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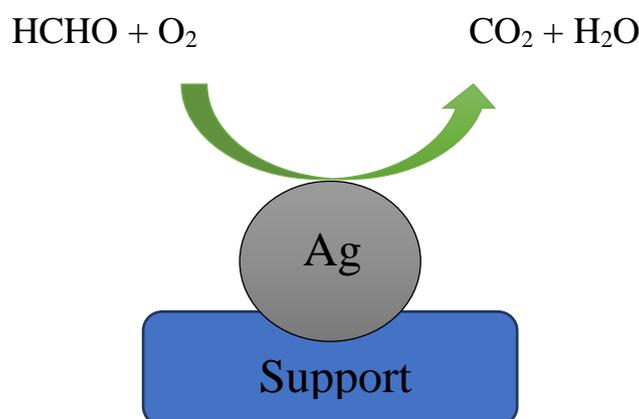
Ag-based Catalysts in different supports: Activity for Formaldehyde Oxidation

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Graphical Abstract



Abstract

Through the impregnation method, Ag catalysts with different support (such as TiO_2 and $\gamma\text{-Al}_2\text{O}_3$) were prepared and then tested for catalytic oxidation of formaldehyde (HCHO) at low temperatures. The Ag/ TiO_2 catalyst exhibited strong catalytic performance, converting HCHO to CO_2 and H_2O at around 95 °C. However, the Ag/ Al_2O_3 catalysts showed much lower activity and reaching 100% conversion at 125 °C. The Ag-based catalysts were next characterized by several methods (XRD, TEM, FT-R, BET and H_2 -TPR). Results of characterization revealed that support have a dramatic impact on the size and dispersion of Ag particles. The XRD analysis showed the existence of different peaks of the silver on the surface of Al_2O_3 in the contrast with TiO_2 no specific peaks exist. Therefore, the size of the Ag particles and their dispersion are the most important factors that affect their catalytic performance for formaldehyde oxidation. In terms of catalytic performance for HCHO oxidation, the Ag/ TiO_2 catalyst possess the best Ag dispersion, as well the smallest Ag particle size.

Key words: formaldehyde oxidation, TiO_2 , Al_2O_3 , Silver (Ag), impregnation, Sol-gel

1. Introduction

In the indoor environment, formaldehyde (HCHO) is a major source of indoor air pollution, which is harmful to human health. Exposure to HCHO over a long period of time can cause irritation in the eyes, deficits in spatial memory, allergic reactions and even cancer. In response to the increasing concern about this hazard, huge efforts have been made to eliminate indoor HCHO. The pollution caused by HCHO can be eliminated via a variety of methods, but catalytic oxidation gas proven to be the most promising [8]

There have been certain types of catalysts that showed highly catalytic activity for oxidizing HCHO. It has been shown that noble metals supported catalysts, such Pt/TiO₂, Pt/MnO_x-CeO₂⁸, Pt/MnO₂¹⁵, Pt/Fe₂O₃¹⁶, Pt/SiO₂¹⁷, Pd-Mn/Al₂O₃¹⁸, Pd/Beta²⁰, Pd/TiO₂⁹, Au/ZrO₂²², Au/CeO₂¹⁰, Au/Fe₂O₃²¹, Au/CeO₂-Co₃O₄²⁷ are active at room temperature for complete oxidation of HCHO to CO₂ and H₂O. Then, the high price of Pt, Au and Pd, prevents their wide application and encourage studies of supported Ag-based catalysts, although it has a much lower price, it still shows considerable efficiency for oxidizing HCHO at low temperature. Lei et al¹³ prepared Ag/CeO₂ nanosphere catalysts by a one-step hydrothermal method and it displayed 110 °C as the complete oxidation temperature. According, to a recent study Ag/TiO₂¹⁴ could catalyze the 100% conversion of HCHO at 95 °C. Using Ag/MnO_x-CeO₂ catalysts (Tang et al, 2006a, b^{1,2}) it was found that HCHO could be transformed into harmless H₂O and CO₂ at temperature below 100 °C. In order to promote the catalytic activity of Ag-based catalysts, some factors have been investigated, including support, additives, and active oxygen species. For the oxidation of HCHO, Chen et al (2011)³ compared the catalytic activity of Ag-based catalysts with different support. In their study, they found that Ag/MCM-41 displayed the best properties of all the catalysts, while the support played a significant role in catalytic activity. It was found that adding additives to Ag-based catalysts could enhance their catalytic activity. (Bai and Li, 2014⁴) found that the HCHO (100 ppm) removal efficiency increased to 55% at room temperature and 100% at 70°C over a 1.7 %K-Ag/Co₃O₄ catalyst. In a recent study, Chen et al. (2017⁵) found that single Ag could facilitate the activation of gaseous oxygen, thereby increasing the amount of active oxygen species that are beneficial to catalysis. The effect of pretreated condition investigated by Qin et al (2017)⁶ shown that the pretreatment condition of O₂ at 500 °C followed by H₂ at 300 °C has more effective catalytic activity on the oxidation of toluene over Ag/SBA-15 due to the small and highly dispersed Ag nanoparticles. In this study, we prepared the Ag-based catalysts with supports of TiO₂ and Al₂O₃ by sol-gel and impregnation method, the silver content in the

