# An alternative method for the incorporation of silver in Ag-$VO_x/TiO_2$ catalysts for the total oxidation of benzene

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## Abstract:

An alternative way of synthesis, the "onion" method, was used to deposit silver nanoparticles on a $VO_x/TiO_2$ catalyst. This synthesis method consists in the impregnation of organic vesicles containing the metallic silver nanoparticles. In situ calcination is needed to remove the organic vesicles and to offer an access of the reactants to the silver nanoparticles. This removal is easier in presence of vanadium. The addition of silver induces a higher proportion of $V^{5+}$. The Ag-$VO_x/TiO_2$ catalysts prepared with this method exhibit better performances in the total oxidation of benzene after moderate in situ calcination at 350 °C than at 450 °C. A synergy between silver and vanadium is evidenced after both kinds of calcination with a silver loading of 0.125 and 0.25 wt. %. The extent of this synergy is higher after a moderate calcination. This effect is likely due to the fact that small nanoparticles prepared via the "onions" sinter less after during in situ calcination at 350°C than at 450°C. A clear link between the extent of the synergy and the size of the silver nanoparticles is evidenced. A decrease of the nanoparticle size induces a higher extent for the synergy.

**Key words**: Ag nanoparticles, total oxidation of benzene, vanadium based catalysts

## 1. Introduction

The protection of the environment needs a very good control of the gaseous emission due to human activities [1, 2]. A wide range of very toxic pollutants can indeed be present in these emissions [2-4] and their dispersion in the environment needs to be avoided. The development of catalytic solution for the abatement of these molecules directly at their source of emissions is thus a priority for environmental catalysis [5]. Among these molecules, dioxins are certainly one of the most dangerous for human health since they are very toxic and responsible for several health problems even in very low concentrations [6]. Vanadium based catalyst are widely developed for the total oxidation of dioxins and several ways were already explored to improve the activity of $V_2O_5/TiO_2$ catalysts [7-22]. This kind of catalyst is one of the most efficient for this reaction and presents the major advantage to be resistant against a chlorine poisoning effect. However, the activity of such catalyst still needs to be improved in order to use less and less energy for the abatement of dioxins.

Recently, an innovative way to improve the efficiency of vanadium based catalysts was explored by several authors, namely the addition of noble metals [19, 21, 23-26]. In particularly, our group focused on the addition of Ag to a $VO_x/TiO_2$ formulation [19, 21, 27, 28]. Indeed, the addition of silver could potentially bring electrophilic oxygens [29, 30] which are interesting species in a reaction of total oxidation. A synergistic effect between silver and vanadium was evidenced in the total oxidation of chlorobenzene and benzene [19, 21] which are classical model molecules used to mimick dioxins. This synergy was directly linked to a compromise between the specific surface of the catalysts, the oxidation state of vanadium, the acidity of the surface and the reaction conditions [19, 21]. In these previous works, $Ag\text{-}VO_x/TiO_2$ catalysts were synthesized by a wet impregnation method. Unfortunately, this synthesis method does not allow to study one

particularly important parameter for such kind of catalyst, namely the size of the silver nanoparticles. This parameter can potentially influence strongly the activity of Ag-$VO_x/TiO_2$ catalysts while the wet impregnation induces a broad distribution of the silver nanoparticle size. The study of this parameter thus needs a synthesis method which offers a good control of the shape and the size of the nanoparticles. The "onion" method developed by Faure *et al.* [31] permits such control. Metallic silver nanoparticles are directly synthesized inside organic vesicles. Moreover, this method has already proven its efficiency to deposit metallic silver nanoparticles on titania [27, 28].

The aim of this study is thus to identify a link between the size of the silver nanoparticles and their synergy with vanadia by using an innovative method for the incorporation of silver. The study focusses on four silver loadings. Three loadings (0.125, 0.25, 0.5 wt. %) correspond to the content of silver of wet impregnated catalysts for which a synergy was evidenced in the total oxidation of benzene [19] while no synergy was evidenced with the fourth loading (1 wt. %). The catalysts were characterized by ICP, XRF, $N_2$ physisorption, XRD, XPS, TGA-MS and TEM.

