Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 113 (2006) 182–186

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Application of alumina supported gold-based catalysts in total oxidation of CO and light hydrocarbons mixture

Svetlana Ivanova, Corinne Petit, Véronique Pitchon *

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse,
UMR 7515 du CNRS 25 rue de Becquerel, 67087 Strasbourg, France

Abstract

Gold nanoparticles supported on alumina have been produced using the anionic exchange method and ammonia washing procedure. The catalysts are tested in the reaction of total oxidation of a mixture of light hydrocarbons and carbon monoxide in order to study the possibility of application in the reduction of cold start emissions. The obtained results are promising according to the temperature range observed for the oxidation of unsaturated hydrocarbons. The results obtained for acetylene confirms the difference of oxidation of this hydrocarbon over gold catalysts. An ageing procedure has been employed. This procedure does not affect the comportment of the catalysts versus hydrocarbon oxidation.

Keywords: Gold catalyst; Alumina; Hydrocarbon oxidation; CO oxidation

1. Introduction

Until recently, gold has been considered as one of the least catalytically useful metals because of its chemical inertness and the difficulty to obtain a high dispersion on common support materials. However, it has been widely proved that it is possible to prepare gold nanoparticles deposited on metal-oxide supports and under such conditions, gold exhibits high a catalytic activity towards low temperature CO oxidation. This reaction is important for purification of automotive exhaust though this pollutant is always contained in a mixture of unburned hydrocarbons which also contribute to air pollution. Actually, at around 90% of CO and unburned hydrocarbons emission is produced during the very first minutes that it takes to reach the operating temperature of motor of 300 °C, called cold start. For resolving this problem an introduction of the catalyst capable to oxidise the unburned hydrocarbons at the temperatures lower than 300 °C is required. With this in mind, gold could have an important potential for an application. Nevertheless, after the catalysts are routinely exposed to high temperatures above 600 °C for various periods of time and the exhaust contains a large proportion of humidity. These two factors contribute largely to the deactivation of the metallic phase by sintering.

Waters et al. [1] have studied gold based catalyst for the total oxidation of methane. The most active catalysts is Au/Co_3O_4 and its high activity below 250 °C was attributed to the existence of Au(III) oxidation state. Blick et al. [2] have studied Au/MgO system for the same reaction. A relation between the morphology of the gold particles and activity has been found.

Grisel et al. [3,4] have studied the influence of the method of preparation and additives – different metal oxides (MOx) to the system Au/Al_2O_3 in the reaction of total oxidation of methane. Metal oxide (MOx) stabilise gold nanoparticles on alumina and resulting catalyst is thermally resistant up to 700 °C. The same research group has also studied the total oxidation of propene over gold supported on alumina and alumina-ceria [5–7]. The addition of several additives enhances the catalytic activity and diminishes the temperature of total oxidation. The activity of gold-based catalysts in the complete oxidation of propene has been compared to these of platinum-based catalysts by Ruth et al. [8]. It was found that the platinum-based catalysts are more active. Recently, Kim et al. [9] studied the oxidation of a mixture of CO and propene. They have found that the addition of Au/TiO_2 to Pt/Al_2O_3 either as a physical mixture or as a pre-catalyst removes the CO and lowers the light-off temperature (T_{50}) for C_3H_6 oxidation compared with Pt catalyst alone by ~54 °C in the reaction feed. However, no indication in the

---

* Corresponding author. Tel.: +33 3 90 24 27 33; fax: +33 3 90 24 27 68.
E-mail address: pitchon@chimie.u-strasbg.fr (V. Pitchon).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.11.064

literature was found for the oxidation of a mixture of CO and hydrocarbons. So, the main objectives of this project is to prepare a gold catalyst on alumina which is a common support used in catalytic exhaust devices and to characterise the gold catalyst in terms of activity and resistance to ageing for the oxidation of mixture of carbon monoxide and hydrocarbons for low temperature applications.