catalyst was 5% by weight, and then compared their performance for the catalytic oxidation of HCHO at low temperature. The catalysts are characterized by, the Temperature-programmed reduction (TPR), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), transmission electron microscope (TEM), Fourier-transform infrared spectroscopy (FTIR) and their catalytic performance for HCHO oxidation was evaluated. The results were used to discuss and explain the activity of Ag-based catalysts.

2. Experimental

2.1. Preparation of catalysts

All chemical reagents used to be of pure analytical grade. The TiO₂ with anatase structure and α -Al₂O₃ powder were prepared by sol-gel method. Titanium (IV) isopropoxide (Ti[OCH(CH₃)₂]₄) formed a solution after 30 min of stirring absolute ethanol. Ethylacetoacetate (Eaacac/Ti =1, molar ratio) was added in the solution to control hydrolysis and condensation reaction rates. After 30 min of stirring an aqueous solution of nitric acid (HNO₃, 0,1M) was introduced to the mix (HNO₃/Ti=10, molar ratio), and stirring continued until a yellow gel formed. Then, the sample was dried and the excess solvent was removed in an autoclave under the supercritical conditions, and calcined at 500 °C with ramping rate of 1 °C min⁻¹ under a flow rate 30 mL/min of oxygen. The same steps were used to synthesize the Al₂O₃ with Aluminum-tri-sec-butoxide (C₁₂H₂₇AlO₃) and 1-butanol, the uncolored gel formed was dried in different condition and calcined at 600 °C. The supported catalysts Ag/Al₂O₃ and Ag/TiO₂ were prepared by impregnation with an aqueous solution of silver nitrate (AgNO₃).

2.2. Characterization of catalyst

BET surface area, pore volume and pore diameter of all samples were obtained from N₂ adsorption isotherms using an ASAP 2020 micromeritics analyzer.

X-ray diffraction (XRD) measurements of catalysts were measured by using PANalytical X'pert PRO MPD diffractometer with a CuK α 1 radiation (λ =1.54060 Å) and operated at 40 kV and 40mA. The patterns were taken in the 2 θ range of 10–70°.

The programmed H₂ temperature reduction profiles (H₂-TPR) were carried out on chemisorption analyzer Autochem 2920 equipped with a TCD detector. The TPR technique is based on the determination of hydrogen consumption for the reduction of metal oxides as a function of temperature. The temperature was in the range of 40 to 550 °C using a 5% H₂ /Ar gas mixture with a ramp of 5 °C/min and a flow rate of 30 ml/min.

2.3 Measurement of catalytic activity

The source of formaldehyde used during the tests, therefore, comes from the dissolution of paraformaldehyde at 50 °C overnight with stirring. The activity tests for the catalytic oxidation of HCHO (100 ppm) over the Ag/Al₂O₃ and Ag/TiO₂ catalysts (50 mg) were performed with a fixed-bed quartz flow reactor by passing a mixture gas of 19.5% O₂, 78% N₂, and 2.5% H₂O balance at a total flow rate of 100 cm³ min⁻¹, within the temperature range of 50–350 °C. After reaching the steady state, the effluent gas was analyzed (MKS Multigas 2030) for HCHO conversion and CO₂ selectivity. The HCHO conversion was calculated by this equation:

$$\text{HCHO Conversion (\%)} = \frac{[\text{HCHO}]_{in} - [\text{HCHO}]_{out}}{[\text{HCHO}]_{in}} * 100$$

Where $[\text{HCHO}]_{in}$ and $[\text{HCHO}]_{out}$ are HCHO concentration at the inlet and outlet, respectively.

The apparent selectivity for carbon dioxide, are calculated as presented by the following equation:

$$(Pi) \text{ Selectivity (\%)} = \frac{[Pi]}{\sum [Pj]} * 100$$

Where $[Pi]$ is the product concentration and $\sum [Pj]$ is the sum of all reaction product concentrations.

