Journal of Thermal Analysis and Calorimetry, Vol. 73 (2003) 341–346

COPPER OXIDE ON Cu/Al_2O_3–TiO_2 CATALYSTS
TG, FTIR-CO absorption and catalytic activity in the NO reduction by CO

M. Morán-Pineda [1*], *S. Castillo* [1,2], *M. Asomoza* [1,3] *and R. Gómez* [1,3]

[1]Instituto Mexicano del Petróleo, Simulación Molecular, Eje Central Lázaro Cárdenas 152,
07730 México D. F., México
[2]Instituto Politécnico Nacional, Edif. 7, Unidad Profesional Adolfo López Mateos,
07738 México D. F., México
[3]Universidad Autónoma Metropolitana-I, Chem. Dept.. AP 55-534, 09340 México D. F., México

(Received October 19, 2002; in revised form March 18, 2003)

Abstract

TG, FTIR-(CO absorption), and catalytic activity in the NO reduction by CO were used to characterize Cu/Al_2O_3–TiO_2 catalysts prepared by co-gelling aluminum tri-sec-butoxide and titanium iso-propoxide at pH 9 and at pH 3 gelling conditions. Under nitrogen flow, copper oxide decomposition, oxygen storage capacity (OSC) and sample dehydroxylation (total mass loss) was followed by TG. The CuO decomposition forming Cu^0, Cu^{+1} was observed by means of FTIR (CO absorption) spectra. In pH 9 sample the large amount of Cu^0 was observed. At low total mass loss and high $Cu^0/Cu^{+1}+Cu^{+2}$ ratio (pH 9 sample) a lowest light-off in the NO reduction by CO was observed.

Keywords: alumina–titania sol–gel catalysts, CO adsorption on alumina–titania catalysts, copper alumina–titania oxidation state, NO reduction by CO, TG sol–gel alumina–titania

Introduction

Supported noble metals like platinum, palladium and rhodium or combinations between them were reported as the most effective catalysts for the NO reduction [1–2]. The essential support is alumina or ceria and lanthanum doped alumina. The main role of rare earth oxides has been related to improving the textural properties of alumina, however oxygen storage capacity (OSC) on doped alumina was observed [3]. The OSC effect increases CO oxidation rate, while the NO reduction by CO is inhibited [4]. Then a compromise between the improvement of the textural properties of supports and the importance of the OSC effect in the NO reduction must be reached.

Less expensive catalysts like supported copper have been reported as alternative ones to substituted noble metal supported catalysts [5]. Copper–lanthanum–manganite has been reported as a good catalyst the CO oxidation and NO reduction by CO. The composite shows oxygen storage capacity [6].

---

[*] Author for correspondence: E-mail: fmarina@imp.mx

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Titania is known as a reducible oxide [7]. When metals are deposited on its surface metal oxidation and titania reduction processes occurs. The oxidizing reducing cycle Ti^{4+} to Ti^{3+} and Cu^0 to Cu^{+1} have been reported on reduced Cu/TiO_2 catalysts [8, 9].

In the present work we study Cu/Al_2O_3–TiO_2 catalysts, with the aim to stabilize titania on the alumina matrix and to study the oxidation reducing cycles of copper on the support. The mixed oxides were prepared by the sol–gel method using titanium and aluminum alkoxides as starting materials and $CuCl_2{\cdot}2H_2O$ as copper precursor. The catalysts characterization was made by means of TG-FTIR, FTIR (CO absorption) and by the NO reduction by CO as catalytic test.

