Functionalization of hydroxyapatite with silver for application in total oxidation of formaldehyde

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Significance and Relevance

New "in flow" and conventional "batch" methods (IFM and BM) were used for the preparation of Ag-modified hydroxyapatite (Ag-HAP) catalysts. HAP supported Ag_3PO_4 NPs were synthesized by BM while most part of silver appears as highly dispersed Ag species on HAP when using IFM. The best intrinsic activity for HCHO oxidation into CO_2 in moist air (RH=50%) was achieved over Ag-HAP prepared by IFM and subsequently calcined at 500°C. The highly dispersed Ag NPs and the presence of water likely promote HCHO oxidation through a hydroxide-active oxygen pathway. This work offers valuable insight for design of new efficient Ag-HAP catalysts.

Preferred and 2nd choice for the topic: Air cleaning and combustion, Automotive and stationary emission control
Preferred presentation: Oral preferred

Introduction and Motivations

Formaldehyde (HCHO) is an irritant and carcinogenic volatile organic compound (VOC) released primarily by the degassing of wood-based panels which may cause serious health hazards. Much effort has been devoted to eliminate HCHO, with catalytic oxidation being one of the most effective methods.

Noble metal-based catalysts such as Pt and Au exhibit high activities on formaldehyde oxidation. However, due to the high cost of precious metals, developing low-cost catalysts remains a significant challenge. Among the various alternatives, Ag-based catalysts are much cheaper and show considerable efficiency for HCHO oxidation at low temperature[1].

The aim of this work is to study the catalytic performances of new silver-functionalized calcined hydroxyapatite (HAP, $Ca_{10}(OH)_2(PO_4)_6$) for the total oxidation of formaldehyde in dry/wet air. HAP, the most abundant CaP mineral, can serve as a catalytic support thanks to its high specific surface area, versatile ion-exchange property and surface area exposed to OH^-, PO_4^{3-}, and Ca^{2+} entities[2]. Functionalization of as-synthesized hydroxyapatite with silver was carried out using "batch" and "in-flow" methods, and the effect of subsequent calcination temperature (300°C-500°C) on physical properties and catalytic performances in HCHO oxidation was investigated.

Materials and Methods

IFM: A flowing $AgNO_3$ aqueous solution (100 mL- 1.3 mL/min) was allowed to pass through the compact bed of HAP. The solid F-Ag/HAP was obtained after a vacuum treatment and drying.

BM: An aqueous solution of $AgNO_3$ (250 mL) was added to HAP (~6 g). The reaction mixture was stirred for 24 h at 40°C. The suspension was filtered, washed and dried (120°C-16 h) to get B-Ag/HAP. The Ag content was calculated to obtain a nominal Ag loading of 3 % w/w in both cases.
The as-prepared samples (≈ 500 mg) were calcined at 300 °C and 500 °C (2°C/min) in dry flowing air (0.2 L/min) to get the B-Ag/HAP-T F-Ag/HAP-T samples (where T stands for the temperature in °C).

Catalytic tests were performed with 200 mg of catalyst (100 < particle size < 200 µm) loaded in a glass tubular micro-reactor (inner diameter: 10 mm). The powders were activated 1 h at 100 °C in a dry air flow (100 mL/min) before being submitted to 100 ppmv HCHO/synthetic air for 4 h (GHSV: 30 L /(g.h).

Results and Discussion

Silver content for B-Ag/Hap and F-Ag/Hap of 1.9 and 0.8 wt% differs from a factor 2 in line with the IFM ensuring a minimization of the contact time between Ag and HAP. XRD results show that HAP supported Ag_3PO_4 NPs with a crystalline structure were synthesized by BM while most part of silver appears as highly dispersed Ag(I) species on HAP with a minor contribution of $Ag_3(PO_4)$ when using IFM. The calcination step at 300°C shows persistence of the diffraction peaks relative to the cubic $Ag_3(PO_4)$ phase for B-Ag/HAP while it is noted the quasi-absence of Ag related phase for F-Ag/HAP. After calcination at 500°C it is only observed the peaks characteristic of HAP which implies the high dispersion of Ag species on HAP on both samples. However, the H_2/Ag ratios determined from the H_2-TPR experiments are below 0.5 for B-Ag/HAP-500 suggesting that Ag(I) species are not completely reduced to Ag(0). By opposition, the absence of H_2 consumption peaks indicates the full conversion of Ag(I) species into Ag(0) NPs in the preparation step, as shown in Fig. 1a for F-Ag/HAP-500, which are recognized to activate O_2. The textural properties analysed from nitrogen sorption isotherms show minimal differences among the different series of catalysts as compared to those of the HAP support. Interestingly, XPS atomic ratios Ag/Ca and Ag/P (with Ag 3d corrected from the Ca 2p energy loss) indicate a better Ag dispersion for the catalysts of the IFM series. The CO_2 yield (Y_{CO2}) for HCHO total oxidation at 100°C in dry (non-calcined catalysts) and moist air (RH = 50%) for 4 h on time-on-stream (TOS) are given in Fig. 1b, showing the beneficial role of a calcination step at 500°C on the conversion of HCHO into CO_2 while calcination at 300°C leads to low efficient catalysts.

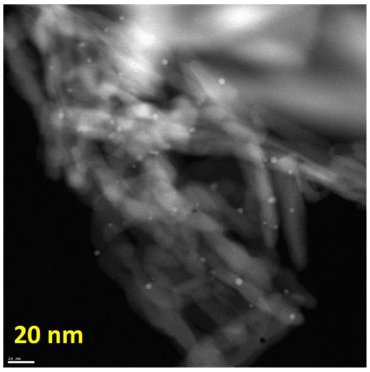

Fig. 1a : STEM-HAADF image of F-Ag/HAP-500

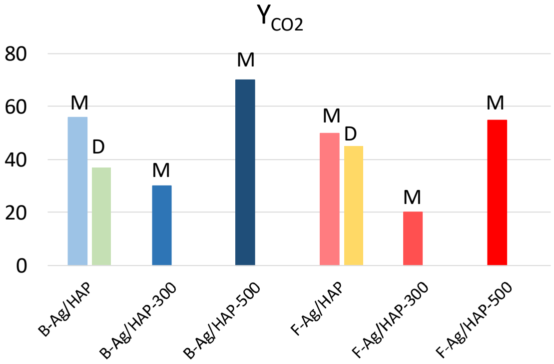

Fig. 1b : Y_{CO2} (%) for HCHO total oxidation over catalysts at 100°C after a TOS of 4h in dry (D) and moist (M) air.

The results showed that the mode of preparation affects the Ag content and the nature/distribution of silver species. The highly dispersed Ag(0) nanoparticles on IFM samples, combined with the presence of water, likely enhance HCHO oxidation via a hydroxide-active oxygen pathway. This mechanism results in superior catalytic activity, also considering the lower Ag concentration compared to BM samples.

References

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