## 2. Experimental

### 2.1 Preparation of the catalysts

#### a) Synthesis of $VO_x/TiO_2$

$TiO_2$ Degussa P25 (85% anatase - 15% rutile, 49 $m^2.g^{-1}$) was used as support and was dried overnight at 110°C before the impregnation. The $NH_4VO_3$ precursor (Vel, >99%) was dissolved in distilled water and treated with oxalic acid (Aldrich, >99%, molar ratio vanadium:oxalic acid = 1:2 [9]). An appropriate amount of support was then added to the solution. The suspension was mixed for 2h at room temperature and water was evaporated in a rotary evaporator under reduced

pressure at 40°C. The material was dried overnight in an oven at 110°C and finally calcined in air in a muffle furnace (20h, 400°C). The vanadium loading always corresponds to 2.49 wt. % which is equivalent to 0.75 theoretical monolayer on the titania support.

b) The incorporation of silver

A new route for the preparation of supported Ag NPs catalysts was proposed recently [28, 31]. Silver NPs are first prepared by the spontaneous reduction of $Ag^+$ inside organic microreactors called “onions” [28]. Onions are organic vesicles made of closely-packed concentric bilayers of surfactant (Scheme 1). The formation of silver nanoparticles takes place at room temperature under the sole reducing effect of the surfactant. The vesicles loaded with ~5 nm sized Ag NPs were then transferred onto a support ($TiO_2$ or $VO_x/TiO_2$) by a simple impregnation step followed by evaporation and drying.

Onions were prepared by shearing an appropriate amount of Genamin T020 (Scheme 1) directly with an identical quantity of a silver solution (0.44 M) with a spatula in a glass vial until a homogeneous paste was obtained. The salt was thus directly encapsulated inside the vesicles. The paste was allowed to incubate for 40 min (at ~25°C). A precise amount of this paste (~100 mg) was dispersed into 2 ml of distilled water to obtain a colloidal suspension. Impregnation was performed by magnetically stirring for 2 hours 1g of $TiO_2$ (Degussa P25) or $VO_x/TiO_2$ in 100 ml of water after the addition of the suspension of silver nanoparticles-loaded onions. Water was then evaporated in a rotavapor (50°C; ~100 mbar) and the material was dried for one night at 80°C in an air oven. Finally, the catalysts are calcined in the catalytic reactor in air, namely in situ, at 350°C or 450°C during one hour. Four loadings of silver were explored: 0.125, 0.25, 0.5 and 1 wt. %.

Table 1 shows the different types of catalysts synthesized and their generic names. The generic name is built as follows: OAgT-x, x corresponding to the Ag loading (wt. %) and O indicating the “onion” method

## 2.2 Catalytic test

The catalytic tests were performed in a metallic fixed-bed microreactor operating at atmospheric pressure. The reactor was made of an inconel tube of 1 cm internal diameter. The catalytic bed was composed of 200 mg of catalyst powder selected within the granulometric fraction 200-315 µm and diluted in 800 mg of inactive glass spheres (315-500 µm). The gas stream contained 100 ppmv of benzene in He (Praxair, 99.995%), 20% of $O_2$ (Praxair, 99.995%) and He (Praxair, 99.996%) as diluting gas to obtain 200 $ml.min^{-1}$ (GSVH = 37000 $h^{-1}$). The total oxidation of benzene was performed at 250°C. During the test, the catalysts were stabilized for 150 min at this temperature.

The analysis of reactants and products ($CO_2$, CO) was continuously performed by on line gas chromatography (Varian CP 3800 GC). This equipment allowed to detect potential intermediate products of the reaction like hydrocarbons.

The conversion is defined as the ratio reactant transformed/reactant in the inlet (in %). The selectivity of $CO_2$ is systematically between 95 and 100 %, CO being the only other product. In this work, we will assume that there is a synergy between Ag and vanadium if the catalytic performances of the Ag-$VO_x/TiO_2$ catalyst are higher than the sum of the individual performances of the two corresponding reference catalysts, namely $Ag/TiO_2$ and $VO_x/TiO_2$.

