Research & Reviews: Journal of Chemistry

Characterization of Rh-Ge/TiO$_2$ and Pt-Ge/TiO$_2$ Catalysts by Fourier Transform Infrared Spectroscopy of Adsorbed CO

Ekou T[1,2]*, Ekou L[1], Lafaye G[2], Especel C[2] and Marécot P[2]

[1]Université Nangui Abrogoua, LTPCM 02 Bp 801, Abidjan 02, Ivory Coast
[2]Université de Poitiers, IC2MP, UMR 7285 CNRS, TSA 51106-86073 Poitiers, Cedex 9, France

Research Article

ABSTRACT

The Rh-Ge/TiO$_2$ and Pt-Ge/TiO$_2$ bimetallic catalysts are prepared and characterized by Fourier transform infrared (FT-IR) spectroscopy of adsorbed CO. The catalytic reduction procedure induces modifications of the intensity of the bands, indicating thus some changes on the surface of the Rh metallic phase. FTIR investigation of adsorbed CO reveals that the intensity of each peak associated to the different CO absorbed species falls when the germanium content of the catalyst increases. These different modifications show the existence of an interaction between the germanium and rhodium on the bimetallic Rh-GeTiO$_2$ catalysts, and germanium and the platinum on the bimetallic Pt-Ge/TiO$_2$ catalysts.

INTRODUCTION

Metal oxides are important classes of catalytic materials [1-4]. Notably, titanium dioxide is used in heterogeneous catalysis, as photocatalyst, in solar cells for the production of hydrogen and electric energy, as gas sensor, as white pigment, as a corrosion-protective coating, as an optical coating, in ceramics, and in electric devices. It was reported that Pt supported on high temperature pre-reduced TiO$_2$ shows a high catalytic activity for photo-assisted water decomposition and water gas shift reactions [5]. TiO$_2$-supported metal catalysts also show striking decreases of CO and H$_2$ uptake with increasing reduction temperature, this phenomenon being attributed to the strong metal support interaction (SMSI) [6]. High catalytic activity and selectivity are often reported for such systems [7].

CO adsorption is typically used in the characterization of supported metal catalysts [8]. In general, it is found that the CO adsorption depends on the metals themselves, their dispersion and oxidation state, as well as the nature of the support.

Carbon monoxide adsorption experiments were studied on reduced and oxidized Pt/TiO$_2$ with FT-IR. On reduced Pt samples, two kinds of CO species adsorbed linearly were observed and assigned as adsorption on Pt close-packed sites and on Pt open sites [9]. In the case of Rh-based supported catalysts, the adsorption of CO is known to produce three distinct adsorption modes: dicarbonyl species, linear-bound CO and bridged-bound CO, as demonstrated by Trautmann and Baerns [10] in their early and very detailed work dedicated to FT-IR of CO adsorption on Rh/Al$_2$O$_3$. The adsorption sites involved in the different adsorption modes are constituted of Rh atoms either in a metallic state (Rh^0) or in an oxidized form (Rh^{+1} or Rh$^{>+1}$) [10-19].

This paper is devoted to the study by infrared spectroscopy of the CO adsorption on Rh-Ge/TiO$_2$ and Pt-Ge/TiO$_2$ catalysts prepared by addition of germanium via the catalytic reduction method on Rh and Pt monometallic catalysts.

EXPERIMENTAL

Preparation of the support

The support used is the titanium dioxide P25 from Degussa, with a specific surface area of 50 m^{2}g^{-1} and a pore diameter of

8.3 nm. The powder of TiO_2 is grinded and sifted to retain only the grains with diameter included between 0.04 and 0.1 mm. To eliminate some possible impurities, the oxide support undergoes calcination under dry air (60 cm^3min^{-1}) at 500°C (heating ramp of 10°C.min^{-1}) during 4 hours.

