Catalysis Today 176 (2011) 116–119

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Investigation of Au/hydrotalcite catalysts for toluene total oxidation

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ARTICLE INFO

Article history:
Received 30 September 2010
Received in revised form 14 January 2011
Accepted 24 January 2011
Available online 18 February 2011

Keywords:
Hydrotalcite
Gold based catalyst
Toluene oxidation
CO oxidation

ABSTRACT

X_6Al_2HT hydrotalcites, where X represents Ni, Co, Mn or Mg, have been investigated before and after gold deposition for toluene and CO total oxidation reactions. Specific area and XRD measurements of these solids have been done. No change in the structure of the hydrotalcite support due to the introduction of gold is detected for the Co_6Al_2HT and Mn_6Al_2HT support. However the deposition of gold on these oxides has a beneficial effect on the activity. Concerning the total oxidation of toluene, the best activity is obtained with Au/Mn_6Al_2HT catalysts with a T_{50} at 240 °C. However catalytic behaviour of Au/X_6Al_2HT catalysts in oxidation of toluene depends mainly on the nature of the support: no clear correlations have been observed between catalytic properties and the average size of the Au particles.

1. Introduction

Volatile organic compounds (VOCs) in industrial gas represent a serious environmental problem. Many metals deposited on a support were shown to be active for catalytic VOCs oxidation. However, it was found that the support plays an important role in the improvement of the efficiency of the catalyst, particularly in oxidation reaction. During the past decade, many studies have established that nanosized Au-on-reducible support has a remarkable catalytic activity for many important oxidation reactions [1–6]. In a previous paper we have shown that gold catalyst supported on Ce–Ti mixed oxide prepared by deposition-precipitation method provide small gold particle size and high catalytic activity in propene oxidation [3,4]. Moreover, it was shown that an interesting way to obtain mixed oxides catalysts is through the use of hydrotalcites. 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 [7,8]. Indeed, after calcination treatment mixed oxides are formed and possess unique properties like high surface area and porosity, good thermal stability, good mixed oxides homogeneity basic properties and undergo high metal dispersion [9]. The partial or the total substitution of Mg^{2+} and Al^{3+} is possible by divalent cation or trivalent cation in the hydrotalcite structure.

In the present study, X_6Al_2HT hydrotalcites (samples called HT, where X represents Ni, Co, Mn or Mg) have been investigated before and after gold deposition for toluene and CO total oxidation reactions. The HT supports and the gold based catalysts have been studied by several physico-chemical techniques (BET measurements and XRD). Therefore, the aim of this work is the preparation of gold particles on HT and the attempt of understanding the effect between gold and the HT support on the catalytic oxidation of CO and VOC.

2. Experimental

2.1. Catalysts preparation and characterization

Hydrotalcite (HT) like compounds with XAl molar ratio 6:2 (denoted as X_6Al_2 where X correspond to Ni^{2+}, Mn^{2+}, Mg^{2+} or Co^{2+}) were prepared by coprecipitation. An aqueous solution containing appropriate amounts of nitrates elements (Ni, Mn, Mg or Co and Al) was added, under stirring, dropwise into Na_2CO_3 solution. During the synthesis the temperature and pH were maintained respectively at 60 °C and 10 by addition of NaOH solution. The solution was dried at 60 °C during 18 h. The resulting suspension was filtered off and washed several times with hot deionized water (50 °C) and dried at 55 °C during 48 h. The suspension was filtered washed and then dried at 100 °C during 24 h. The thermal treatment was performed under flow of air ($4\,L\,h^{-1}$ – $2\,°C\,min^{-1}$ – 4 h at 500 °C).

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doi:10.1016/j.cattod.2011.01.034

Gold based catalysts were also prepared with the Deposition Precipitation method using sodium hydroxide as precipitating agent. One gram of the hydrotalcite support was added to an aqueous solution at 80 °C containing the suitable amount of gold to obtain 4 wt% in the solid. The pH of $HAuCl_4$ solution was adjusted to 8 by addition of NaOH (0.1 mol L^{-1}) drop by drop under stirring during 4 h. The suspension was filtered, washed several times with hot water in order to eliminate Na^+ and Cl^- ions. The catalyst was then dried in the oven at 80 °C followed by a thermal treatment under air at 400 °C (1 °C min^{-1}) during 4 h. The code names of these catalysts are respectively: Au/X_6Al_2HT (where X represents Ni, Co, Mn or Mg).