2. Experimental

2.1. Catalysts preparation

We have developed a novel method of preparation based upon the direct anionic exchange (DAE) of the gold species with the hydroxyl groups of the support [10]. This method permits to have a high and homogeneous dispersion of gold on alumina. An important advantage of this method is to have final gold amount on the support close to the theoretical amount introduced in the solution. This is not the case of deposition precipitation method by sodium carbonate or hydroxide widely used in the literature. Aqueous solutions of $HAuCl_4$ of concentration 10^{-4} mol L^{-1} (pH 3.5) were made in order to obtain a final Au loading of 2 wt.%. The support γ-Al_2O_3, with a BET surface of 190 $m^2 g^{-1}$ was sieved with the fraction 125–250 μm retained. The gold solution was heated to 70 °C and the support was added. Then the slurry was filtered, washed, dried in an oven at 120 °C overnight and calcined in air at 300 °C for 4 h.

The mechanism of direct anionic exchange (DAE) of gold precursor with hydroxyl groups of alumina was proposed previously [11] and explains the preparation step-by-step: starting by the evolution of gold complexes in the solution, its interaction with alumina and the influence of applied drying and washing procedures.

2.2. Washing procedures

The washing procedures have been applied in order to remove the chlorine which is responsible for the gold particles sintering during the calcination. The washing agent was aqueous solution of ammonia ($NH_3 \cdot H_2O$) with concentration 25 mol L^{-1}. The employed washing procedure was a short washing for 20 min.

Caution/ safety note: The contact of ammonia with gold solution could provoke the formation of gold ammonia complexes which are explosive [12]. The use of this procedure is not dangerous if the gold complexes are strongly attached to the support by DAE. The assurance that there is no gold in the solution before adding of ammonia is required.

2.3. Characterisation, catalytic test and ageing procedures

Chemical analysis of Au and Cl in the samples was performed by inductively coupled plasma atom emission spectroscopy at the CNRS Center of Chemical Analysis (Vernaison, France). The detection limit is 150 ppm for Cl. Chemical analysis was performed after sample calcination. The Au weight loading of the samples is expressed in grams of Au per grams of calcined sample: wt.% Au = [mAu/(mAu + mAl_2O_3)] × 100. The gold loading was found to be 1.37 wt.% of gold and chlorine below 150 ppm.

Various unburned hydrocarbon species may be emitted from hydrocarbon flames. In general, there are two classes of unburned hydrocarbons: (1) small molecules that give the intermediate products of combustion resulting from the breaking of the C–C chain and (2) larger molecules that are formed by pyro-synthesis in hot, fuel-rich zones within flames (e.g. benzene, toluene, xylene, and various polycyclic aromatic hydrocarbons). Small unsaturated molecules are usually difficult to oxidise and compose mainly the product of incomplete combustion. Therefore, the study was focussed on this type of molecules and the catalysts were tested in the oxidation reaction of several hydrocarbons (C_2H_6, C_2H_4, C_2H_2). The reaction was performed at atmospheric pressure using a fixed-bed quartz micro-reactor packed with 200 mg catalyst and a gas mixture of 1% CO, 1500 ppm of hydrocarbon and 5% O_2 in helium with a flow rate of 75 $cm^3 min^{-1}$ (GHSV ~ 15000 h^{-1}). The flow was adjusted by means of Tylan flow controllers. The temperature was monitored and controlled by a Eurotherm system. The analysis was performed by Rosemount Infrared analysers for both CO and CO_2, and by gas chromatography for hydrocarbon (DB-Wax column, 2 m long and 2.5 mm of interior diameter). The experiment was repeated several times in order to measure the reproducibility and the results for CO and hydrocarbon oxidation presented as "fresh catalyst" are indeed the results from the second catalytic run . Before each test, the catalyst was treated at 300 °C in air during 2 h.

Two ageing procedures were used, i.e., heating in situ in air at 600 °C for 12 h or heating ex situ at 600 °C in air containing 5% H_2O at a flow rate 200 $cm^3 min^{-1}$ for 12 h.

