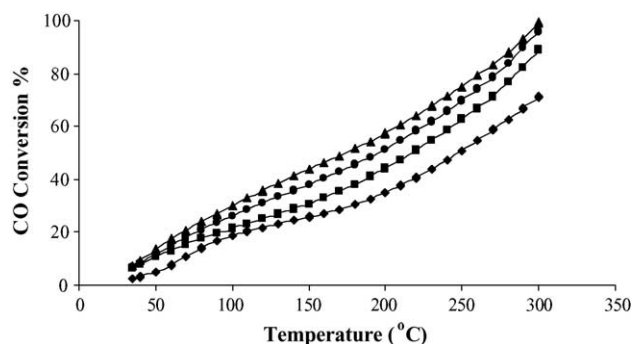


Fig. 4. Effect of washing procedure on CO oxidation activity for Au/Mg₄Al₂: without washing (▲); washed in ammonia (●); washed in ammonia 'in situ' (■); washed in warm water (◆).

3.3. Effect of the washing procedure

The poisoning effect of chloride has been investigated in detailed by Oh et al. [23]. The residual chloride was found to affect the activity in two different ways. It facilitates the agglomeration of Au particles during the heat treatment (calcination step) by the formation of Au–Cl–Au bridges [28], and it inhibits the catalytic activity by poisoning the active site. According to the literature results, the average gold particle size is bigger for the catalysts with higher residual Cl⁻ content [23].

One objective of this work is to confirm whether Cl⁻ has any direct effect on the catalytic activity. It could be accomplished by examining the changes in Au particle size and the catalytic activity when Cl⁻ was removed.

In order to remove the remaining Cl⁻ ions, part of the catalyst prepared by DAE using 1.05×10^{-2} M gold concentration was washed by different washing procedures. Three procedure were developed. The first two methods consist in washing the solid after filtration in either warm water or 4 M ammonia solution under vigorous stirring for 1 h, and the third one, so-called in situ washing, is performed by adding concentrated ammonia 25 M, to the suspension, i.e. without washing, under vigorous stirring for 1 h and then to filtrate. The influence of washing procedure on the catalytic activity Au/Mg₄Al₂ in CO oxidation is presented in Fig. 4. and Table 3.

The highest CO conversion was obtained for the sample washed in warm water. To explain this fact, all the samples were investigated by elemental analysis, XRD and TEM techniques. The XRD patterns are presented in Fig. 5. The sample prepared without washing contains the Au(111) reflection at $2\theta \sim 38^\circ$, corresponding to an average particle size

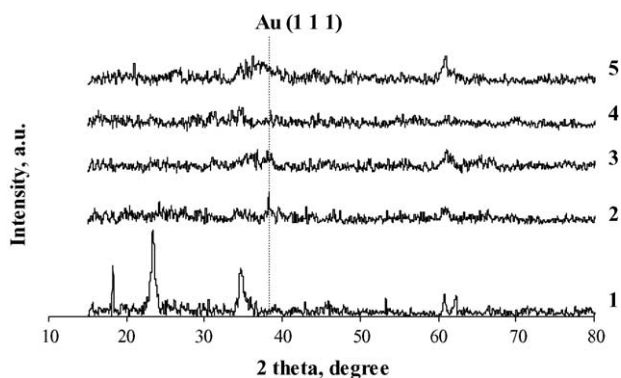


Fig. 5. Diffractograms of Au/Mg₄Al₂ depending on the washing procedure: (1) Mg₄Al₂; (2) without washing; (3) washing in warm water; (4) washing in ammonia; and (5) washing in ammonia 'in situ'.

of crystallites 22 nm, calculated by Scherrer equation using peak (1 1 1). After washing with warm water, the gold particle size decreases down to 12 nm and chloride is removed from the sample, as shown in Table 3. The diffractogram of the sample washed in ammonia solution contain Au(1 1 1) reflection at $2\theta \sim 38^\circ$, corresponding to an average particle size of crystallites 7 nm. The broadening of Au(1 1 1) reflection for the sample washed in ammonia in situ is observed. It

could be attributed to the fact that the particle size is too small to be detected. But a concomitant increase in the activity in CO oxidation for the samples washed in ammonia is not observed.