Preparation of Rh and Pt monometallic catalysts

The metals are dispersed on the TiO_2 support in order to increase the available active area and to acquire certain stability due to the interactions with the support. The preparation method used is an impregnation by ionic exchange from $RhCl_3$ and H_2PtCl_6 precursor. A quantity of metallic salt (1 wt.%) is introduced on the TiO_2 support. The pH of the metallic salt solution is adjusted either to eleven (Rh salt) by an ammonia concentrated solution (28% commercial) or to one (Pt salt) by addition of acid hydrochloric solution. After exchanging during 12 hours, the aqueous solution is evaporated with a rotary evaporator. Then the impregnate support is dried a night in a stove at 120°C.The monometallic catalysts are activated by a calcination under dry air, followed by a reduction under hydrogen, according to the operating conditions reported in **Table 1.** The calcination under dry air permits to decompose the metallic precursors and to eliminate the humidity traces that promote generally the metal sintering. After reduction, the catalysts display a metal phase with zero oxidation degree.

Table 1. Activation of the monometallic catalysts.

		Calcination	Reduction
Gaz flow		60 cm^3.min^{-1} [Air]	60 cm^3.min^{-1} [Hydrogen]
Temperature	Rh/TiO_2	300°C	300°C
	Pt/TiO_2	400°C	500°C
Temperature ramp		10°C.min^{-1}	10°C.min^{-1}
Time of treatment		4 hours	4 hours

Preparation of Rh-Ge and Pt-Ge bimetallic catalysts

Bimetallic catalysts are prepared by the "catalytic reduction" method [8]. The monometallic catalysts synthesized previously (parent catalysts) are modified by superficial reaction between the hydrogen activated on the first metal and the cation of the second metal following the reaction:

$$nH_{ads.} + M^{n+} \rightarrow M_{ads.} + nH^+$$

Where $H_{ads.}$: is the hydrogen adsorbed on the parent metal (Rh or Pt), M^{n+} the cation of second metal (Ge^{4+}), $M_{ads.}$: The second metal adsorbed (Ge).

The reaction is performed under hydrogen flow. Adsorbed hydrogen is so constantly renewed on the metallic surface in order to charge catalysts with variable germanium contents according to the quantity of precursor salt ($GeCl_4$) introduced in solution. The bimetallic catalyst after a drying step under hydrogen at 100°C is finally activated at the same temperature that the one used for the corresponding parent sample (300°C and 500°C for the Rh and Pt samples, respectively), with a heating ramp of 2°C.min^{-1}. The bimetallic catalysts are denoted Pt-X%Ge/TiO_2 or Rh-X%Ge/TiO_2, X being the germanium quantity really deposited on the catalyst.

Fourier transformed infrared spectroscopy (FT-IR) of adsorbed CO

Experimental protocol: Transmission FT-IR spectra are collected in the single-beam mode using a NICOLET Magna 550 spectrometer with a resolution of 2 cm^{-1}. Catalysts are grinded in order to obtain a fine and homogeneous powder pressed further into self-supported wafers with a diameter of 12 mm. After introduction in the IR cell, the sample is reduced in-situ at 300°C (Rh-based samples) or 500°C (Pt-based samples) (2°C.min^{-1}) during 1 hour under hydrogen flow followed by an evacuation of the gas at the temperature of reduction (secondary vacuum). In fact, numerous impurities are often present on the catalytic materials coming from their contact with the atmosphere. These species present on the metallic particles surface can disrupt the adsorption of the probe molecule. After cooling to the ambient temperature, a reference spectrum is saved. Some doses of carbon monoxide are introduced in the cell until saturation of the catalysts. Still at room temperature, the cell is then ejected (primary vacuum) for retaining only the carbon monoxide strongly bound on the catalysts surface. For each step, some spectra are registered.