Experimental

The Al_2O_3–TiO_2 supports were synthesized as following: 0.64 mol of aluminum tri-sec-butoxide (Aldrich, 99.9% purity) was dissolved in 100 mL of ethanol (Baker 99.9%) and refluxed under constant stirring. For basic medium preparation, the solution was adjusted to pH 9 with NH_4OH (Baker 35% NH_3 in water), while for acidic gelation the solution was adjusted to pH 3 with HCl (Baker, 36.5% in water). Under continuous stirring 0.07 mol of titanium isopropoxide (Aldrich, 99.9%) was added drop by drop to the ethanolic solution (10 mass% TiO_2). Hydrolysis was accomplished by adding 0.83 mol of bidistilled dropwise water. The solution was maintained under reflux until the gel was formed. Samples were dried at 70°C for 12 h and calcined at 550°C for 4 h in a static oven. Metal supported catalysts were prepared by impregnation of the calcined Al_2O_3–TiO_2 supports with a $CuCl_2{\cdot}2H_2O$ aqueous solution, the concentration was in order to obtain 1.0 mass% Cu on the catalysts. Impregnated catalysts were dried at 70°C overnight and calcined at 550°C in air for 4 h.

Thermogravimetric analyzer, TG 2950 TA Instruments, coupled to a FTIR Nicolet Protege 460 spectrophotometer was used. The system allows the analysis by FTIR of the evolved gases from room temperature to 550°C. In previously calcined samples placed on the TG pan, a heating rate of 10°C min^{-1} from 25 to 150°C in N_2 carrier flow was applied. Then the temperature was hold for 60 min at 150°C and after the sample was heating to 800°C. Afterwards, instead of N_2 flow, air flowing was admitted in the system and the sample cooled from 800 to 50°C by shooting off the heating program [10].

The catalytic activity was measured under atmospheric pressure in the non-selective reduction of NO by CO using a fixed bed quartz reactor applying a heating program rate of 5°C min^{-1}. The reactant mixture containing 1.5 vol% CO, 0.5 vol% NO, balance N_2, flow $LHSV$=3600 h^{-1} (liquid hourly space velocity), catalyst mass 50 mg. Temperature range 100–400°C. The catalytic system was coupled to a FTIR spectrometer Nicolet-8220 gas analyzer permitting the identification of desorbed species. The activity was followed as NO total conversion.

The CO adsorption on the metallic catalysts was study by means of FTIR-CO absorption spectra using a Nicolet model 710 apparatus. Samples pressed as thin self-supported wafers were placed in a Pyrex glass cell equipped with CaF_2 windows. The calcined samples were reactivated 'in-situ' at 400°C for 30 min under vacuum

($1\cdot10^{-5}$ torr); afterwards, the cell was cooled to –85°C with liquid nitrogen. CO (20 torr) was then admitted into the cell. The excess of CO was evacuated during fifteen minutes and then the FTIR spectra were recorder.

Results and discussion

Before thermogravimetric analysis the samples were previously calcined at 800°C and re-exposed to air after the thermal treatment. In Fig. 1, two mass loss steps can be observed. The first mass loss comprised from room temperature to 150°C correspond to H_2O desorption as it was identified by the FTIR corresponding bands. The second mass loss comprised between 150 and 800°C was assigned to copper oxide decomposition, oxygen storage capacity (OSC) and dehydroxylation of the mixed oxide. The mass loss observed after water release, (6.7 mass%) for pH 9 sample and 8.7 mass% for pH 3 sample is due to the big capacity of sol–gel materials to be re-hydroxylated. Alumina or titania sol–gel are oxides who show high hydroxylation after air exposure. The evolution of the copper oxidation states from initial Cu^{2+} to Cu^{1+} and Cu^0 as the thermal treatment increases, could be supported by the coloration of the samples observed when they were annealed. Initially (150°C) the samples show green color which turns to dark green color and finally around 800°C the samples became bluish gray color. Similar effect of color evolution has been reported by Del Arco *et al.* [9], on Cu/TiO_2 catalysts thermally treated. The evolution of the coloration of the samples was attributed to Cu^{2+} to Cu^{1+} and Cu^0 oxidation states and is a reversible process, since when the samples were cooling in air flow from 800 to 50°C the samples acquires the initial green color. This behavior was repetitive for each heating–cooling cycle given to the sample. The mass variation (W) divided by the initial mass of the sample (W_0) in function of the temperature is shown in Fig. 2. We can see that the pH 3 sample loss is 20% higher than that observed for the pH 9 sample. The total mass loss involves copper oxide reduction, support oxygen release (OSC), and dehydroxylation, then, we are not in the possibility to quantify the amount corresponding to the oxygen storage capacity. But this phenomenon cannot be

