CONVERSION OF METHANOL TO FORMALDEHYDE ON TiO₂ SUPPORTED Ag NANOPARTICLES

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ABSTRACT

TiO₂ supported Ag nanoparticles with metal loading ranging from 2.0 to 12.0 wt.% have been prepared by reduction of a silver precursor with formic acid under mild conditions. XPS showed that silver remains in a reduced state and TEM has demonstrated that the procedure was effective to produce silver nanoparticles. Only small changes in the metal particle size from 2.0-3.4 nm occurs when the Ag content increases from 2.0 to 12.0 wt.%. O₂ TPD has revealed the presence of different types of adsorbed oxygen species being the one assigned to the active specie called O_b, which one displayed the highest proportion in the catalysts with higher metal loading. Catalytic activity in the conversion of methanol to formaldehyde showed that those samples with metal loading higher than 7.0 wt% displays higher yields compared to the unsupported silver catalyst.

Keywords: silver nanoparticles, catalysts, methanol, formaldehyde

INTRODUCTION

Formaldehyde is one of the most important chemical products worldwide (production of ~4-5x10⁷ tons per year) [1] for the production of urea-phenolic, acetal and melamine resins. Two important routes are used in the industrial production of formaldehyde. One is carried out over a ferrite molybdate catalyst by oxidation of methanol in an excess of air at temperatures close to 400° C [2-4]. The second route uses a thin layer of electrolytic silver catalyst [5-11] with a feed of a mixture of methanol and air (approximately 1:1) molar ratio in the temperature range 580 to 650°C. Typical yield of formaldehyde are close to 90%. Nowadays, about 55% of the industrial production is based on silver catalyst. The overall process is regarded as a combination of partial oxidation and dehydrogenation of methanol:

The total reaction is highly exothermic and fast, requiring short contact time (< 0.01 s) [12]. The main by-products are CO₂, CO, H₂, H₂O, formic acid and methyl formate. Thus, the selectivity may be limited by several side reactions such as the total oxidation of methanol or formaldehyde, formaldehyde dehydrogenation, water gas shift reaction among others. Silver catalysts deactivate by sintering due to the severe exothermic reaction. The addition of extra water vapour to the reaction mixture, may be useful to reduce the sintering of Ag particles because of its large heat capacity, therefore water vapour may remove a great deal of reaction heat preventing the sintering of the catalyst [13,14]. However, water addition is limited by the requirement of the final products strength and of the additional water needed for tail-gas-scrubbing.

Silver catalysts can also be used dispersed on various supports in order to minimize the sintering. Thus, pumice, alumina, silica-alumina and silica have been used as support of silver catalysts [15, 16]. The traditional method based on the impregnation of a metallic precursor followed by oxidation and reduction usually lead to large silver crystallites. Sol-gel method also provide an interesting procedure to prepare highly dispersed supported catalysts, which may have an excellent resistance to sintering [17-19]. Cao et al have shown that a silica supported silver catalyst prepared by the sol-gel method displays a high activity and selectivity in the oxidative dehydrogenation of methanol to formaldehyde [15]. Reduction of AgNO₃ aqueous solution either with hydrazine sulfate or thermal reduction with hydrogen at 650° C in the presence of a support has also been used to prepare silver supported catalyst [5].

In order to obtain highly dispersed silver nanoparticles by chemical reduction, Wang et al. [20] have used silver nitrate as a Ag precursor in the presence of polyvinylpyrrolidone (PVP) using glucose as reducer, leading to silver particles in the range 20-70 nm.

In this work, supported silver catalysts have been prepared by coating the support with silver nanoparticles obtained by reduction of aqueous silver

nitrate with formic acid [21]. Catalysts with different Ag loadings in the range 2 to 12 wt. % were prepared and characterized by surface area measurements, TEM, XRD, O₂-TPD and XPS. The catalysts were evaluated in the conversion of methanol to formaldehyde in a flow reactor in a temperature programmed mode in a range of 150-600°C and also isothermally at 480 and 560°C.

2. EXPERIMENTAL

2.1. Preparation of the catalysts

x wt.% of Ag/TiO₂ catalysts were prepared by coating the support (TiO₂ DEGUSSA P-25 (72 m²/g) with silver nanoparticles. They were obtained by the reduction of silver nitrate with an aqueous formic acid containing a 50% in excess of the necessary amount to achieve a complete reduction of Ag(I). The reduction was carried out in the presence of the support under continuous stirring while the temperature was continuously increased from room temperature up to boiling and it was maintained at this temperature for 15 min. Then, the solid was cooled down, filtered and dried at 120°C. A series of catalysts with silver loading ranging from 2.0 to 12.0 % wt. % was obtained.