The specific surface areas of solids were determined by the BET method using a QSurf M1 apparatus (Thermoelectron), and the gas adsorbed at −196 °C was pure nitrogen.

X-ray diffraction (XRD) measurements were carried out on a Bruker AXS D8 Advance diffractometer equipped with a copper anode ($\lambda = 1.5406$ Å) and a LynxEye detector. The scattering intensities were measured over an angular range of $20° \leq 2\theta \leq 80°$ for all the samples with a step-size of $\Delta(2\theta) = 0.02$ and a count time of 4 s per step. The diffraction patterns have been indexed by comparison with the JCPDS files. Crystallite size (d) of gold nanoparticles was calculated (with a graphics based profile analysis program "TOPAS from Bruker AXS") from the line broadening of the Au diffraction line using the Scherrer equation.

2.2. Catalytic tests

The activity for the toluene total oxidation of the catalysts (100 mg) was measured in a continuous flow system on a fixed bed reactor at atmospheric pressure. Toluene was chosen as probe molecule for the catalytic oxidation, because they are often found in industrial exhausts and present high photochemical ozone creation potentials (POCP) [10,11].

Before each test, the catalyst was reactivated in flowing air (2 L h^{-1}) at 400 °C for 4 h. The flow of the reactant gases (100 mL min^{-1} with 1000 ppm of C_7H_8 and balance with air) was adjusted by a Calibrage CAL PC-5 apparatus constituted of a saturator and mass flow controllers. After reaching a stable flow, reactants passed through the catalyst bed and the temperature was increased from room temperature to 400 °C (1 °C min^{-1}). The feed and the reactor outflow gases were analyzed on line by a micro-gas chromatograph (VARIAN CP4900).

CO oxidation reaction was conducted at atmospheric pressure in a quartz flow microreactor containing 100 mg of catalyst in a fixed bed, using a series of mass flow controllers with diluted gases. The catalytic tests were made using a gas mixture containing 5000 ppm CO and 10% O_2 (He as eluant gas) with a flow of 100 mL min^{-1}, in the temperature range 20–200 °C with a ramp rate 1 °C min^{-1}.

Model 4400IR (Mitchell Instrument) infrared analyzers were used to perform the analysis both CO and CO_2. Before the reaction, a pre-treatment in air at 400 °C 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 15 min at room temperature. The furnace was heated from 20 to 200 °C, with a ramp rate 1 °C min^{-1}. This procedure was repeated in order to verify the reproducibility of the experiments. The catalysts performance was assessed in terms of T_{50} temperature, defined as the temperature, when 50% conversion was obtained.

Table 1
Code name, BET specific area and temperature of 50% toluene conversion (T_{50}) of catalysts.

Catalysts	Specific area (m^2/g)	T_{50} (°C)
Co_6Al_2HT	123	287
Au/Co_6Al_2HT	122	265
Mn_6Al_2HT	110	249
Au/Mn_6Al_2HT	94	235
Ni_6Al_2HT	225	357
Au/Ni_6Al_2HT	190	330
Mg_6Al_2HT	216	>400
Au/Mg_6Al_2HT	201	>400

3. Results and discussion

Table 1 indicates the code name and the evolution of specific surface areas of HT support after gold deposition and thermal treatment at 400 °C under air. No significant decrease of the specific area after gold deposition is observed. This phenomenon seems indicate that gold could be well dispersed on HT surface.

The catalytic behaviour of the samples for toluene oxidation is represented in Fig. 1 and Table 1. The catalytic performance of the samples according to the T_{50} values follows the order:

$$Au/Mn_6Al_2HT > Au/Co_6Al_2HT \gg Au/Ni_6Al_2HT \ggg Au/Mg_6Al_2HT$$

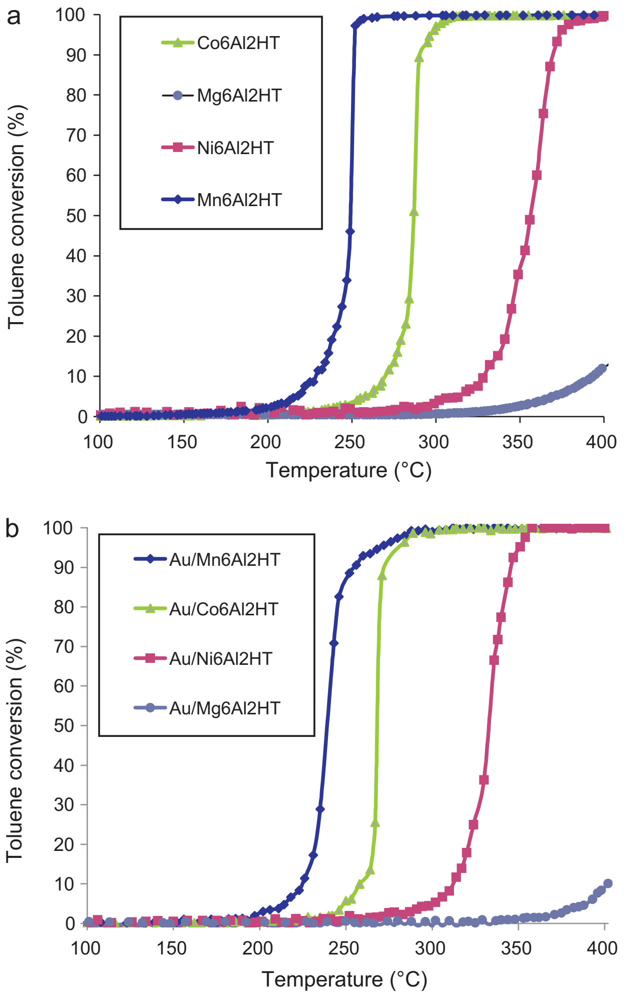

Fig. 1. Toluene conversion on hydrotalcite supports (a) and on gold based catalysts (b).

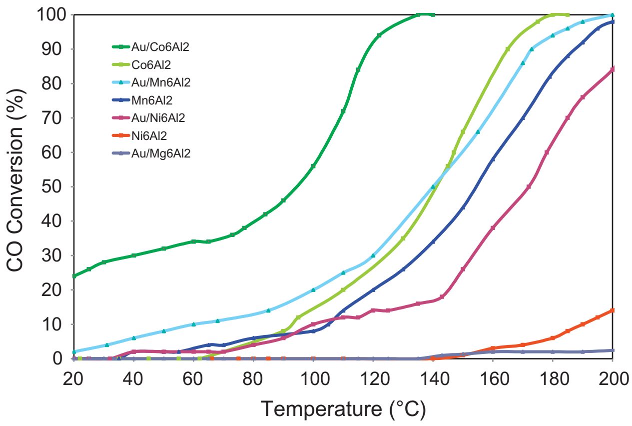

Fig. 2. CO conversion on HT support and gold catalysts.

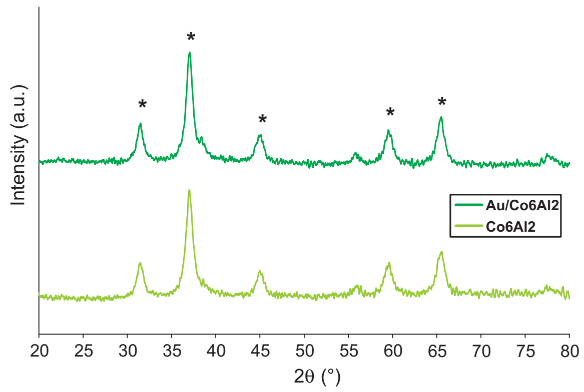

Fig. 3. XRD patterns of Co_6Al_2HT and Au/Co_6Al_2HT catalysts ($* = Co_3O_4$ and $CoAl_2O_4$).

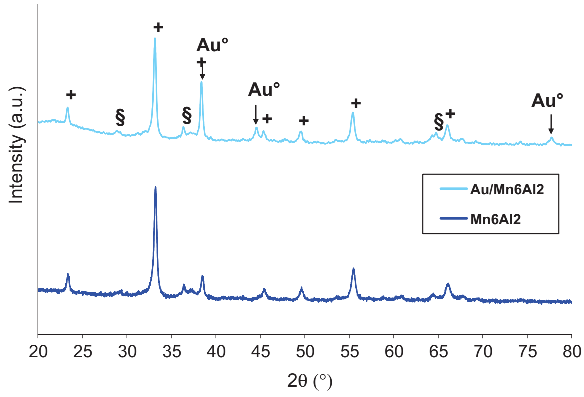

Fig. 4. XRD patterns of Mn_6Al_2HT and Au/Mn_6Al_2HT catalysts ($+ = Mn_2O_3$, $§ = Mn_3O_4$).