TEM was used in order to confirm the decrease of the particle size especially, in the case of the samples washed with ammonia, and to determine more accurately the particles size and their distribution. TEM images for the catalysts prepared by DAE, washed by different procedures are presented in Fig. 6. Particle size distribution of gold for all those samples have been calculated and are presented in Fig. 7.

For the sample Au/Mg₄Al₂ prepared by DAE without washing procedure, the majority of the particles are the fraction of size of 5–25 nm. The mean particle size calculated according to formula (2.3) is 16.7 nm. It is coherent with the average particle size of crystallites 22 nm, as calculated by Scherrer equation from XRD. For the catalyst washed with warm water, the particle size distribution is rather broad and agglomerates larger than 20 nm are observed. The mean particle size is 12.8 nm. The removal of chloride before the calcination causes a remarkable decrease of T_{50} from 250 to 175 °C for those samples, as it was presented in Fig. 4. The smallest gold particles were obtained either for the sample washed with ammonia or for the in situ ammonia washed

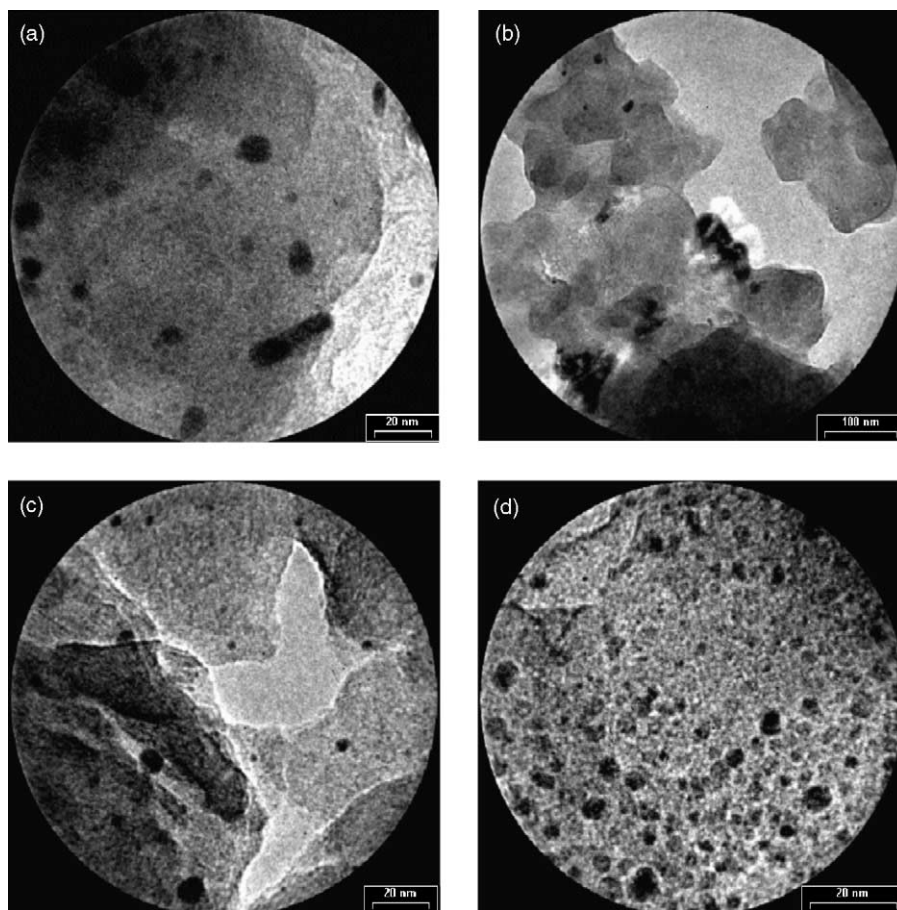


Fig. 6. TEM images of Au/Mg₄Al₂ depending on washing procedure: (a) without washing; (b) washing in warm water; (c) washing in ammonia solution; and (d) washing in ammonia 'in situ'.