As comparison Ag unsupported catalyst provided by OXIQUIM was used. It was prepared by electrodeposition of a AgNO₃ dissolution. Ag crystals with a wide particle size distribution were obtained. A fraction ranging from 10-20 mesh (50-500 mm) and surface area of 0.22 m²/g was used. This fraction corresponds to the smallest particle size industrially used.

2.2. Characterization

Nitrogen physisorption at 77K was carried out in to Micromeritics ASAP 2010 apparatus. X-ray diffraction (XRD) patterns were obtained on a Rigaku diffractometer using a Ni filter and Cu Kα₁ radiation. Intensity was measured by scanning steps in the 2θ range between 3° and 70° at 1°/min⁻¹. X-ray photoelectron spectra were acquired with a VG ESCALAB 200R spectrometer (VG-Scientific) provided with a hemispherical analyser, operated in a constant pass energy mode and non-monochromatic MgKα X-ray radiation (hν = 1253.6 eV) operated at 10 mA and 12 kV. The system was provided with a reaction cell, which allows pre-treatment at high temperatures. The catalysts were reduced *in situ* in hydrogen at 773 K for 2 h and then transported to the analysis chamber without air contact. The surface Ag/Ti atomic ratios were estimated from the integrated intensities of Ag 3d_{5/2} and Ti 2p after background subtraction and corrected with the atomic sensitivity factors [22]. The line of O 1s was also analyzed. Ag 3d peaks were decomposed into several components assuming that the peaks had Gaussian-Lorentzian shapes. TEM studies were carried out by using a Jeol Model JEM-1200 EXII System and SEM micrographs in a JEOL JSM-6380 scanning electron microscope (SEM). TPD-O₂ profiles were carried out in a TPD/TPR 2900 Micromeritics system provided with a thermal conductivity detector. The samples were exposed to a mixture of 5%O₂/He (40 cm³/min) and a heating rate of 10°/min up to 400°C and kept at this temperature

for 90 min. Then, it was cooled down to room temperature, the gas was shifted to He (40 cm³/min) and once the baseline was restored the samples were heated at 10°/min up to 900°C.

2.3. Catalytic tests

Catalytic tests have been carried out in a stainless steel reactor of 12 mm of diameter. In each experiment 50 mg of unsupported Ag catalyst or 300 mg of Ag/TiO₂ catalyst was used. Methanol was fed by an ELMEX liquid pump and oxygen from a flow mixture 20%O₂/He. The total reactant flow was 255 mL/min and the O₂/CH₃OH molar ratio was ½ for standard experiments. In other experiments, in which the effect of the O₂/CH₃OH was studied, the molar ratio was changed from 0.33 to 0.50. In most of the evaluations the temperature raised at heating rate of 1°C/min. Some experiments were also performed at constant temperatures of 480 or 560°C.

The analysis of reactants and products were carried out by gas chromatography connected to a spectrometry of masses (GC-MS) using a column B-dex 225 of 30 m.

3. RESULTS AND DISCUSSION

3.1. Surface area and Transmission Electron Microscopy

Nitrogen adsorption isotherms at 77 K on Ag/TiO₂ catalysts exhibit type IV isotherms in the BDDT classification, characteristic of mesopore solids and specific surface areas evaluated by BET method are shown in Table 1. It can be seen a decrease in the surface area as the Ag loading increases. This behaviour usually occurs when a active phase is deposited on a carrier, and a partial blockage of the pores structure of the support takes place. This effect is more significant at higher metal loading.

Table 1. Surface area, m²/g obtained from N₂ adsorption isotherms at 77 K and metal particle size obtained from XRD and TEM for Ag/TiO₂ catalysts.