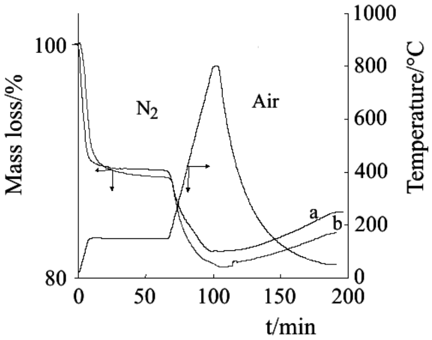

Fig. 1 TG on $Cu/Al_2O_3–TiO_2$ catalysts showing the decomposition and reoxidation cycle: a – pH 9; b – pH 3. The mass loss from 150 to 800°C will correspond to copper oxide decomposition, OSC phenomenon, and dehydroxylation (total mass loss) of the samples after exposure to air

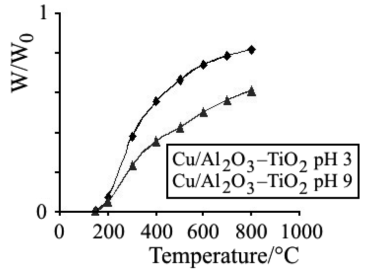

Fig. 2 TG mass variation on function of temperature for the $Cu/Al_2O_3–TiO_2$ pH 9 and $Cu/Al_2O_3–TiO_2$ pH 3. The Fig. shows a higher total mass loss for the sample prepared at pH 3

discarded and it would be higher in the pH 3 sample. The OSC phenomenon has been observed on TiO_2 [9].

The CO absorption spectra of $Cu/Al_2O_3–TiO_2$ pH 9 and $Cu/Al_2O_3–TiO_2$ pH 3 at –85°C are shown in Fig. 3. Three bands around 2104, 2117 and 2150 cm^{-1} can be observed and they were assigned to CO absorption on copper Cu^0, $Cu^{1+}$and Cu^{2+}respectively [10]. In the sample prepared at pH 9 it can be observed greater density of Cu^0 and Cu^{1+} if compared with the pH 3 sample. Thus, in the sample prepared at pH 9 the amount of copper on low oxidation state is indicative that in such sample, the decomposition of copper oxide is faster achieved.

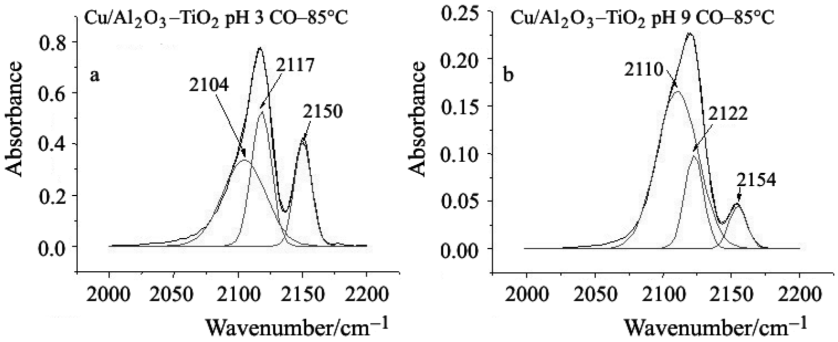

Fig. 3 FTIR (CO adsorption) on $Cu/Al_2O_3–TiO_2$ catalysts: a – prepared at pH 9; b – prepared at pH 3; Cu^0 (2104–2110 cm^{-1}), Cu^{1+} (2117–2122 cm^{-1}) and Cu^{2+} (2150–2154 cm^{-1})