Data exploitation: The reference spectrum corresponds to the spectrum characteristic of the metallic phase and of the support, obtained after thermic treatment eliminating all humidity and previously adsorbed gas traces. The spectrum characteristic of carbon monoxide strongly adsorbed on the catalyst surface (irreversible CO) is obtained by the difference between the spectrum of the sample after evacuation of carbon monoxide and the reference spectrum. Some previous works concerning the carbon monoxide adsorption on rhodium and platinum catalysts are used as references to decompose the spectra in elementary bands (Peakfit software) [20-25].

RESULTS AND DISCUSSION

In order to evaluate the interaction between the two metals formed the active phase, the Rh-Ge/TiO_2 and Pt-Ge/TiO_2

catalysts prepared by catalytic reduction are characterized by Fourier transformed infrared spectroscopy. Firstly, the study of the monometallic catalysts is needed.

Effect of the preparation method of the bimetallic catalysts on the parent Rh/TiO$_2$ catalyst

During the preparation of the bimetallic catalysts by the catalytic reduction method, the parent catalysts undergo an immersion in an aqueous solution containing the Ge precursor salt under hydrogen flow. In order to evaluate the modifications induced by this protocol, blank samples are prepared by treating the parent samples as indicated previously but without Ge addition in the aqueous solution (the activation treatments before and after the immersion step are maintained).

The IR spectra of CO adsorbed on the Rh/TiO$_2$ parent and blank catalysts according to the pressure of CO are compared on **Figure 1.** The spectra are taken with the increasing of CO in the cell before the final evaluation.
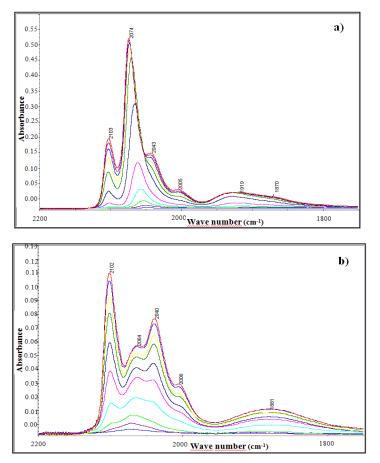

Figure 1. Spectra of adsorbed CO (with increasing CO amounts) on Rh/TiO$_2$ monometallic catalysts: a) parent sample, b) blank sample.

The blank sample is the catalyst prepared in the same condition as the bimetallic catalyst but without the germanium added.

Five distinct bands distinct are observed around 2100 and 2040 cm^{-1}, near 2070 and 2005 cm^{-1} and a wide band between 1920 and 1850 cm^{-1}. Different bands have been observed in this paper as those reported in the literature [16,23,26-28]:

i. The peaks 2074 cm^{-1}, 2064 cm^{-1} and at lower wavenumbers correspond to the vibration of linear Rh^0-CO and bridged (Rh^0)$_2$-CO species, respectively, relative to CO adsorbed on the surface of Rh^0 atoms.

ii. The peaks (2040, 2043) cm^{-1} and (2102, 2013) cm^{-1} correspond to vibrations of germinal dicarbonyl Rh^{+1}-(CO)$_2$ species (asymmetric and symmetric mode, respectively), relative to CO adsorbed on the surface of Rh^{+1} atoms.

iii. The peaks 2006 cm^{-1} and 2005 cm^{-1} correspond to the vibration of bridged (Rh^{+1})$_2$-CO species.

In the case of the geminal dicarbonyl species, the formation of Rh^{+1} in a highly dispersed state is believed to be the result of an oxidative disruption of the Rh-Rh bonds in the Rh crystallites at room temperature and under CO atmosphere, due to the higher energy of the Rh-CO bond as compared to the Rh-Rh one [10]. Consequently, the presence of the gem-dicarbonyl bands in the spectra should be interpreted as isolated Rh^{+1} islands on the larger Rh^0 crystallites.

Figures 1a and 1b clearly show that the catalytic reduction procedure induces modifications of the intensity of the five adsorption bands, indicating thus some changes on the surface of the Rh metallic phase. Consequently, the bimetallic catalysts will be further compared systematically to their corresponding blank sample.