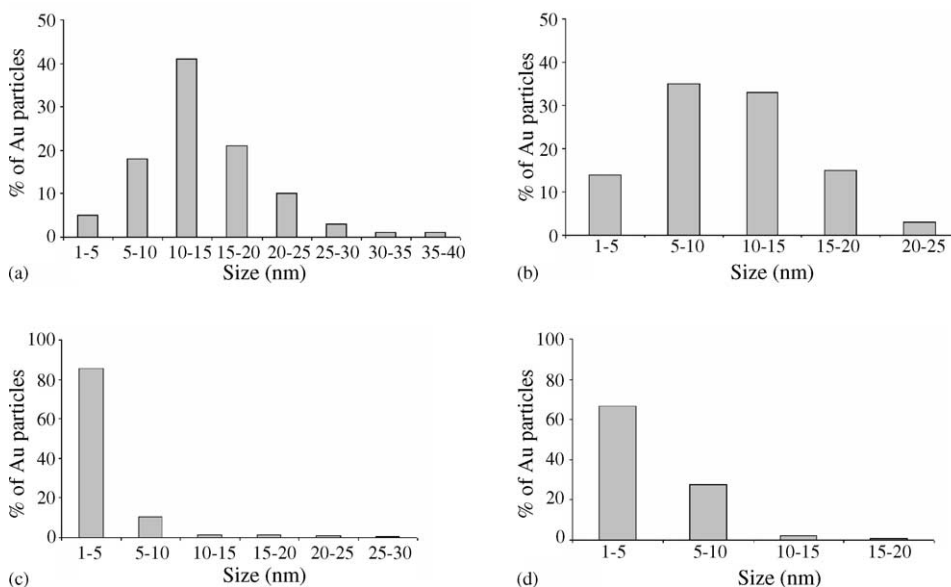


Fig. 7. Histograms of particle size distribution for Au/Mg₄Al₂ depending on washing procedure: (a) without washing; (b) washing in warm water; (c) washing in ammonia solution; and (d) washing in ammonia 'in situ'.

sample. The mean particle diameters are 6.1 and 4.2 nm, respectively (Table 4).

In the case of Au/TiO₂, for example, the existence of gold particles smaller than 5 nm enables significant CO oxidation activity even sub-ambient conversion. In the case of the sample washed in situ with concentrated ammonia and although the particles size is small, i.e. average size of 4.2 nm, ambient activity is not observed. For the water washed sample, although a larger particle size is obtained, i.e. 12.8 nm, a highest CO activity is observed. The low activity of the well dispersed sample, washed in concentrated ammonia, can be related to the an effect of the medium used during for the washing step. Although ammonia is much better than water to remove chloride, and therefore preventing the sintering of gold during the calcinations. It is possible, that the interaction between ammonia and HT caused some changes in the structure of the support, affecting the activity in CO oxidation. It confirms that the activity of gold catalyst does not only depends upon the particle size, but also of the nature of the interaction with the support which favours the formation of the most stable complex [29].

This study confirms the poisoning influence of chloride on the catalytic activity in CO oxidation. According to the liter-

Table 4

The mean particle diameters for Au/Mg₄Al₂ depending on the washing procedure calculated from TEM experiments

Washing procedure	Mean diameter (nm) ^a
Without washing	16.7 (6.6)
Washing in warm water	12.8 (5)
Washing in ammonia	6.1 (3.4)
Washing in ammonia 'in situ'	4.2 (2.8)

^a The standard deviations, calculated according to formula (2.4), are indicated in parentheses.

ature, the average gold particle size is higher for the catalysts with a high residual chloride content [2]. All the proposed procedures of washing allow the removal of chlorine and prevent the agglomeration of gold particles. Depending on the washing procedure, different activity and different particle size were obtained. However, all procedures caused the loss of gold, instead of 2.6 wt.% for non-washed sample, 1.5 wt.% after washing step was obtained.