The previous selectivity values will make it possible to calculate the yields of these products as shown on the equation:

$$(Pi) \text{ Yield (\%)} = \text{HCHO Conversion} * S(Pi)$$

3. Results and discussion

3.1. Catalytic test

The catalytic activities and the selectivity of by-products, of pure supports (TiO₂ and Al₂O₃) and the catalysts (Ag/TiO₂ and Ag/Al₂O₃) were evaluated for the HCHO oxidation as shown in **fig. 1**. It is evident that the most efficient catalyst for HCHO oxidation was the Ag/TiO₂, while the worst active catalyst was pure Al₂O₃ the order of activity observed was Ag/TiO₂ >> Ag/Al₂O₃ > TiO₂ > Al₂O₃. To more understanding the effect of support modification, the catalytic properties of TiO₂ and Al₂O₃ without silver were studied.

The results obtained showed that the pure supports have an average activity but cannot completely convert HCHO into CO₂ and H₂O. The main by-products found in the outlet of gases is the CH₃OH and CO with a low selectivity of dioxide of carbon (CO₂).

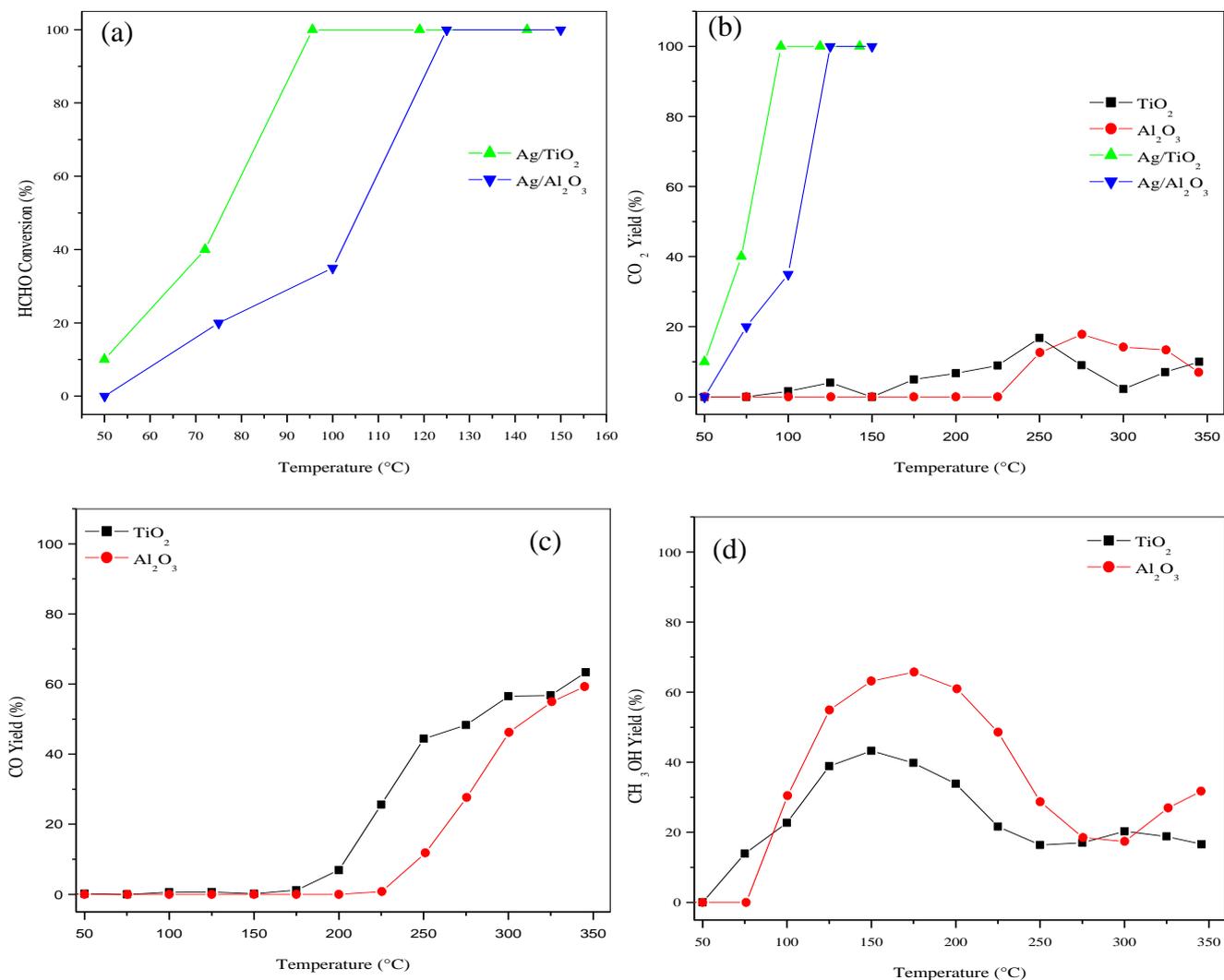


Fig 1. HCHO conversions (a), CO₂ yield (b), CO yield (c), CH₃OH yield (d) on TiO₂, Al₂O₃, Ag/TiO₂ and Ag/Al₂O₃. Reaction conditions: HCHO 100 ppm, catalyst mass 50 mg, O₂ 19,5 vol%, total flow rate 100cm³min⁻¹, GHSV 84000h⁻¹