The catalytic activity of the samples evaluated on the NO reduction by CO without oxygen is shown in Fig. 4. The activity on function of the temperature shows that the catalyst prepared at pH 9 reach 50% light-off conversion at 280°C, while for the samples prepared at pH 3 50% is reached at 370°C. We can assume then that the low light-off showed by the pH 9 catalyst could be related to a low OSC effect. The reaction of NO with CO in absence of oxygen can be described as follows:

$$2NO+CO \rightarrow N_2O+CO_2$$

$$N_2O+CO \rightarrow N_2+CO_2$$

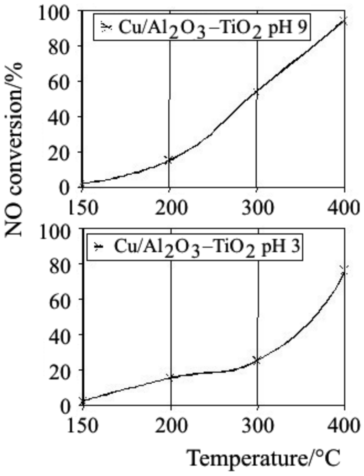

Fig. 4 NO conversion on Cu/Al_2O_3–TiO_2 catalysts as a function of the temperature during the NO reduction by CO. Light-off for NO conversion (50%) at 260 and at 370°C for pH 9 and pH 3 samples respectively can be observed

When the reaction occurs in presence of oxygen as reactant or with oxygen released from the support, the large affinity of CO for oxygen inhibit the reduction of NO due to stoichiometric conditions [11].

Conclusions

Even when a quantitative evaluation of the OSC phenomenon cannot be obtained, we can assume that it is present in both samples and it can be detected by the catalytic activity behavior of the samples and by the Cu^0/Cu^{1+} and Cu^{2+} ratio. In the first case a low OSC phenomenon could present in pH 9 catalyst (low light-off). In the second case, the $Cu^0/Cu^{1+}+Cu^{2+}$ ratio of pH 9 sample is higher than that obtained for the pH 3. At least OSC will correspond a highest Cu^0 oxidation concentration. Such results let us to propose that the TG thermogravimetric analysis as a helpful technique for the interpretation of the Cu/TiO_2–Al_2O_3 sol–gel gas exhaust catalytic converter reactions.

* * *

We are indebted to IMP-Molecular Engineering Program for financial support. The authors thank Tec. Rufino Vazquez for his assistance and technical support in this work.

References

1 G. P. Ansell, A. F. Diwell, S. E. Golunski, J. W. Hayes, R. R. Rajaram, T. J. Treux and A. P. Walker, Appl. Catal. B: Environ., 2 (1993) 81.
2 M. Sirilumpen, R. T. Yang and N. Tharapiwattananon, J. Mol. Catal. A: Chemical, 137 (1999) 273.
3 V. I. Parvulescu. P. Grange and B. Delmon, Catal. Today, 46 (1998) 223.

4 M. Iwamoto, T. Zengyo, A. Hernández and H. Araki, Appl. Catal B: Environmental, 17 (1998) 254.
5 M. Haneda, Y. Kintaichi, T. Mizushima, N. Kakuta and H. Hamada, Appl. Catal. B: Environmental, 31 (2000) 81.
6 F. Patcas, F. C. Buciuman and J. Zsaco, Thermochim. Acta, 360 (2000) 71.
7 H. Bosch and F. Janssen, Catal. Today, 2 (1988) 364.
8 P. A. Sermon, K. Rollings, P. N. Reyes and M. J. Davies, J. Chem. Soc. Faraday Trans., I, 83 (1987) 134.
9 M. del Arco, A. Caballero, P. Malet and V. Rives, J. Catal., 113 (1988) 120.
10 O. Scarlatioana and M. Zaharuscu, J. Therm. Anal. Cal. 68 (2002) 861.
11 A. Dandekar and M. A. Vannice., Appl. Catal., B: Environmental, 22 (1999) 179.
12 M. Shelef and G. W. Graham, Catal. Rev. Sci. Eng., 36 (1994) 431.