3.4. Effect of the pre-treatment temperature of Mg₄Al₂

The effect of the pre-treatment temperature of hydrotalcite on CO conversion was undertaken by pre-treating two different Mg₄Al₂ samples, at either 60 °C or 450 °C. The results for Au/Mg₄Al₂, prepared by the DAE method using an initial gold concentration of 1.05 × 10⁻² M, is shown in Fig. 8 and Table 5.

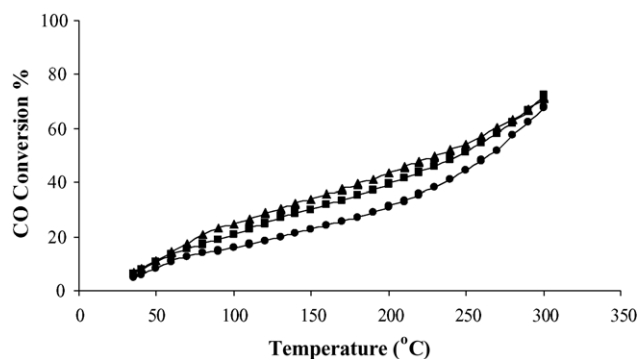


Fig. 8. Activity of Au/Mg₄Al₂, prepared using hydrotalcite calcined at 450 °C: without washing (■); washed in warm water (▲) washed in ammonia (●).

Table 5
Effect of the pre-treatment temperature of Mg_4Al_2 on % of CO conversion and gold loading for Au/Mg_4Al_2

The pre-treatment temperature °C	Washing procedure	T_{10} (°C)	T_{50} (°C)	Au (%)	Cl (ppm)
60	Without washing	70	250	2.63	0.15%
	Washing in warm water	48	175	1.48	≤200
	Washing in ammonia	48	198	1.5	≤200
450	Without washing	48	246	1.67	316
	Washing in warm water	48	235	1.16	≤200
	Washing in ammonia	56	265	1.20	≤200
Mg_4Al_2 (60°C)	–	248	300	–	–
Mg_4Al_2 (450°C)	–	250	–	–	–

The activity in CO oxidation for Au/Mg_4Al_2 prepared by DAE without washing step is independent of the pre-treatment temperature of the hydrotalcite. In comparison with the samples prepared using Mg_4Al_2 , pre-treated at lower temperature, there is a significant difference of gold loading and amount of remaining chloride as shown by elemental analysis. Using Mg_4Al_2 calcined at 450°C causes a loss of gold during the preparation. The amount of gold for the washed samples is about 1.2%. Simultaneously, there is a smaller amount of residual chloride. During the preparation of Au/Mg_4Al_2 using HT calcined at 60°C an increase of pH from 1.8 to 6.0 and from 1.8 to 7.3, for HT calcined at 450°C was observed. The increase of pH of a gold solution causes the formation of different gold complexes. According to Nechayev et al. [26], with an increase of pH, less chlorinated gold species are formed which would explain the significant difference in amount of residual chloride in the prepared samples. When HT calcined at higher temperature was used as a support, a higher increase in the pH value was noticed, as less chlorinated species were formed and exchanged with the support, causing lower amount of residual chloride.

In comparison with the samples prepared using HT without calcination, an increase in CO conversion was not observed because of the lower gold loading.

The XRD patterns of Au/Mg_4Al_2 without washing in comparison with Mg_4Al_2 calcined at 450°C are presented in Fig. 9. The diffractograms for the samples after washing procedures are not presented because the gold loading is always less than 1.5 wt.%.

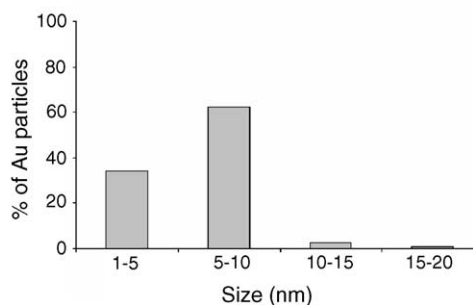
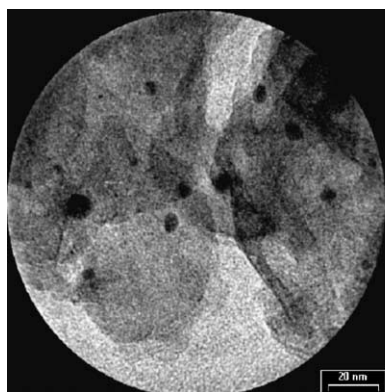


Fig. 10. TEM image of Au/Mg_4Al_2 , prepared using Mg_4Al_2 calcined at 450°C, washed in warm water and the histogram of particle size distribution.