zhang and all⁷ proved that TiO₂ and Al₂O₃ showed no activities for HCHO oxidation in the range of temperature 35-125 °C. The study of Hang and al⁸ showed that TiO₂ and hydrogenated TiO₂ have a little activity after 200 °C. According to these data the catalytic activity of the supports synthesized by sol-gel method significantly important. Therefore, the supports modification by impregnation of silver in the surface, results in increase of catalysts performance as well as selectivity of formaldehyde oxidation to CO₂. The Ag/TiO₂ catalyst has better oxidation activity, the complete HCHO conversion to CO₂ is achieved at 95 °C.

Totally elimination of formaldehyde over Ag/Al₂O₃ catalyst is exhibited at 125 °C. We can conclude that the addition of Ag can provide sufficient active sites for the HCHO oxidation reaction. Note that the efficiency of the Ag/TiO₂ catalyst in the conversion of HCHO at low temperature (particularly T₅₀) is better than some literature data **table 1**

Table 1. Catalytic activity of silver-based catalysts in the HCHO oxidation

Catalysts	Reactions conditions	T ₅₀ (°C)	References
Ag/TiO ₂	100 ppm HCHO, O ₂ 19,5 vol%, GHSV 84000h ⁻¹	79	This work
Ag/CeO ₂	810 ppm HCHO, O ₂ 20 vol%, 84,000 h ⁻¹ SV	90	[33]
Ag-HMO	400 ppm HCHO, 10 vol% O ₂ , 30,000 ml(gh) SV	80	[34]

With GHSV: gas hourly space velocity

3.3. Characterization of the catalysts

Fig 2 display the XRD patterns of TiO₂ and Ag/TiO₂ catalysts. Diffraction peaks at 25.44°, 38.0°, 48.3°, 54.43° and 63.4 correspond to (101), (004), (200), (105) and (204) and were well matched of tetragonal anatase TiO₂ (JCPDS 01-071-1166). The XRD pattern of Ag/TiO₂ showed an increase in peaks intensities with no additional peak related to the silver. These results showed that Ag species were widely dispersed on TiO₂ support that may have been caused by the strong interaction metal-support⁹. XRD patterns of Al₂O₃ and Ag/Al₂O₃ catalysts are shown in **Fig 3**. Only the phase γ -Al₂O₃ was detected Al₂O₃¹⁰. As for the Ag/Al₂O₃ the diffraction peaks of Ag₂O at 38,2° and 64,5 were observed, which assigned as (111) and (220) crystal planes. In addition, a peak of Ag⁰ was detected at 44,3° corresponded to the (200) lattice plane, which could be indexed to face-centered cubic phase¹¹. The crystallite sizes of the synthesized catalysts were calculated using the Debye-Scherrer equation and are presented in **Table 2**.

Table 2. Material properties of synthesized catalysts

Catalyst	S _{BET} (m ² /g) ^a	Pore volume (cm ³ /g) ^a	Average pore diameter (Å) ^a	Crystal size (nm) ^b
TiO ₂	132	0.38	84	-
Al ₂ O ₃	322	0.69	62	-
Ag/Al ₂ O ₃	247	0.40	59	25