## 2.3 Physicochemical characterization

The weight percentages of V and Ag in all the catalysts were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on an Iris Advantage apparatus from Jarrell Ash Corporation. These analyses were performed at the Earth and Life Institute (ELI), Université catholique de Louvain-la-Neuve, Belgium. For some catalysts, the elementary measurements of Ag and V were realized with a Philips Minipal PW4025. The system is controlled by an analytical program called Minipal. The radiation source is an X-ray tube, consisting of a rhodium anode, whose specifications are 30 kV and 1 mA. The detector is a SI-PIN diode high resolution, hermetically isolated, but with a small opening in beryllium. The sample powders were placed into small cup whose bottom is formed of a thin transparent plastic film. The calibration of the apparatus was realized with chemical compositions obtained previously by ICP-AES.

$N_2$ physisorption experiments were performed at -196°C on a Micromeritics TriStar 3000 instrument. The samples were outgassed overnight at 150°C under vacuum (2 Pa) before the measurement. The specific surface area was determined from the BET method in the 0.05 – 0.30 $P/P_0$ range.

X-ray diffraction (XRD) measurements were performed on the catalysts with a Siemens D5000 diffractometer using the Kα radiation of Cu (λ = 1.5418 Å). The source tube was operating at 40 kV and 40 mA. The 2θ range was recorded between 5 and 75° at a rate of 0.028° $s^{-1}$. The samples were deposited on zero background specimen holder made of Si single crystals. The ICDD-JCPDS database was used to identify the crystalline phases.

Surface characterization was done with an X-ray photoelectron spectroscopy (XPS) on a Kratos Axis Ultra spectrometer (KratosAnalytical, Manchester, UK) equipped with a monochromatized aluminium X-ray source (powered at 10 mA and 15 kV). The pressure in the analysis chamber was about $10^{-6}$ Pa. The analyzed area was 700 μm x 300 μm. The pass energy of the hemispherical analyzer was set at 160 eV for the wide scan and 40 eV for narrow scans. Charge

stabilization was achieved by using the Kratos Axis device. The electron source was operated at 1.8 A filament current and a bias of –1.1 eV. The charge balance plate was set at -2.8 V. The sample powders were pressed into small stainless steel troughs mounted on a multi specimen holder. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, Ti 2p, Ag 3d, V 2p and C 1s again to check for charge stability as a function of time, and the absence of degradation of the sample during the analyses. Special care was taken to make sure that vanadium and silver were measured fast enough in order to avoid their reduction under vacuum. This was done by measuring these elements at first as soon as the vacuum level was low enough to allow proper XPS measurements.

Data processing was performed with the CasaXPS program (Casa Software Ltd., UK). The binding energy (BE) values were referred to the C–(C, H) contribution of the C 1s peak at 284.8 eV. Molar fractions [%] were calculated using peak areas normalized on the basis of acquisition parameters after a linear background subtraction, experimental sensitivity factors [32], and transmission factors provided by the manufacturer. Concerning vanadium, we only considered the V $2p_{3/2}$ peak. Indeed, it has been shown that the V $2p_{1/2}$ peak is too close to the O 1s peak and can therefore undergo deformations [33, 34]. The V $2p_{3/2}$ peak was decomposed into two components, respectively $V^{5+}$ and $V^{4+}$, with the following constraints [34]: difference of 1.2 eV between the positions of the two components, identical full width at half maximum (fwhm), position of the component assigned to $V^{5+}$ fixed between 517.1 and 517.3 eV

Transmission electron microscopy (TEM) measurements were performed on a JEOL 2000FX, working under an acceleration voltage of 200 kV. For the analysis, the sample powder was dispersed in 2-butanol (Sigma-Aldrich, > 99%) and homogenized by agitation. A droplet of the suspension was deposited on a copper grid coated with a porous carbon film and the solvent was then evaporated at room temperature.

The thermogravimetric analysis (TGA) was performed on a *TGA/SDTA 851$^e$* apparatus (Mettler-Toledo) under dry air flow (100 ml.min$^{-1}$). The sample (20 mg) was placed in an alumina sample holder. The temperature program starts at 25°C and finishes at 700°C, the temperature slopes being 10°C.min$^{-1}$. During the analysis, the products are identified by mass spectrometry ($CO_2$, $H_2O$, $NO_2$, etc.).