Ag/TiO ₂ wt%	S _{BET} , m ² /g	Metal particle size, nm	
		XRD	TEM
0.0	72	---	---
2.0	55	7.8	2.0
4.5	49	8.4	3.4
7.0	44	11.5	2.7
9.5	41	9.7	3.0
12.0	36	17.0	2.8

Figure 1 shows a representative TEM micrograph and metal particle size distribution for one of the prepared Ag/TiO₂ catalyst. All samples exhibit a narrow metal particle size distribution and the average are in the range 2.0 to 3.4 nm and the obtained results are compiled in Table 1. A rather modest increases with the metal loading was observed, in line with the preparation procedure used [22]. These results are also in line with XPS findings. It is worthwhile that the obtained Ag particle are much smaller compared to those observed by other procedures, such as the traditional based on an impregnation of a precursor followed by calcination and reduction. The one used in the present study is based on the impregnation of Ag nanoparticles produced by reduction of Ag ions under mild conditions with H₂ generated by decomposition of HCOOH leading to very small silver nanoparticles which are deposited on a porous carrier. These particles do not show tendency to sintering. In fact, when the Ag/TiO₂ catalysts were used in the formaldehyde conversion at temperatures of 560°C for several hours, the metal particle size remains almost constant. This feature is extremely important because one of the disadvantages of the industrial unsupported silver catalysts is the tendency to sintering.

Fig. 1. a) TEM micrograph and b) silver particle size distribution of 7.0% Ag/TiO₂ catalyst.

3.2. X-Ray diffraction

XRD studies on Ag/TiO₂ catalysts were also performed. As it is well known this support contains mainly anatase and rutile in a minor extent. The reflexions corresponding to both phases appear in all the patterns and it can be seen a slight increases in the lines at $2\theta=38.1^\circ$, 44.2° , 64.5° , of the TiO₂ with silver loading and also lines at $2\theta=77.4^\circ$ y 81.5° appear for the catalyst with higher Ag content. The enhancement in the intensity of the mentioned lines of TiO₂ may be attributed to the presence of crystalline silver. In fact, diffraction lines at 38.1° ; 44.2° ; 64.5° and 77.4° are characteristic of Ag: (111); (200); (220); (311); and (220) respectively.

Metal particle size of the silver catalysts were estimated by using the Debye-Scherrer equation [23] based in the broadening of the Ag (111) diffraction line and the obtained results are compiled in Table 1. An important increase in the particle size with the silver content is observed. However, due to the weak signals and the characteristic of the procedure used to calculate the particle size, the obtained values are higher than those obtained by TEM. This can be understood if it is bear in mind that this technique is sensitive only to particles larger than 3.0 nm.

3.3 X-Ray Photoelectron Spectroscopy

The chemical state of Ag for all catalysts has been studied by XPS. For all samples the binding energies of Ag 3d_{5/2} are in the range 367.9-368.1 eV, being indicative that silver is essentially in a zero valent state. Core level spectra of Ti 2p_{3/2} and O 1s were also studied and the binding energies are displayed in Table 2.

Table 2. Binding energies (eV) of Ag 3d_{5/2}, Ti 2p_{3/2} and O 1s core levels and Ag/Ti atomic surface ratio of Ag/TiO₂ catalysts.

Ag/TiO ₂ wt%	Binding energy, eV			
	Ag 3d _{5/2}	Ti 2p _{3/2}	O 1s	(Ag/Ti) _s
2.0	367.9	458.5	529.8 (53) 531.9 (47)	0.052
4.5	367.9	458.5	529.8 (56) 531.8 (44)	0.056
7.0	368.1	458.5	529.7 (86) 532.0 (14)	0.347
9.5	368.1	458.5	529.8 (89) 532.3 (11)	0.390
12.0	368.1	458.5	529.6 (77) 532.1 (23)	0.441

It can be seen that O 1s display two signals placed at B.E. of 529.8 and 531.9 eV attributed to Ti-O-Ti and surface Ti-OH bond respectively [24, 25]. With regard to the Ag/Ti surface atomic ratio an important enhancement with Ag loading is observed, indicative of an increases in the amount of Ag surface atoms.