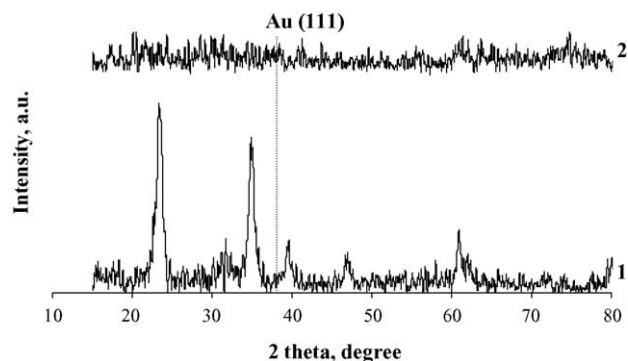


Fig. 9. Diffractograms of the sample Au/Mg_4Al_2 prepared without washing: (1) Mg_4Al_2 and (2) without washing.

The XRD pattern for the Au/Mg_4Al_2 does not contain clear Au(1 1 1) reflection at $2\theta \sim 38^\circ$. It could be related to the fact that the particle size is too small to be detected using this method. In order to define gold particle size accurately, TEM was used and the images of the sample washed in warm water along with the histogram of particle size distribution are presented in Fig. 10.

A majority of particles in the fraction 1–10 nm is obtained. The mean particle diameter calculated according to formula (2.3) is 8.6 nm. This value is lower than for the sample prepared using hydrotalcite pretreated at 60°C (12.8 nm).

According to the literature and measurements results obtained in the Institute of Chemical Process Fundamentals CAS (Prague, Czech Republic), the surface area of Mg_4Al_2

Table 6
Effect of Mg_4Al_2 precursor on percentage of CO conversion and gold loading for Au/ Mg_4Al_2

Mg_4Al_2 precursor	Washing procedure	T_{10} ($^{\circ}C$)	T_{50} ($^{\circ}C$)	Au (%)	Cl (ppm)
Sulfate	Without washing	48	246	1.67	316
	Washing in warm water	48	235	1.16	≤ 200
	Washing in ammonia	56	265	1.2	≤ 200
Nitrate	Without washing	192	–	1.53	0.85%
	Washing in warm water	200	–	1.48	0.82%
	Washing in ammonia	190	–	1.38	0.74%
Mg_4Al_2 sulfate	–	250	–	–	–
Mg_4Al_2 nitrate	–	290	–	–	–

increases from the initial $55 \text{ m}^2/\text{g}$ to a maximum of $160 \text{ m}^2/\text{g}$, when the HT is calcined at $450 \text{ }^{\circ}C$ [19]. According to Narayanan et al., the change in the surface area may be explained by changes in structural features of the HT [20]. A calcination disturbs the layered structure with the formation of a $MgO-Al_2O_3$ mixed oxides phase. It is also possible that during the calcination, the carbonate anions are removed as CO_2 accompanied by dehydroxylation. This creates voids and contribute to the surface area. It could be concluded that the increase of the surface area of hydrotalcite contribute to better dispersion of gold.

3.5. Effect of Mg_4Al_2 precursor

The effect of hydrotalcite precursor on CO conversion was undertaken. As a supports for gold, two different Mg_4Al_2 prepared with either sulphate or nitrate precursors and calcined at $450 \text{ }^{\circ}C$, were investigated. The influence of HT precursor on activity in CO oxidation and gold loading for 2% Au/ Mg_4Al_2 , prepared by DAE method using the initial gold concentration $1.05 \times 10^{-2} \text{ M}$, is shown in Table 6.