These results show that the gold catalysts are active for toluene oxidation. CO_2 and H_2O are the only products detected at 100% of conversion. The conversion of several hydrotalcite support calcined at 500 °C is compared with gold based catalyst. Thus, the use of gold has a little effect on the activity. Moreover, it could be noticed that the activity (Fig. 1) depends strongly on the composition of the hydrotalcite support. Concerning the total oxidation of toluene, the best activity is obtained with Au/Mn_6Al_2HT catalysts with a T_{50} conversion at 240 °C.

For a better understanding of these catalytic results, CO total oxidation was carried out. Indeed, the CO conversion on gold catalyst could be contributed to a better knowledge of the gold dispersion on support. Several authors [12–15] have shown that there is a relationship between catalyst activity and gold metallic particle size. More smaller is the crystallite size, better is the activity for the CO conversion into CO_2.

In Fig. 2 is presented the catalytic behaviour of the samples for CO oxidation. The catalytic performance of the samples follows the order:

$$Au/Co_6Al_2HT > Co_6Al_2HT \approx Au/Mn_6Al_2HT > Mn_6Al_2$$

$$HT > Au/Ni_6Al_2HT \gg Ni_6Al_2HT > Au/Mg_6Al_2HT$$

These results show that the gold catalysts are active for CO oxidation. The conversion of several hydrotalcite support calcined at 500 °C are compared with gold based catalyst. Thus, the use of gold has a beneficial effect on the activity and depends on the composition of the HT support. Well interaction between gold and the Co_6Al_2HT support was also evidenced. However, concerning the Mg_6Al_2HT solid, no CO conversion was observed until 200 °C (result no mentioned in Fig. 2). Moreover, the deposition of gold on this support is not very efficient since the CO conversion is very low at 200 °C. Thus, the nature of the HT support is crucial to well disperse gold nanoparticles and enhances the catalytic performance.

In order to investigate the size and structure of the samples, XRD patterns were performed. Thus, XRD patterns of Co_6Al_2HT support and the Au/Co_6Al_2HT catalyst are presented in Fig. 3. For the both diffractograms, Co_6Al_2HT and Au/Co_6Al_2HT, several diffraction peaks can be attributed to those of a spinel-type structure. The broadness of diffraction peaks can be also explained by the presence of a mixture of two oxide spinel phases very difficult to differentiate by XRD Co_3O_4 (JCPDS 42-1467), and $CoAl_2O_4$ (JCPDS 44-0160) [16]. The formation of Co_3O_4 is due to the easy oxidizability of Co^{2+} ions and the thermodynamical stability of Co_3O_4 (than CoO) in air [17]. No Au° diffraction lines at $2\theta = 38.2°$ and 44.4° were detected in this sample. It could be related to the fact that the particle size is too small to be detected using this method and probably that the gold crystallites was highly dispersed on the Co_6Al_2HT support according to the BET measurements.

However, concerning the other HT based catalysts, the XRD patterns of Au/HT sample (Figs. 4, 5 and 6) present besides the characteristic peaks of the structure of the HT support, the reflections due to the presence of metallic gold (patterns at $2\theta = 38.2°$, 44.4° and 77.6°). These last peaks are identified by comparing with ICDD JCPDS file No. 04-0784. For Au/Mn_6Al_2HT and Au/Mg_6Al_2HT solids, gold metallic particles size has been deduced using Scherrer equation on the peak at = 77.6° since at this angle no overlap with support HT pattern is observed. Thus, the gold particle size has been estimated respectively at 6.7 nm for Au/Mn_6Al_2HT and 15.3 nm for Au/Mg_6Al_2HT catalyst. The worst gold dispersion is obtained