^a Determined by BET, ^b Determined by XRD

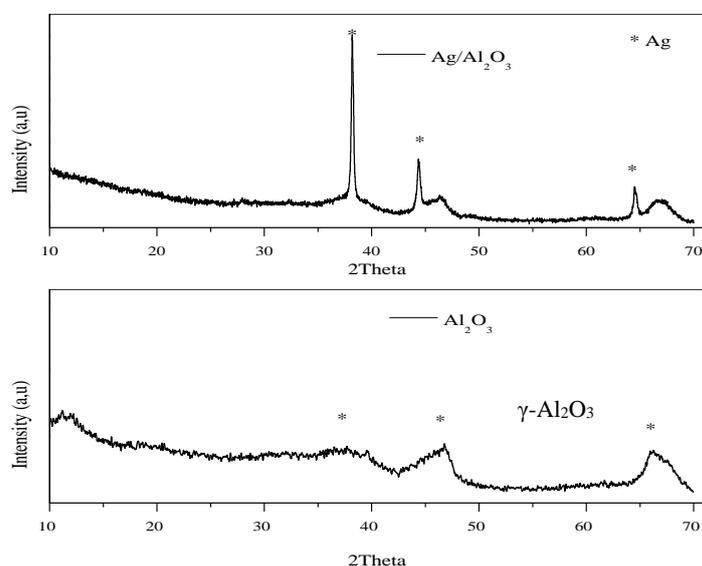


Fig. 2 X-ray diffraction patterns of : Al₂O₃ and Ag/Al₂O₃

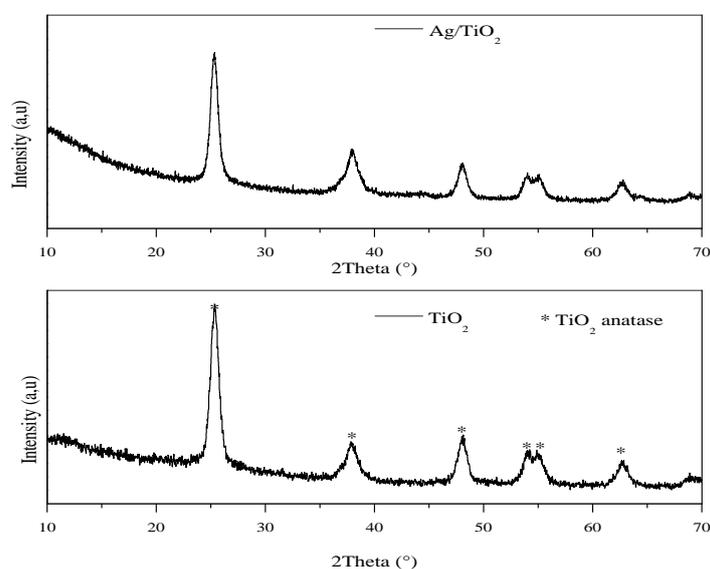


Fig. 3 X-ray diffraction patterns of : TiO₂ and Ag/TiO₂

The N₂ adsorption-desorption isotherms of Al₂O₃, Ag/Al₂O₃, TiO₂ and Ag/TiO₂ samples are presented in **Fig 4a** and **b** show the isotherms of Al₂O₃ support and Ag/Al₂O₃ catalyst. Both solids belonged to type IV with a type H3 hysteresis, typically indicates the presence of closely packed slit pores¹². As shown, in Fig 3b the isotherm of TiO₂ and Ag/TiO₂ samples

resembled the type IV curves with H2 hysteresis loop, corresponding to mesoporous textures and in-bottle shaped. The Barrett-Joyner-Halenda (BJH) pore size distribution (**Fig 5a, b**) Al_2O_3 , $\text{Ag}/\text{Al}_2\text{O}_3$, TiO_2 and Ag/TiO_2 catalysts indicating that all samples characterized by a monomodal size distribution. The Brunauer-Emmett-Teller (BET) surface area, pore volume and average pore diameter obtained from N_2 adsorption-desorption measurement were showed in **Table 2**. The surface area of both TiO_2 and $\gamma\text{-Al}_2\text{O}_3$ supports gradually decreased after silver impregnation.

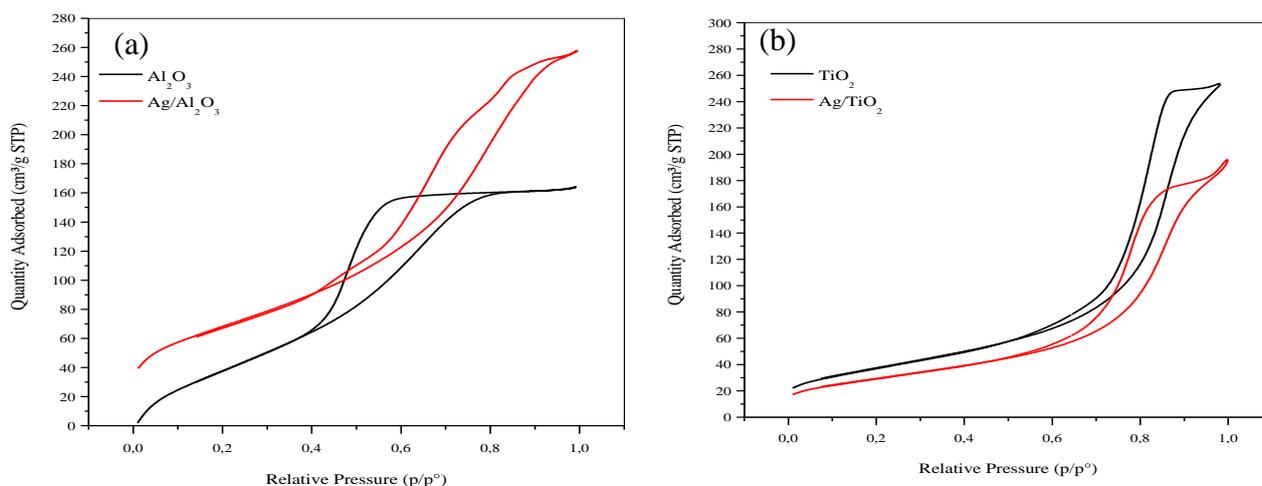


Fig. 4 The curves of nitrogen adsorption-desorption isotherms of : Al_2O_3 , $\text{Ag}/\text{Al}_2\text{O}_3$ (a) and TiO_2 , Ag/TiO_2 (b)