3.5. Oxygen Temperature Programmed Desorption (O₂-TPD)

It has been pointed that surface chemisorbed species represent the active centres of silver catalysts for the formation of both formaldehyde and carbon dioxide [26-28]. Silver adsorbs oxygen in a variety of states, the formation of which strongly depends on the sorption conditions and the surface structure of the silver. Waterhouse et al. [29] after a detailed O₂ chemisorption and a combined TPD and Raman spectroscopy study, were able to detect three types of adsorbed oxygen denoted as O_α, O_β, y O_γ. Initially, O₂ is adsorbed dissociatively on silver leading to form surface atomic oxygen. This may occur on silver planes which bind oxygen strongly adsorbed (Ag (110), denoted as O_α) or on Ag (111) denoted as O_β. Neither of these oxygen species is thermally stable at 700 °C, temperature at which the conversion of methanol to formaldehyde usually takes place) and will be desorbed as O₂ or diffuse into the catalysts subsurface to form O_β through interstitial mechanism and grain boundary diffusion. O_β may diffuse back to the catalysts surface by the same mechanism by which it is formed or transform into O_γ via volume diffusion through the (111) textural facets. O_α is desorbed in the temperature range 25 to 250°C; O_β between 400 y 650°C and O_γ between 650 and 800°C. The activity in the methanol conversion has been mainly assigned to the O_β.

In order to detect the presence of these reported oxygen species and to quantify the extent of each type, in this work, O₂ TPD was also performed. Figure 3 shows the obtained profile. The one due to a bulk Ag catalyst under the studied conditions only shows a broad peak centered at 500°C, attributed

to O_β species. On the other hand, the profile of the 2 wt% Ag/TiO₂ catalyst displays two peaks, one at lower temperatures centered at 170 °C and a second at 707°C, assigned to O_α and O_β respectively. The catalysts with higher Ag loading show profiles, containing the expected three peaks, in the temperature range 90 to 110°C, 550 to 515°C and 700 to 720°C for O_α , O_β and O_γ respectively. The absence of the second peak in the O₂-TPD profile of the 2 wt% Ag/TiO₂ catalyst may be due to the lower metal content and smaller particle size.

Fig. 2. XRD diffraction patterns of Ag/TiO₂ catalysts.

Fig. 3. Temperature Programmed Desorption of O₂ on Ag/TiO₂ catalysts.

Figure 4 shows a percentage of each type of species as a function of silver loading. It can be seen a significant enhancement in the extent of O_β species with Ag content. An important increases in the extent of O_β species occurs mainly from 7 wt% of Ag and then it remains almost constant. These species associated to active sites should be related to the catalytic activity as will be discussed below.

Fig. 4. Percentage of oxygen adsorbed species as a function of metal content in Ag/TiO₂ catalysts.

3.6. Catalytic activity measurements

Catalytic conversion of methanol to formaldehyde on Ag/TiO₂ catalysts using a stoichiometric mixture CH₃OH/O₂ at different temperatures was studied and the obtained results are displayed in Fig. 5. The lowest activity is shown by the 2wt.%Ag/TiO₂ catalyst, whereas the one with 4.5% Ag and the bulk Ag obtained by electrolytic via display comparable behavior. Catalysts with silver loading higher than 7.0wt. % present conversion level continuously increases with Ag loading.

Fig. 5. Effect of the reaction temperature on the conversion level of CH₃OH over Ag/TiO₂ catalysts.

The observed enhancement in catalytic activity may be attributed to a higher amount of active sites. In fact, Ag/TiO₂ catalysts display similar metal particle size and consequently, comparable metal dispersion and therefore as metal content increases a parallel increases in the silver surface atoms take place. However, the activity of Ag surface atoms may show significant differences. Thus, it is more convenient to compare the activity with the O_β species which appears as the active catalytic species. As discussed previously, the samples with Ag loading ≥ 7.0 % are those with higher proportion of O_β species in agreement with catalytic results.

The selectivity to formaldehyde at different reaction temperatures is given in Fig. 6. At temperatures lower than 250° C (not shown) most of the catalysts display selectivities to formaldehyde close to 100% (but low conversion levels) which is explained considering that under these conditions only dehydrogenation of methanol, takes place. When the temperature is higher than 400°C, catalytic oxidation of methanol also occurs, showing selectivity levels close to 70% for those catalysts with higher metal loading. Table 3 shows a comparison of the selectivity to formaldehyde at two conversion levels. The higher selectivity values are displayed by the catalysts with higher Ag loading.

Fig. 6. Effect of the reaction temperature on the selectivity to formaldehyde in the conversion of CH_3OH over Ag/TiO_2 catalysts.

Table 3. Selectivity to the conversion of CH_3OH over Ag/TiO_2 catalysts at two different conversion levels.