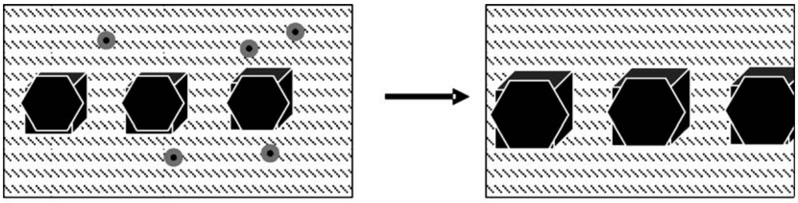
3. Results

High resolution TEM photographs were taken of this sample in order to study the dispersion and morphology of gold particles. It was observed, in accord with the literature, a non-spherical symmetry suggesting hemispherical morphology for particles smaller than 3 nm [13]. The average gold particle size for the fresh catalyst is found to be 1.9 nm. In this sample, gold particles smaller than 1 nm were observed. The TEM characterisations of aged samples [14], show a slight increase of gold particle size after ageing procedures to 2.6 nm after an ageing at 600 °C. Gold particles smaller than 1 nm observed before test on the support disappear and few large particles, higher than 9 nm, are present. The model of the particles size distribution for the two types of catalyst is present in Scheme 1.

3.1. Unsaturated hydrocarbons

The ethylene does not change its comportment in whole range of temperature in the presence or absence of CO (Fig. 1).

On the other hand, the oxidation reaction is inhibited as acetylene is mixed with CO, less for hydrocarbon (Fig. 2) than



(A) (B)

Scheme 1. Gold particles size distribution (A) fresh catalyst (B) spent catalyst.

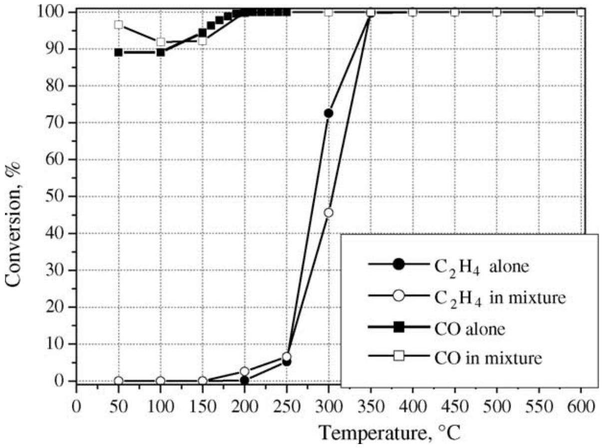


Fig. 1. Conversion of ethylene and CO separately or in mixture.

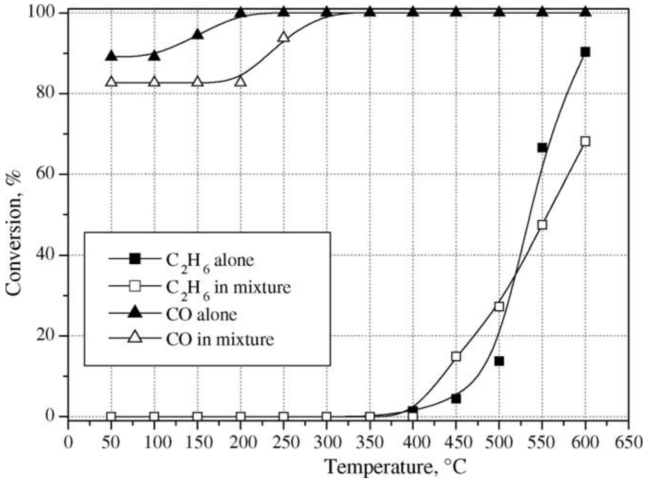


Fig. 3. Conversion of ethane and CO separately or in mixture.

for CO. The oxidation of acetylene has priority and once the conversion of hydrocarbon becomes 100% CO is immediately oxidised.

3.2. *Saturated hydrocarbons*

The oxidation of saturated hydrocarbons is more difficult that the oxidation of unsaturated one. It seems that the existence of π–bond facilitate the oxidation over gold based catalysts. Ethane (Fig. 3) start to convert at 450 °C which is a temperature rather distant for considering it as a catalyst for cold start application.