A significant difference in CO oxidation activity for Au/ Mg_4Al_2 prepared by DAE using $1.05 \times 10^{-2} \text{ M}$ gold concentration, depending on HT precursor is observed. Simultaneously, in the case of the sample obtained using nitrate salts of Mg and Al as HT precursors, much bigger amount of residual chloride, is measured by elemental analysis. In spite of the higher gold loading for those samples, the activity is much lower. This confirms the poisoning effect of chloride on the catalytic activity in CO oxidation. All the procedures used for washing did not allow a complete removal of chloride from the samples. Probably, this could be explain the differences in the interaction of the gold precursor with HT, depending on the investigated support.

The addition of HT prepared from a nitrate precursor to the gold solution causes a continuous increase of pH from 1.8 to 10.2 with the time. The increase of pH is larger than during the preparation of the sample from hydrotalcite obtained from a sulfate precursor (7.0). When the pH of the gold solution is so high, the precipitation of $Au(OH)_3$ is observed. This species does not contain chloride. Therefore, the higher amount of residual chloride in those samples comes from the adsorption of chloride ions by the structure of HT which can be rather strongly bonded.

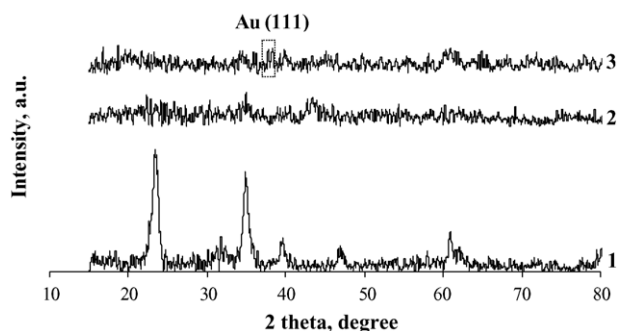


Fig. 11. Diffractograms of HT prepared with: (1) sulfate; (2) nitrate; and (3) Au supported on HT prepared using nitrate salts precursors.

As shown from the XRD patterns (Fig. 11.), Mg_4Al_2 prepared from a nitrate precursor does not present a high degree of crystallinity in comparison with HT prepared from the sulfate precursor. The XRD pattern of the sample prepared without washing contains the Au(111) reflection at $2\theta \sim 38^{\circ}$, corresponding to an average particle size of crystallites 31 nm, calculated by Scherrer equation. As it could be seen in Fig. 9, the particle size of gold supported on HT-sulfate is much lower than in the case of HT-nitrate where no as clear as in the previous case Au(111) ray is obtained. Both the large particle size of gold and a significant amount of residual chloride causes the low activity with HT obtained from nitrate salts of Mg and Al as precursors.

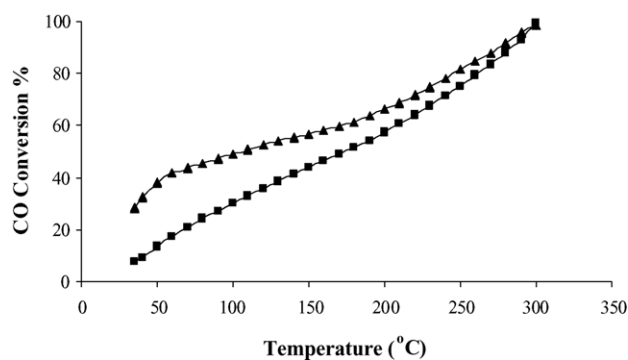


Fig. 12. The influence of metal loading on CO conversion for washed in warm water samples: 5% Au (▲); and 2% Au (■).

Table 7
Effect of gold loading on CO conversion for Au/Mg₄Al₂ catalysts

Expected gold loading (wt.%)	Washing procedure	T ₁₀ (°C)	T ₅₀ (°C)	Au (%)	Cl (ppm)
2	Without washing	70	250	2.63	0.15%
	Washing in warm water	48	175	1.48	≤200
	Washing in ammonia	48	198	1.5	≤200
5	Without washing	20	240	3.14	380
	Washing in warm water	20	106	2.85	≤200
	Washing in ammonia	20	192	2.77	≤200

3.6. Effect of gold loading on CO conversion

The influence of metal content on CO conversion for Au/Mg₄Al₂ was investigated. A series of samples by DAE were prepared with different gold loading, e.g. 2 and 5 wt.% of Au supported on HT pre-treated at 60 °C. The comparison of catalytic activity for the samples washed in warm water is presented in Fig. 12. The influence of the metal loading on CO conversion for all samples is summarized in Table 7.