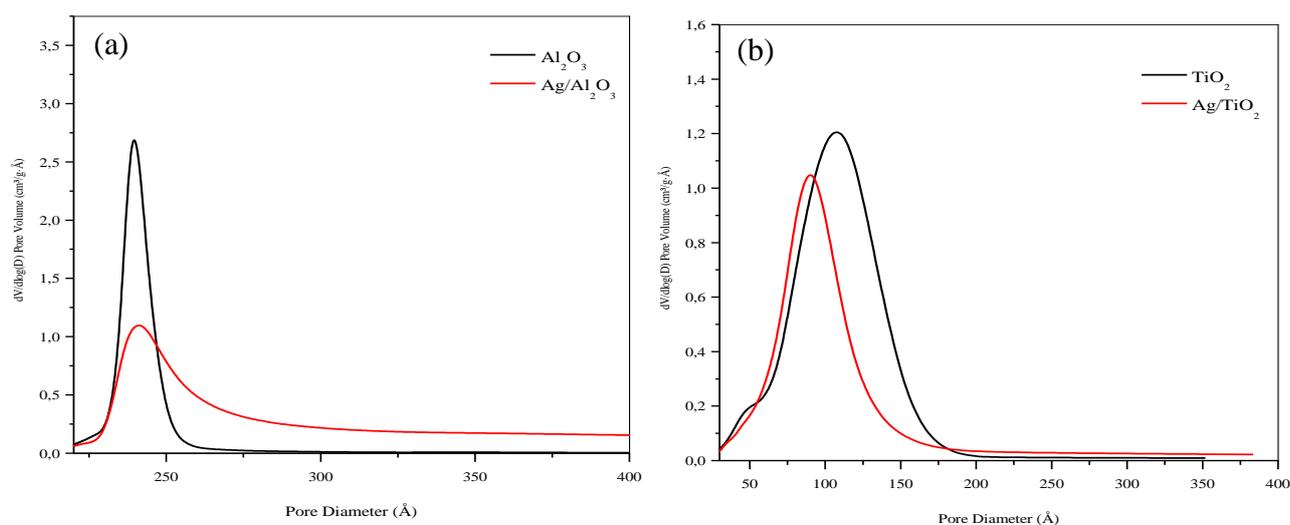


Fig. 5 Pore size distribution curves of : Al_2O_3 , $\text{Ag}/\text{Al}_2\text{O}_3$ (a) and TiO_2 , Ag/TiO_2 (b)

The optical analysis of FT-IR was used to determine the functional groups and vibration bonds in the samples in the range of 4000-400 cm^{-1} . **Fig 6** show the FT-IR of Al_2O_3 support and $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst. The absorption peak at 3480 cm^{-1} is related to the vibration bonding of the hydroxyl groups OH. The peak of water molecules is formed at 1630 cm^{-1} . The vibrations peaks generated in the range of 700-500 cm^{-1} correspond to Al-O-Al, that proves the existence of γ -form¹³. **Fig 7** presents the FT-IR spectra of TiO_2 and Ag/TiO_2 . The adsorption band in the range of 3800-3000 cm^{-1} are assigned to the stretching vibrations of OH. The peak absorption at 1620 cm^{-1} is ascribed to the adsorbed water molecules. The observed peaks at the range of 900-450 cm^{-1} is associated with the vibration of Ti-O-Ti^{14, 15}.