## 3. Results and discussion

### 3.1 Physicochemical characterizations

The impregnation of the onions induces a decrease of the specific surface regarding to the support (50 m².g$^{-1}$) (Table 2). This decrease is more and more pronounced with the silver loading. Such decrease was already observed for the catalysts prepared by wet impregnation [19, 21]. In this study, we suggested that the impregnation of silver could potentially lead to the obstruction of the interstitial spaces between the $TiO_2$ particles which are responsible of the specific surface of titania [19, 21]. This hypothesis is still relevant with the impregnation of the onions. However, here the trend can be additionally explained by the increasing amount of surfactant. Indeed, the amount of surfactant is directly proportional to the silver loading. The more pronounced decrease of the specific surface observed for the highest silver loadings can thus be correlated with the increasing quantity of surfactant used for the synthesis of the onions.

The composition of the materials is given in Table 2. The silver and vanadium contents are systematically lower than the nominal data. This trend is easily explainable. Indeed, there is still a high amount of surfactant present at the surface of the catalyst (between 4 and 5 wt. %). The

silver and vanadium loadings were calculated to obtain the nominal loading after the calcination which will carried out inside the reactor. The samples characterized being only dried, the presence of the surfactant induces thus a virtual decrease of the silver and vanadium loadings. Moreover, the transfer of the onions from the glass vial to the solution of impregnation is quite problematic as the onions are very sticky. It is thus possible to lose a small part of silver during this transfer. A previous study showed that the mass balance measured on silver based catalysts prepared with the onion method is in good agreement with the expected loadings [27, 28].

The XRD measurements highlight only the peaks of the anatase and rutile phases for the OAgT and the OAgVT catalysts (Fig. 1). The absence of Ag peak is in good agreement with the expected size of the silver nanoparticles. Indeed, the onion method should lead to the formation of metallic nanoparticles with a diameter under 5 nm [27, 28, 31]. These nanoparticles should thus not be detectable by XRD. Nevertheless, the absence of silver peak could also come from the low loadings used for the synthesis of the catalysts.

The Ag/Ti ratios (Table 3) are lower than those obtained with impregnated catalysts [19, 21]. This result is again likely due to the presence of the surfactant. These organic molecules induce a higher amount of C atoms at the surface of the catalyst which leads to a relative decrease of the silver signal. Indeed, silver is present on the surface of the catalyst. Since the intensity of the signal decreases exponentially with the depth, its contribution to the XPS signal is proportionally more important than the contribution of the support. The presence of the surfactant on the surface of the catalyst has thus a bigger effect on the signal of Ag than on the signal of Ti which is located deeper in the sample. In other words, the surfactant leads to a lower Ag/Ti ratio even if it does not contain Ag or Ti.

This phenomenon is evidenced indirectly with the sample OAgT-0.25-C. This sample corresponds to the OAgT-0.25 sample which underwent a calcination at 450°C. This calcination step induces the removal of the organic matter at the surface of catalyst and results in a higher relative signal for Ag and Ti. However, this effect is really more important for Ag than for Ti due to exponential decrease of the XPS signal with the depth. Therefore, we observe an increase of Ag/Ti ratio after this calcination step.

It is interesting to notice that the impregnation of onions already influences the $V^{5+}$ proportion. This proportion increases with the silver loading as it was already observed with co-impregnated catalysts [19, 21]. This result is quite surprising as the silver is normally not accessible because the nanoparticles are still included in the organic vesicles. However, XPS analyses performed on the OAgVT-0.25 sample before and after the drying step showed that the carbon atomic concentration decreases during this step from 21.6 to 20.4 %. This evolution suggests that the removal of the surfactant already starts during this drying step for the OAgVT catalysts. This result is in agreement with the autocatalytical effect of vanadium on the combustion of the surfactant observed in a previous study [27]. The removal of the surfactant implies that the accessibility to the silver particles increases, so that the potential contact between silver and vanadium increases as well. Some silver particles could thus potentially already influence the vanadium properties.