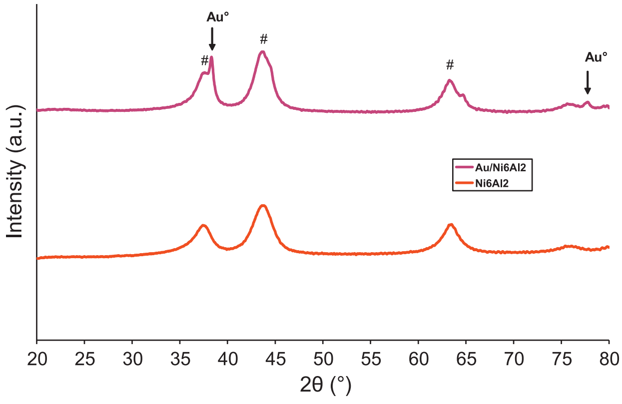

Fig. 5. XRD patterns of Ni_6Al_2HT and Au/Ni_6Al_2HT catalysts ($\# = NiO$).

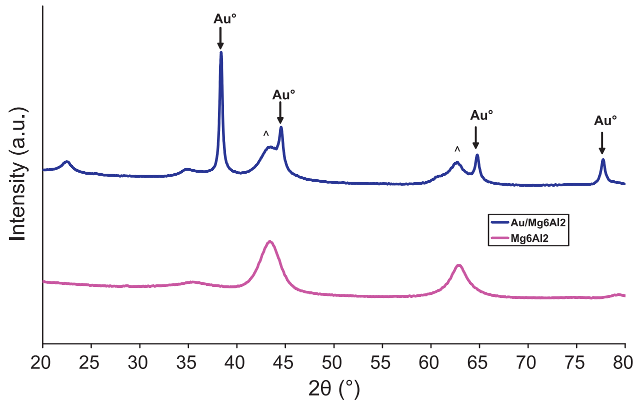

Fig. 6. XRD patterns of Mg_6Al_2HT and Au/Mg_6Al_2HT catalysts (^ = MgO).

using Mg_6Al_2HT as support. This observation is in correlation with the previous results concerning their activity for the CO conversion. Thus, the Mg_6Al_2HT is not a suitable support for gold in this case.

Concerning the XRD patterns of Mn_6Al_2HT and Ni_6Al_2HT solids (Figs. 4 and 5), no change in the structure of the HT support due to the introduction of gold is detected. For the Au/Ni_6Al_2HT XRD pattern, no estimation of the gold crystallite size is possible due to the overlap of NiO and Au° patterns.

From CO oxidation test and XRD measurements, a better gold dispersion is obtained on the Co_6Al_2HT, Mn_6Al_2HT and Ni_6Al_2HT than on Mg_6Al_2HT. This observation indicates that the catalytic behaviour of Au/HT support catalysts for the oxidation of toluene depends mainly on the nature of the support. Thus, the Mg_6Al_2HT does not appear like a suitable support for gold. However, no clear correlations have been observed between catalytic properties and the dominating size of the Au particles. Indeed, Au/Mn_6Al_2HT catalyst is more active in the toluene oxidation than Au/Co_6Al_2HT then this one is better in the CO oxidation. The best activity of Au/Mn_6Al_2HT catalyst in the toluene oxidation can be explained by the manganese oxides since in the Mn_6Al_2HT based solids, oxides Mn_2O_3 (JCPDS 41-1442) and Mn_3O_4 (JCPDS 24-0734) were evidenced by XRD (Fig. 4). Indeed, manganese oxides are reported to be very efficient phases for VOC oxidation [18,19]. These results lead us to the conclusion that the choice of the divalent cation in the hydrotalcite materials is very important in order to obtain an efficient catalyst for the VOC oxidation.

4. Conclusion

The use of gold has a beneficial effect on the catalytic activity for the toluene and CO oxidation and depends mainly on the composition of the HT support. Indeed no clear correlations have been observed between catalytic properties and the dominating size of the Au particles for the toluene oxidation. However a better gold dispersion is obtained on the Co_6Al_2HT than on the Mn_6Al_2HT support which could explain the better activity of Au/Co_6Al_2HT catalyst for the CO oxidation. The best activity in the catalytic toluene oxidation observed on Au/Mn_6Al_2HT solid can be explained by the presence of manganese oxides. Moreover, this study has revealed that the choice of the divalent cation in the hydrotalcite materials is a key factor in order to obtain an efficient catalyst for the VOC oxidation.

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