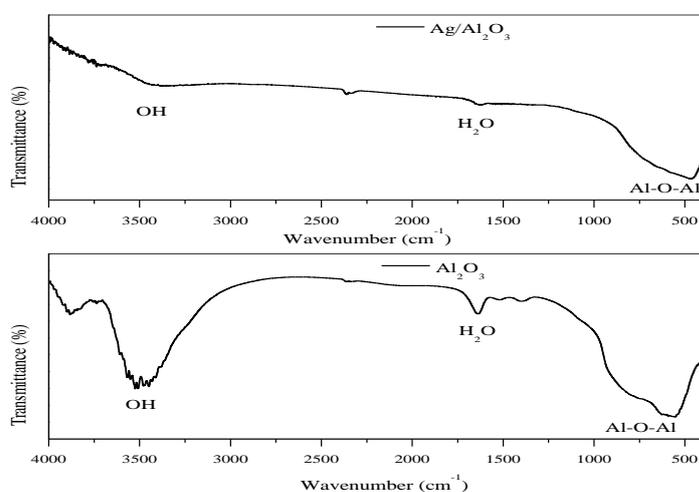


Fig. 6 FT-IR spectrum of Al_2O_3 and $\text{Ag}/\text{Al}_2\text{O}_3$

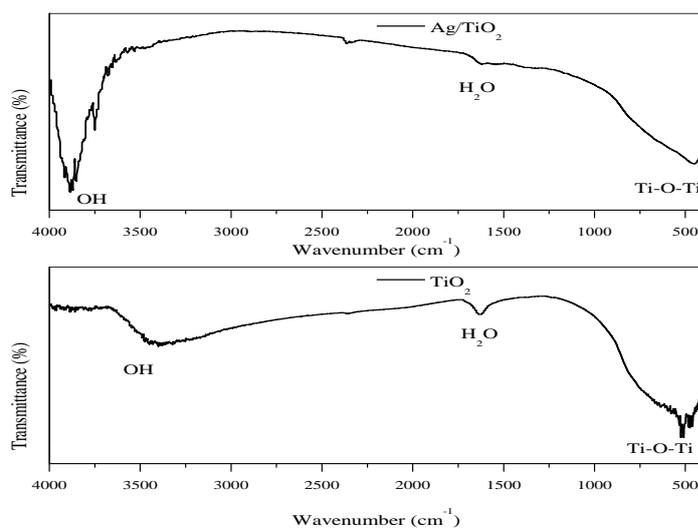


Fig. 7 FT-IR spectrum of TiO_2 and Ag/TiO_2

Transmission electron micrographs (TEM) of Ag/Al₂O₃ and Ag/TiO₂ catalysts are shown in **fig 8** and **fig 9**. The image of Ag/Al₂O₃ showed a distribution of Ag particles with nonuniform shapes, the silver present in the form of huge agglomerates composed of large particle sizes (**Table. 1**). In contrast in Ag/TiO₂ it can be observed that the Ag particle sizes is much smaller, and the distribution was relatively uniform. The addition of silver in the surface of TiO₂ support caused some black spots with a hexagonal structure. The results of TEM indicate that the impregnation of silver is very affected by the support used.