During the TGA analyses, the main weight loss occurs around 285°C for OAgT-0.25 (Fig. 2) while it occurs at a much lower temperature for the OAgVT catalysts (Fig. 3). Indeed, the weight loss mainly occurs in this case at 230°C: a downward shift of more than 50°C is highlighted. A clear link can be established between these main weight losses and the combustion of the

surfactant (Fig. 2 and 3). In both cases, all combustion products are indeed detected in parallel with the weight loss. The top of the peaks of combustion products corresponds to the temperature of the weight loss (Fig. 2 and 3) and their shapes closely fit the shape of the weight loss derivative peak. In addition, the weight loss peaks and the combustion products peaks are sharper for the O-AgVT catalyst. All these results are clearly linked to the good combustion properties of $VO_x$ catalysts. These properties are still highlighted by the second weight loss. A shoulder is noticed around 415°C for OAgT-0.25 (Fig. 2) while this peak is less marked and shifted downwards by about 70°C (down to ~345°C) for OAgVT (Fig. 3). No peak of $CO_2$, $H_2O$ or $NO_2$ was observed when the same experiment was carried out with the bare $TiO_2$ support (not shown).

Since the combustion of the surfactant mainly occurs at 285°C for OAgT, it means that the silver nanoparticles are not exposed to the gaseous phase below this temperature because the surfactant still impedes the access to the nanoparticles. Actually, it has been shown that Ag nanoparticles are active only from ~350°C when the OAgT samples are directly used in catalytic test after the drying step [27]. Moreover, the peak observed around 415°C evidenced that a fraction of the surfactant is only removed at higher temperature. Thus, higher accessibility of the nanoparticles and higher activity could presumably be reached with a further “cleaning” of the surface at higher temperature. On the other hand, the activity of the nanoparticles at 350°C decreased after that the catalyst was brought to 400°C [27]. A sintering is a plausible explanation for this observation.

The presence of V improves the removal of the surfactant by calcination. The organic molecule burns at different temperatures depending on the nature of support onto which it is deposited. This effect of vanadia can be linked to its well-known ability to catalytically oxidize organics

following a MVK cycle [35]. $V_2O_5$ exhibits labile surface oxygen atoms which act as oxidant for organic compounds. This result is relatively important because it means that a lower calcination temperature is needed to expose the silver nanoparticles to the gas phase. A lower calcination temperature leads to lower sintering of the nanoparticles. It should be thus possible to determine if the size of the nanoparticles has an effect on the synergy between silver and vanadium by using two different temperatures for the calcination step.

TEM analyses were performed on the OAgT and OAgVT samples. Unfortunately, the low loadings of silver and the presumed low size of the nanoparticles did not allow to observe many nanoparticles. Moreover, the contrast was worse than with the wet impregnated catalyst. It was thus particularly difficult to identify the silver nanoparticles and to evaluate their average size. A representative picture of the OAgVT-0.5 catalyst is presented in Fig. 4. The silver nanoparticles identified on this picture exhibit a size lower than 5 nm. This size is in agreement with the XRD results. We can thus reasonably assume that the silver nanoparticles obtained with the onion method present a size lower than 5 nm.

### 3.2 Total oxidation of benzene

The VT, OAgT and OAgVT catalysts were tested at 250°C after in situ calcinations in air at 350°C or 450°C during one hour (Fig. 5). 450°C would have been chosen to ensure complete removal of the surfactant if one would not be aware of the effect of vanadia. From our TGA experiments, it appears that a treatment at 350°C is sufficient to remove completely the surfactant from the OAgVT catalyst. The performances of these catalysts are compared to the theoretical sum of the VT reference catalyst and the OAgT corresponding catalyst. It is important

to notice that the VT reference catalyst is slightly more active when treated at 450°C because it is presumably better oxidized. On the opposite, the OAgT catalysts were systematically less efficient after a calcination step at 450°C than at 350°C. These lower performances are certainly due to a higher sintering of the nanoparticles at 450 °C than at 350 °C [28].

The OAgTV catalysts are more active after a treatment at 350°C. Moreover, in this case, a synergy is observed for a silver loading from 0.125 to 0.5 wt. % while the extent of this synergy is significantly lower (or even absent) after a calcination at 450°C. The systematic absence of synergy for the OAgVT-1 catalyst was already observed for wet impregnated catalyst with an equivalent silver loading. This behaviour can be linked to the decrease of the specific surface. Indeed, the heat treatment applied to remove the organic molecules induced a decrease of the specific surface. However, the whole specific surface is certainly not recovered as it was the case for wet impregnated catalyst with similar silver loading [19, 21].