The presence of CO does not affect the oxidation of ethane. However, slightly lower degree of conversion for both gases is observed where the ethane and CO are mixed.

For tested alkanes or alkene like CH_4, C_3H_6, and C_3H_8 no influence of CO addition was found.

3.3. *Influence of ageing procedures*

The oxidation of CO has priority at low temperature. The activity of the catalyst versus ethylene oxidation does not change after the ageing treatments. However, the activity in CO oxidation of the catalysts sensibly decreases at low tempera-

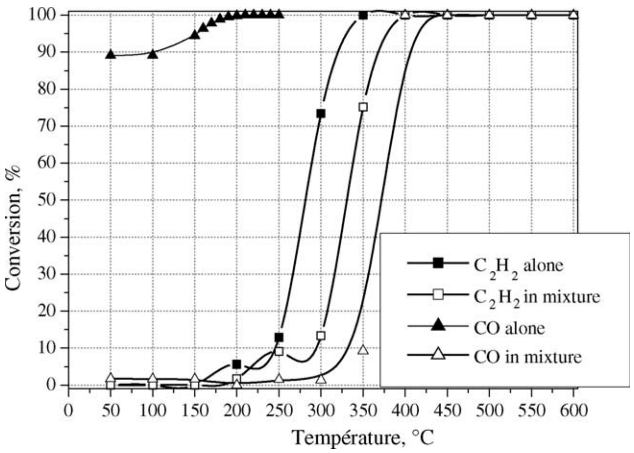


Fig. 2. Conversion of acetylene and CO separately or in mixture.

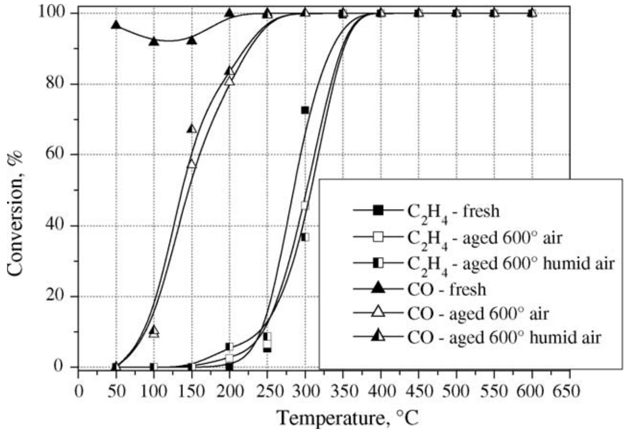


Fig. 4. Influence of ageing procedures on the conversion of a mixture CO and C_2H_4.

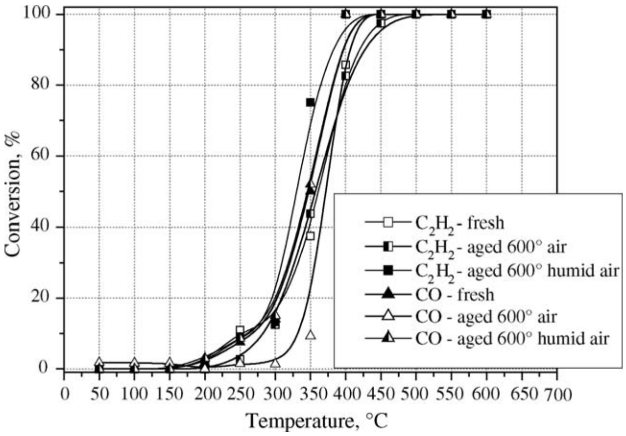


Fig. 5. Influence of ageing procedures on the conversion of a mixture CO and C_2H_2.

tures but still 100% of CO is oxidised at temperature less than 250 °C (Fig. 4).

The same comportment for aged sample as the fresh one was observed during the oxidation of acetylene. Once the hydrocarbon is converted the CO oxidation starts. Both gases are combusted in the temperature range of 300–400 °C (Fig. 5).

The saturated hydrocarbon–ethane (Fig. 6), present exactly the same trend of activity as the unsaturated hydrocarbons. The oxidation of hydrocarbon is not affected by the ageing procedures. As for the melange ethylene–CO, thermal treatment of the catalysts up to 600 °C in the presence or not of water provoke a decrease in activity versus CO oxidation which is more marked for the sample pre-treated without water.