Catalyst Ag/TiO_2 , wt%	Selectivity, %	
	Conversion 60%	Conversion 70%
2.0	69	65
4.5	65	65
7.0	84	71
9.0	95	93
12.0	97	93
unsupported Ag	81	70

The yield to formaldehyde under the studied conditions is given in Fig. 7. It can be seen that bulk silver catalyst lead to yield that increases with reaction temperature, being 60% at 550°C. Catalysts with 4.5 wt.% Ag or lower, display comparable behavior than bulk silver sample. Conversely, those Ag/TiO_2 catalysts having Ag content higher than 7.0 % lead to higher formaldehyde yield.

Fig. 7. Effect of the reaction temperature on the yield to formaldehyde in the conversion of CH_3OH over Ag/TiO_2 catalysts.

The effect of the reaction mixture on the catalytic behavior was studied at two different temperatures 480 and 560° C on the 12.0 wt. % Ag/TiO_2 catalyst and over Ag catalyst as comparison. Fig.8 shows the yield to formaldehyde as a function of the $\text{O}_2/\text{CH}_3\text{OH}$ molar ratio. The composition of the reaction mixture varied from 0.33 to 0.50 to keep out of the explosive region. 0.300 g of catalyst was used in each experiment, except in that of Ag catalyst (0.050 g). It can be seen that the yield increases as the amount of O_2 in the mixture increases reaching a maximum at composition in the range 0.42 to 0.45 and then it decreases slightly. At low O_2 content in the mixture the yield is lower in spite of a high selectivity to formaldehyde displayed under these conditions, however, the conversion is lower. As the mentioned ratio increases the selectivity remains constant and the conversion increases and therefore the

yield is higher. When the $\text{O}_2/\text{CH}_3\text{OH}$ molar ratio is higher than 0.45 a slight decrease in the selectivity to formaldehyde probably due to the presence of side reactions, leading to a decreases in the yield. The activity is higher at higher temperatures and the trend is rather similar for both catalysts but in the Ag/TiO_2 catalysts at 560° C the maximum shift to $\text{O}_2/\text{CH}_3\text{OH}$ of 0.47.

Fig. 8. Effect of the reaction temperature on the yield to formaldehyde in the conversion of CH_3OH over Ag/TiO_2 catalysts at different $\text{O}_2/\text{CH}_3\text{OH}$ molar ratios.

These two catalysts were also tested during 24 h using a $\text{O}_2/\text{CH}_3\text{OH}$ molar ratio of 0.42 at 480° C. The results displayed in Fig. 9 show slight changes in the yield to formaldehyde during the first 5 h on stream and after 24 h the level appears rather stable with yields of 58 y 82% for Ag and 12.0% Ag/TiO_2 catalysts respectively. Then, the samples were removed from the reactor and they were examined by TEM. An increases in the Ag particle size was observed in both samples. The unsupported silver the average particle size showed an increases from 269 to 391nm whereas in the 12.0% Ag/TiO_2 catalyst, changes from 2.8 to 4.4 nm. These results revealed that the main feature responsible of the industrial silver catalyst deactivation is the sintering of metallic particles. In fact, this deactivation is even more drastic because the reaction under industrial conditions usually is performed at temperatures close to 600°C.

Fig. 9. Conversion of CH_3OH over Ag/TiO_2 and Ag catalysts at 480 and 560° C. Yield, % versus time on stream. $\text{O}_2/\text{CH}_3\text{OH}$ molar ratio = 0.47.

4.- CONCLUSIONS

The obtained results showed that the procedure used to prepare highly dispersed Ag nanoparticles on TiO_2 catalysts has been effective, leading to particles in the range 2.0 to 3.4 nm depending on the metal loading.

XPS showed that silver remains in a reduced state and the amount of surface silver atoms increases with metal loading. Temperature Programmed Desorption of O_2 displayed the presence of different types of adsorbed oxygen species. The adsorbed specie having a highest proportion, in the catalyst with higher metal loading, is the one assigned to the active specie called O_2^- .

Catalytic activity in the conversion of methanol to formaldehyde showed that those samples with metal loading higher than 7.0 wt% displays higher yields compared to the unsupported silver catalysts in the temperature range 300 to 560°C. The composition of the reactant mixture also affects the catalytic behavior. At 560°C, the 12.0 wt%Ag/TiO₂ catalyst displays a yield to formaldehyde in the range 60 to 85% being the maximum at O₂/CH₃OH molar ratio of 0.48. The sintering of these Ag/TiO₂ catalysts also occurs but in lower extent than bulk silver catalysts, because of the presence of the titania support.

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