The doping effect of silver is thus significantly higher when the in situ calcination is done at a lower temperature. The doping effect of silver seems linked to the size of the silver nanoparticles if we assume that a higher calcination temperature induces a more marked sintering of these particles [27]. The extent of the synergy increases thus with a decrease of the nanoparticle size. This effect could be linked to the higher amount of silver atoms exposed to gas phase when the size decreases. This increase of the exposed atoms could result in a higher quantity of oxygen activated by silver and reoxidizing vanadium during the test.

## 4. Conclusion

An alternative method was used to deposit silver nanoparticles on a $VO_x/TiO_2$ catalyst. This synthesis method consists in the impregnation of organic 'onions'-looking vesicles containing the metallic silver nanoparticles. The addition of silver induces a higher proportion of $V^{5+}$. This parameter increases with the silver loading as it was already observed with co-impregnated catalysts and can be considered as a doping effect of silver. The presence of vanadium leads to an easier removal of the surfactant. This behaviour facilitates the access to the catalyst surface and to the silver nanoparticles.

The OAgVT catalysts exhibit better performances after moderate in situ calcination at 350 °C. A synergy between silver and vanadium is evidenced after calcination for OAgTV-0.125 and OAgVT-0.25 catalysts. The extent of this synergy is however higher after a moderate calcination. This effect is likely due to the fact that small nanoparticles prepared via the "onions" sinter less after in situ calcination at 350°C than at 450°C. This phenomenon allows developing optimally the synergy between silver and vanadium and clearly indicates the link between the extent of the synergy and the size of the silver nanoparticles: a decrease of the nanoparticle size induces a higher extent for the synergy.

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**Table 1**: Summary of the synthesized catalysts and their generic names.

| Name | First step | Second step |
|---|---|---|
| VT | $VO_x$ | - |
| OAgT | AgT | - |
| OAgVT | $VO_x$ | Ag |

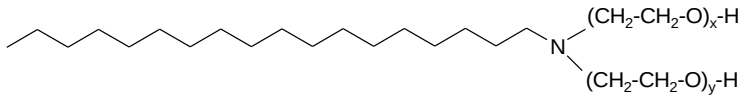
**Table 2:** Specific surface and Ag and V contents for the $Ag/TiO_2$ and the $Ag\text{-}VO_x/TiO_2$ catalysts prepared by wet impregnation.

| Sample | Specific surface ($m^2.g^{-1}$) | Ag loading (wt. %)* | V loading (wt. %)** |
|---|---|---|---|
| VT | 48.3 | - | 2.4 |
| OAgT-0.125 | 44.2 | 0.10 | - |
| OAgT-0.25 | 41.4 | 0.21 | - |
| OAgT-0.5 | 34.3 | 0.45 | - |
| OAgT-1 | 21.8 | 0.87 | - |
| OAgVT-0.125 | 38.2 | 0.09 | 2.4 |
| OAgVT-0.25 | 32.8 | 0.22 | 2.3 |
| OAgVT-0.5 | 24.9 | 0.43 | 2.2 |
| OAgVT-1 | 11.4 | 0.92 | 2.2 |

*determined by ICP; **determined by XRF

**Table 3:** Ag/Ti ratio and proportion of $V^{5+}$ for the $OAg/TiO_2$ and $OAg\text{-}VO_x/TiO_2$ catalysts.

| Sample | Ag/Ti | $V^{5+}$ proportion (%) |
|---|---|---|
| VT | - | 61 |
| OAgT-0.125 | 0.001 | - |
| OAgT-0.25 | 0.001 | - |
| OAgT-025-C | 0.004 | - |
| OAgT-0.5 | 0.003 | - |
| OAgT-1 | 0.005 | - |
| OAgVT-0.125 | 0.002 | 63 |
| OAgVT-0.25 | 0.006 | 74 |
| OAgVT-0.5 | 0.022 | 76 |
| OAgVT-1 | 0.031 | 81 |