Effect of the Ge content on the Rh/TiO$_2$ catalyst

Figure 2 presents the infrared spectra of CO absorbed on the Rh/TiO$_2$ blank sample and on two Rh-Ge/TiO$_2$ bimetallic catalysts with 0.5 and 1.8 wt.% Ge.
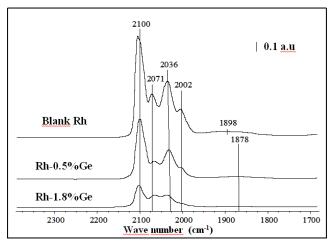

Figure 2. FTIR spectra of CO adsorbed on the Rh-based catalysts (blank and bimetallic Rh–X%Ge/TiO$_2$).

The five bands observed on the blank catalyst are still present on the bimetallic samples: the two intense ones at 2100 and 2036 cm^{-1}, the two smaller others at 2071 and 2002 cm^{-1} and the wide band centered around 1898 cm^{-1} for the monometallic catalyst and 1878 cm^{-1} for the bimetallic catalysts. The attributions of the peaks relative to the adsorption of CO on these catalysts are summarized in **Table 2.**

Table 2. Assignment of the different modes of CO adsorption followed by FTIR observed on the Rh-based catalysts.

Catalysts	Wave number (cm^{-1})				
	Bridged on (Rh^0)$_x$	Bridged on (Rh^{+1})$_x$	Geminal antisymmetric on Rh^{+1}	Linear on Rh^0	Geminal symmetric on Rh^{+1}
Rh/TiO$_2$ blank	1898	2002	2036	2071	2100
Rh-Ge/TiO$_2$	1878	2002	2036	2071	2100

Spectra of **Figure 2** show that the intensity of each peak associated to the different CO absorbed species falls when the germanium content of the catalyst increases. This tendency indicates an increase of the quantity of germanium in contact with rhodium. This observation should confirm the interaction between both metals.

Effect of the Ge content on the Pt/TiO$_2$ catalyst

Figure 3 compares the infrared spectra of CO adsorbed on the monometallic Pt/TiO$_2$ catalyst (blank sample) and two bimetallic Pt-X%Ge/TiO$_2$ catalysts containing 0.2 and 0.4 wt.% Ge.
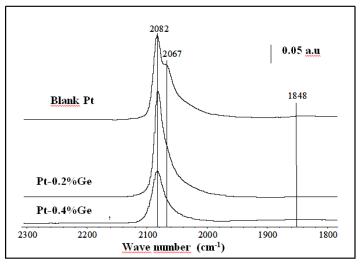

Figure 3. FTIR spectra of CO adsorbed on the Pt-based catalysts (blank and bimetallic Pt–X%Ge/TiO$_2$).

The obtained spectra display three bands, two intense ones at 2082 and 2067 cm^{-1} and a wide band of lesser intensity at 1848 cm^{-1}, attributed according to the literature as follows and gathered in **Table 3** [29-31]:

Table 3. Assignment of the different modes of CO adsorption followed by FTIR observed on the Pt-based catalysts.

Catalysts	Wave number (cm^{-1})		
	Bridged on (Pt^0)$_x$	Linear on Pt^0 "edges"	Linear on Pt^0 "terraces"
Pt-x%Ge/TiO$_2$	1848	2067	2082

i. The peaks at 2082 and 2067 cm^{-1} correspond to vibration of linear species (Pt^0-CO) relative to CO adsorbed on the terraces and edges of Pt^0 atoms, respectively.

ii. The peak at 1848 cm^{-1} corresponds to the vibration of bridged (Pt^0)$_2$-CO species, relative to CO adsorbed on Pt^0 atoms.