The activity in CO oxidation for samples without washing step is independent of the gold loading. But there is significant difference in T₁₀ depending on metal content. Meanwhile, both the chloride and the gold content are smaller than the theoretical value expected in the case of 5%. This could be related to the fact that the number of OH groups at the surface is not large enough to allow complete exchange. Also, the increase in the metal content does not lead to an increase of the gold particle size. A change in the activity was not observed, due to the high remaining chloride content which inhibits reaction. Conversely, an increase of CO conversion with the increase of gold loading, for the sample washed in warm water was observed. The decrease of T₅₀ from 175 to 106 °C, for experimental gold contents of 2.63 and 3.14 wt.% was noticed, respectively, due to the increased of metal loading.

4. Conclusions

The obtained results can be summarised as follows.

There are major differences in CO oxidation activity when gold is supported on HT prepared by different method. An increase of the activity was observed for the catalyst prepared by direct anionic exchange. For that reason further investigations during the different steps of preparation have been undertaken.

The decrease of the initial concentration of the gold solution from 1.05×10^{-2} to 1.4×10^{-3} M and finally to 2.37×10^{-4} M led to a catalyst with higher activity. Simultaneously, the decrease of the concentration leads to the a higher loss of gold during the filtration step. This is related to the changes of pH during preparation. However, at the pH c.a. 6 (1.05×10^{-2} M), the main species is [AuCl(OH)₃]⁻ that is more appropriate to the formation of stronger anchored gold species on the support. The increase of the initial concentration of the gold solution led to agglomeration of gold particles

during the calcination and to a higher content of remaining chloride in the sample.

The effect of chloride has been investigated. This study confirms the poisoning influence of chloride on the catalytic activity in CO oxidation. The average gold particle size is bigger for the catalysts with high residual chloride content. All the procedures used for washing allow the removal of chloride and prevent the agglomeration of gold particles. Depending on the washing procedure, different activities and different particle sizes were obtained. According to XRD and TEM measurements, washing in warm water decreased the gold particle size from 22 to 12 nm and allow the removal of chloride from the sample. The smallest gold particles were obtained either for the sample washed in ammonia or for the sample washed in concentrated ammonia in situ. The mean particle diameters were 6.1 and 4.2 nm, respectively. The existence of gold particles less than 5 nm enables significant activity in CO oxidation even at room temperature, whereas, e.g. the sample washed with ammonia in situ (4.2 nm) is almost not active at such a low temperature. In spite of the fact that the mean diameter of gold was bigger (12.8 nm) for the sample washed in warm water, the highest activity in CO conversion was noticed. It could be possible, that the interaction between ammonia and HT caused changes in the structure of the support. It confirms that the activity of gold catalyst does not only depend on the particle size and that there is a significant influence of the properties of support.

Uncalcined hydrotalcite was found to be good material for supporting gold. During the study of effect of HT pre-treatment temperature, significant differences in the gold loading and in the amount of remaining chloride was observed. When HT calcined at higher temperature was used as a support for gold, a larger increase in the pH was noticed, less chlorinated species were formed and exchanged with the support, resulted in a lower amount of residual chloride. Simultaneously, a higher loss of gold was observed. Higher temperature of calcination increases the surface area of HT, contributing to better dispersion of gold.

A significant difference in CO oxidation activity depending on the HT precursor was observed. Both large particle size of gold and significant amount of residual chloride caused lower activity of samples prepared with HT obtained using nitrate metal salts as a precursor. The various washing procedures did not remove chloride. Mg and Al sulphates a much better precursor for the preparation of active HT support for gold than nitrates. Finally, a significant increase in CO con-

version with the increase of gold loading, especially for sample washed in warm water was observed. The increase in gold content does not increase gold particle size.

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