**Scheme 1:** Chemical formula of the Genamin T020 surfactant (x+y = 2).

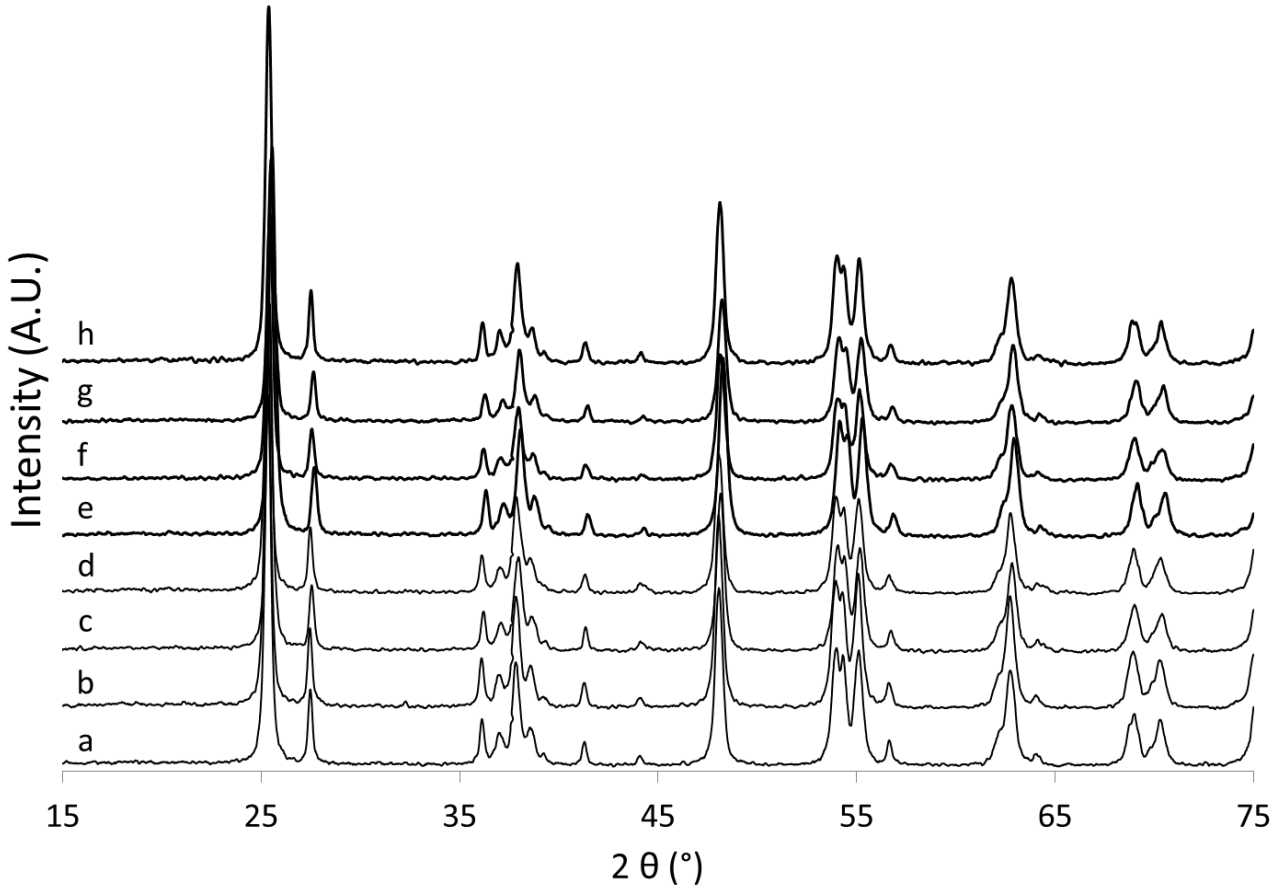



**Fig. 1:** XRD patterns for (a) OAgT-0.125, (b) OAgT-0.25, (c) OAgT-0.5, (d) OAgT-1, (e) OAgVT-0.125, (f) OAgVT-0.25, (g) OAgVT-0.5 and (h) OAgVT-1 catalysts prepared by the onion method.