The addition of a small Ge content on the Pt catalyst involves an increase of the peak intensity relative to CO linear species adsorbed on terraces making the disappearance of the shoulder associated to the linear species associated to edges (2067 cm^{-1}). The intensity of peaks corresponding to these linear species decreases strongly for the highest Ge content. These different modifications show clearly the existence of an interaction between the germanium and the platinum on the bimetallic Pt-Ge/TiO$_2$ catalysts.

Re-adsorption of CO on the Rh-Ge/TiO$_2$ bimetallic catalysts

Series of CO adsorption and desorption are performed on the blank Rh catalyst and on several bimetallic Rh-Ge catalysts **(Figure 4)**.
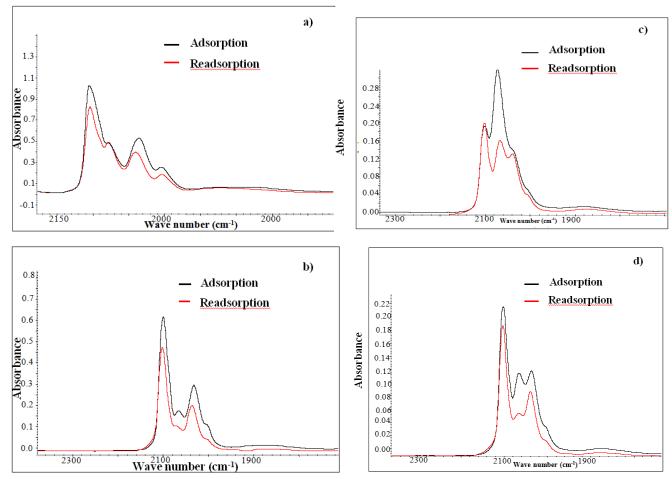

Figure 4. Spectra of CO adsorption and readsorption followed by FTIR on the Rh-X%Ge/TiO$_2$ catalysts: a) X=0 (blank sample), b) X=0.5, c) X=1.6, d) X=1.8.

Previous studies have reported that successive steps of adsorption/desorption/re-adsorption of CO at ambient or high temperature lead to the agglomeration or reduction of Rh^{+1} clusters to Rh^0 species [10,15,21]. The consequence on the FT-IR spectra is an increase of the peaks relative to linear and bridged CO to the detriment of the germinal bands. The results obtained with the blank catalyst are in agreement with the literature: the intensity of peaks attributed to gem-dicarbonyl species, associated to Rh^{+1}, decreases compared to that of the peak corresponding to CO bound linearly to Rh (2071 cm^{-1}). For the bimetallic Rh-Ge/TiO$_2$ catalysts, the observations are different and evolved with the Ge content: it clearly appears that an increase of the Ge content leads to a stabilization of rhodium in the form of small clusters Rh^{+1} since the gem-dicarbonyl bands in symmetric and antisymmetric modes (at 2100 and 2036 cm^{-1}) lose no or little intensity after the re-adsorption step, and to a lesser extent compared to the linear CO band.

CONCLUSION

The absorption bands are interpreted in terms of the traditional bridged and linear CO species. Five bands and three bands of CO adsorption are respectively observed on the Rh-Ge/TiO$_2$ and Pt-Ge/TiO$_2$ catalysts prepared by catalytic reduction. For the Rh-based samples, two intense peaks are located at 2100 and 2036 cm^{-1}, two smaller ones at 2071 and 2002 cm^{-1} and a wide band is finally centered toward 1880-1890 cm^{-1}. For the Pt-based catalysts, two intense peaks appear at 2082 and 2067 cm^{-1} and a wider one at 1848 cm^{-1}. The surface of the Rh and Pt sites is modified by the addition of germanium. After the Ge deposit, the intensity of bands attributed to gem-dicarbonyl species (at 2100 and 2036 cm^{-1}), associated to Rh^{+1}, decreases to the profit of the peak corresponding to CO bound linearly to Rh (at 2071 cm^{-1}).

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