Other hydrocarbons, like CH_4, C_3H_6, and C_3H_8, have also been studied, and for all no influence of ageing procedure over hydrocarbon oxidation was found. On the other hand, the deactivation of catalysts in CO oxidation reaction at low temperature was observed and corresponds probably to gold particles size increase. In CO oxidation, the deactivation of the catalyst is higher than for hydrocarbon oxidation showing that the CO reaction is more sensible to particle size variation.

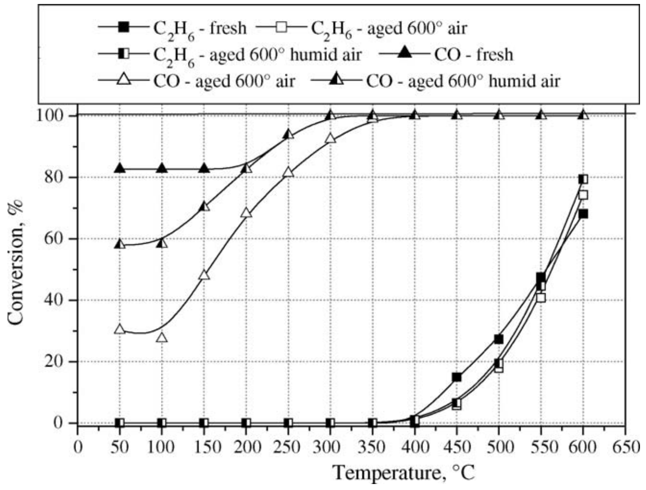


Fig. 6. Influence of ageing procedures on the conversion of a mixture CO and C_2H_6.

4. Discussion

The reaction of oxidation of CO is inhibited in the presence of alkynes but not in the presence of alkenes. This gives us an indication over the mechanism of oxidation–the adsorption of acetylene and CO most probably occurs on the same active site. The adsorption is competitive in favour to acetylene according to CO. The acetylene is strongly adsorbed to the surface at room temperature and occupies all adsorption sites which does not allow an adsorption of CO. However, it provokes an increase in the temperature of acetylene conversion at around 50 °C in whole range of temperatures compared to the conversion of acetylene alone. Once the oxidation of acetylene is complete the oxidation of CO begins. The delayed oxidation of CO indicates that CO could adsorb and react only on the sites totally liberated from acetylene or its products of oxidation. For all other hydrocarbons (CH_4,C_2H_4, C_2H_6, C_3H_6, C_3H_8), presented in this paper by C_2H_4 and C_2H_6, the oxidation of CO is dominate at low temperature.

As reported by Jia et al. [15], ethylene does not adsorb on gold nanoparticles. Our observation confirms it. Ethylene does not cover the adsorption sites of CO which continue to convert to CO_2 at low temperature. The conversion is close to 100% in the whole range of temperatures between 50 and 600 °C. Occupation of the surface is different for acetylene and ethylene, caused by different mode of adsorption which could be related to the additional acid function of acetylene. The occupation of catalyst surface is different for acetylene and ethylene, caused by different mode of adsorption which could be related to the additional acid function of acetylene. Acetylene, where the carbon is sp-hybridized with 50% s - character is much more acidic than ethylene with sp^2 hybridisation and 33% s - character. A mechanism of homogeneous activation of C–H bond of alkyne by Au(I) species was proposed by Wei et al. [16]. The reaction goes through formation of gold acetylide–RCCAuH, which could be one possible explanation of the difference in activity of acetylene and ethylene.

The oxidation of unsaturated hydrocarbons is complete in the range of temperatures 250–350 °C which includes the range of temperature of the cold start emissions. However, a slight improve in catalytic properties of this catalyst is necessary.

The saturated hydrocarbons are not affected either from the presence of CO in the mixture. The oxidation activity is not suppressed but the temperature of oxidation is too far way from the range needed for cold start emission removal.