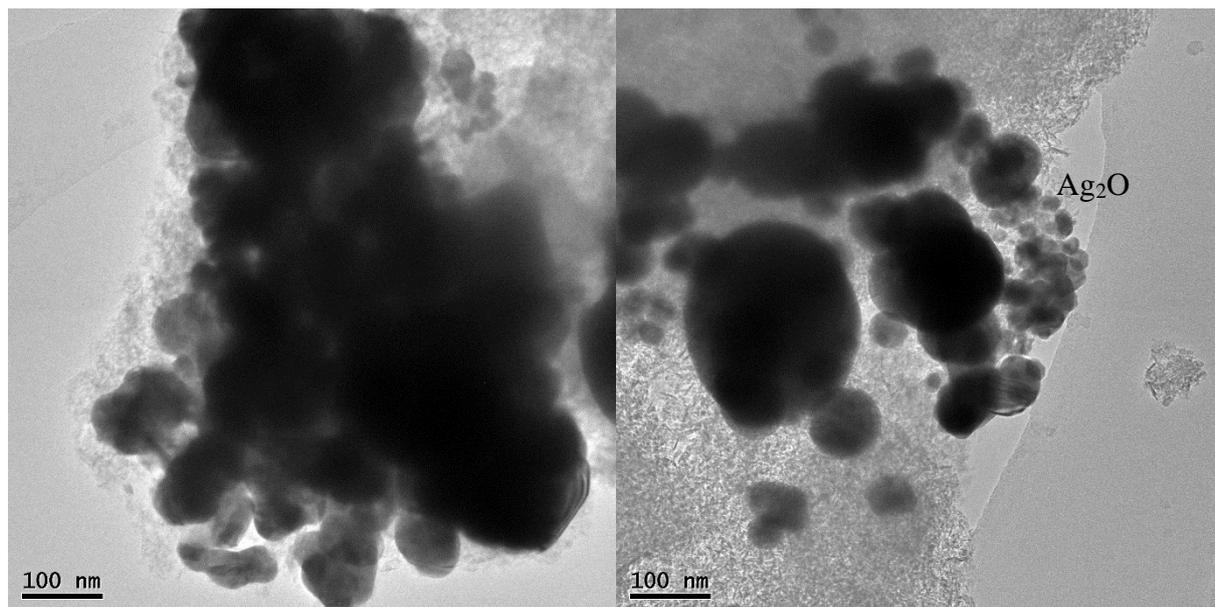


Fig. 8 TEM images of Ag/Al₂O₃

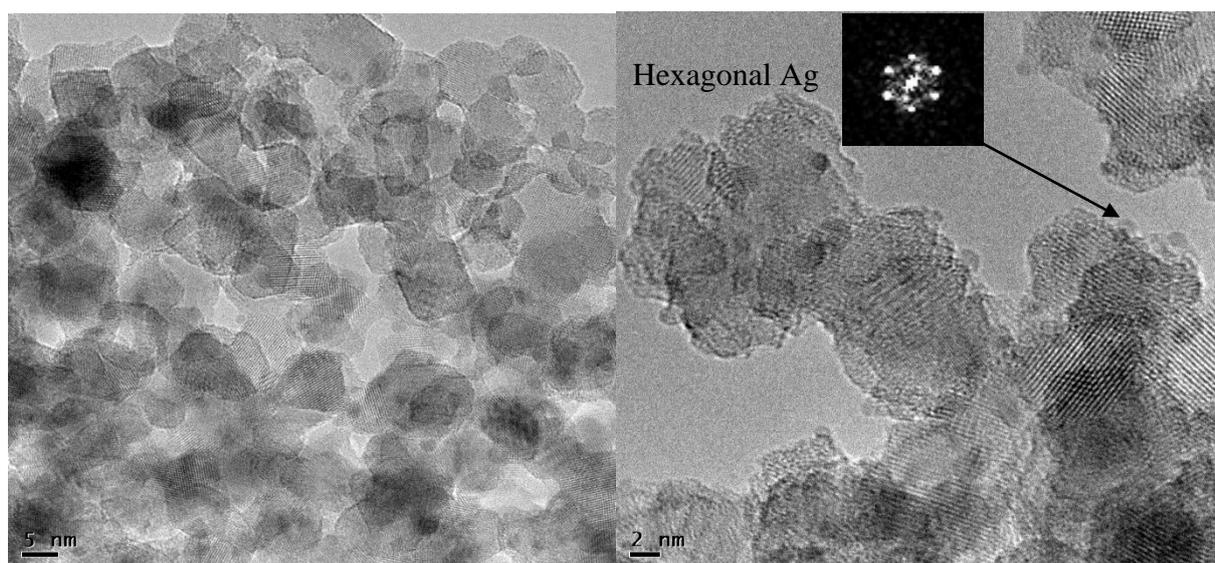
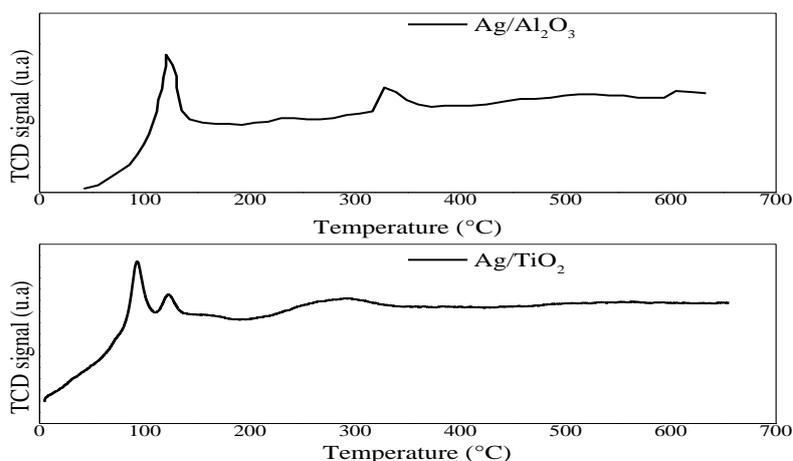


Fig. 9 TEM images of Ag/TiO₂

H₂-TPR experiments were conducted to investigate the redox ability of Ag/Al₂O₃ and Ag/TiO₂ catalysts and the results are shown in **fig 10**. No reduction peaks were observed in the profiles reported for the pure supports TiO₂ and γ -Al₂O₃. Two peaks were detected for Ag/Al₂O₃, peak around 100 °C caused by large Ag₂O clusters and the peak around 350 °C is assigned to small Ag₂O clusters¹⁶. For Ag/TiO₂ the peak below 100 °C was ascribed to reduction of oxygen species absorbed on the dispersed Ag surface, and the second peak was due to the reduction of large Ag₂O groups¹⁷.



H₂-TPR profiles of Ag/Al₂O₃ and Ag/TiO₂ catalysts

Conclusion

Ag/TiO₂ and Ag/Al₂O₃ were effective for the removal of formaldehyde (HCHO) leading to the selective production of carbon dioxide, unlike pure supports which release CO, and methanol as by-products. However, the activity of Ag/TiO₂ (100% conversion at 95 °C) was higher than Ag/Al₂O₃ (100% conversion at 125 °C). Characterization results indicated that Ag particles sizes and their dispersion in the surface of support are the important factors in the catalytic activity for the formaldehyde oxidation. In summary we have reported that the catalytic activity of supported Ag catalysts is dramatically influenced by the support morphology.

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