The ageing of the catalyst does not change its activity versus the hydrocarbon oxidation. However, a deactivation of the catalysts in CO oxidation at low temperature was observed.

Several factors could influence the catalytic activity of gold catalyst such as the oxidation state of metal, the size of gold particles and their morphology. The influence of gold particles size on the catalytic activity in CO oxidation, especially for the gold-based catalyst supported on an inert oxide, such as alumina has been reported by Okumura et al. [17]. Thus the decrease of activity after first catalytic run could be attributed to increase of gold particles size. The TEM study shows the coexistence of two types of gold particles in fresh catalyst, very small particles – lower or equal to 1 nm, and bigger particles with an average diameter of 1.9 nm. For the spent catalyst, it was observed the disappearance of the particles lower than 1 nm and particle size growth to an average diameter of 2.6 nm. The morphology of the particles seems to be preserved.

The particles lower than 1 nm have some special electronic properties due to the structural defects, namely, the high proportion of gold atoms in the kinks, steps and edges sites. So the high activity in CO oxidation in the first catalytic run could be attributed to these defects. The large difference in catalytic activity for the fresh and aged catalyst could be explained by the disappearance of these active sites during the ageing procedures.

The presence of 5% H_2O at the same temperature during the pre-treatment does not affect the average particle size which remains small with a value even slightly lower of 2.3 nm. As the reaction of oxidation of CO is highly structure selective, the increase of gold particles size could explain the subsequent deactivation of the catalysts at low temperature.

5. Conclusions

The gold-based catalyst supported on alumina shows an activity versus unsaturated hydrocarbons and CO in the temperature range slightly distant than required. For saturated hydrocarbons gold catalysts is not applicable for reduction of ‘‘cold start’’ emissions. The oxidative properties of this catalyst should be ameliorated by utilisation par example of other reducible type support which will facilitate oxygen spillover on the catalyst surface.

References

[1] R.D. Waters, J.J. Weimer, J.E. Smith, Catal. Lett. 30 (1995) 181.

[2] K. Blick, T.D. Mitrelias, J.S.J. Hargreaves, G.J. Hutchings, R.W. Joyner, C.J. Kiely, F.E. Wagner, Catal. Lett. 50 (1998) 211.

[3] R.J.H. Grisel, P.G. Kooyman, B.E. Nieuwenhuys, J. Catal. 191 (2000) 430.

[4] R.J.H. Grisel, B.E. Nieuwenhuys, Catal. Today 64 (2001) 69.

[5] R. Grisel, K.-J. Weststrate, A. Gluhoi, B.E. Nieuwenhuys, Gold Bull. 35 (2002) 29.

[6] A.C. Gluhoi, N. Bogdanchikova, B.E. Nieuwenhuys, J. Catal. 229 (2005) 154.

[7] A.C. Gluhoi, N. Bogdanchikova, B.E. Nieuwenhuys, J. Catal. 232 (2005) 96.

[8] K. Ruth, M. Hayes, R. Burch, S. Tsubota, M. Haruta, Appl. Catal. B: Environ. 24 (2000) L33.

[9] D.H. Kim, M.C. Kung, A. Kozlova, S.D. Yuan, H.H. Kung, Catal. Lett. 98 (2004) 11.

[10] S. Ivanova, C. Petit, V. Pitchon, Appl. Catal. A: Gen. 267 (2004) 191.

[11] S. Ivanova, V. Pitchon, Y. Zimmermann, C. Petit, Appl. Catal. A 298 (2006) 57.

[12] J. Fisher, Gold Bull. 36 (2003) 155.

[13] M. Haruta, CATTECH 6 (2002) 102.

[14] S. Ivanova, C. Petit, V. Pitchon, Gold Bull. 39 (1) (2006), in press.

[15] J. Jia, K. Haraki, J.N. Kondo, K. Domen, K. Tamaru, J. Phys. Chem. B 104 (2000) 11153.

[16] C. Wei, C.J. Li, J. Am. Chem. Soc. 125 (2003) 9584.

[17] M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, A. Azuma, M. Haruta, Catal. Lett. 51 (1998) 53.