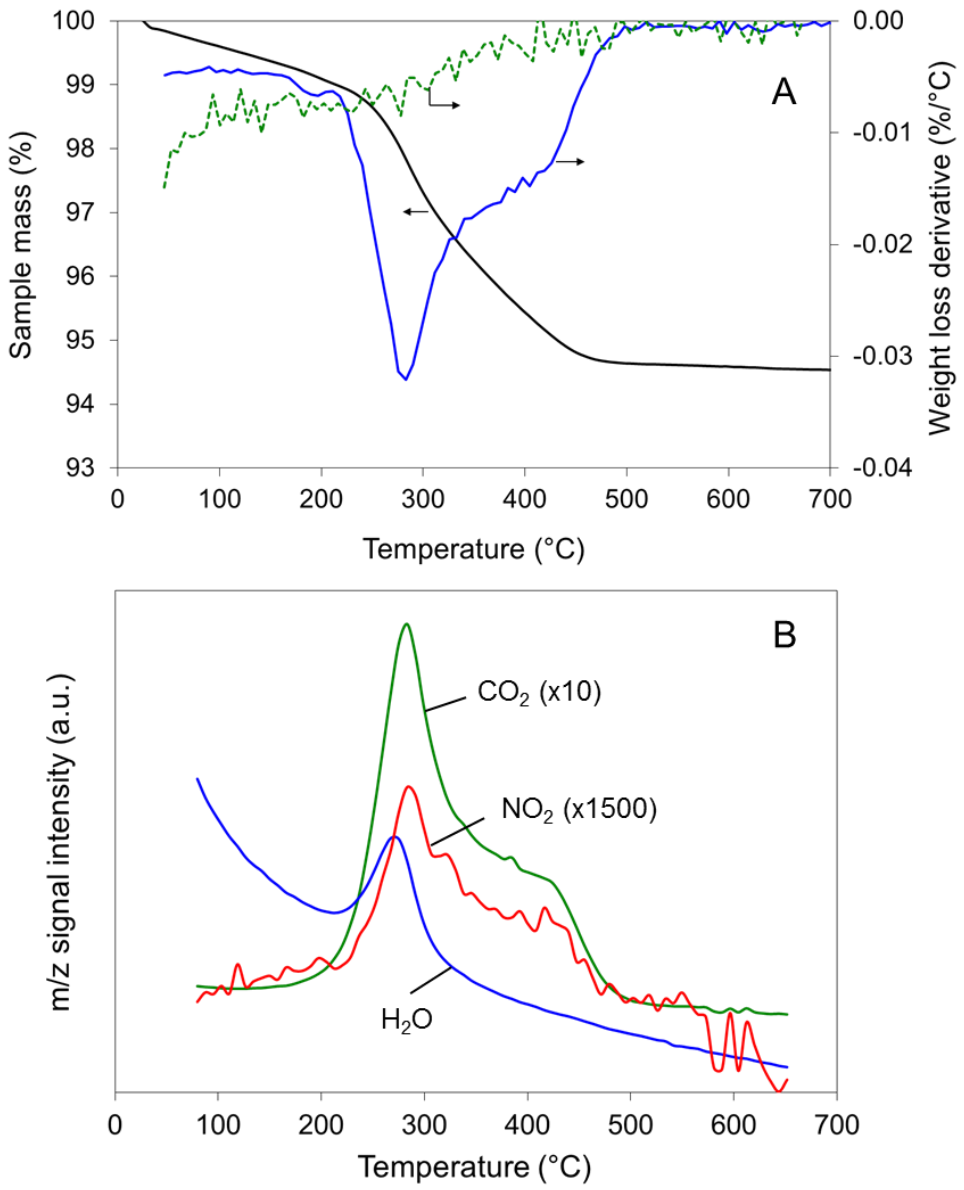



**Fig. 2**: TGA-MS experiments on OAgT-0.25. (A) Thermogravimetric analysis (TGA) and derivative TGA of the catalysts. Arrows indicate the ordinate axis. The dotted line is the derivative TGA obtained with $TiO_2$ or VT catalyst. (B) $CO_2$ (m/z = 44), $H_2O$ (m/z = 18) and $NO_2$ (m/z = 46) evolvement measured from Ag-promoted catalysts during TGA by online MS (signal magnification is indicated in brackets).

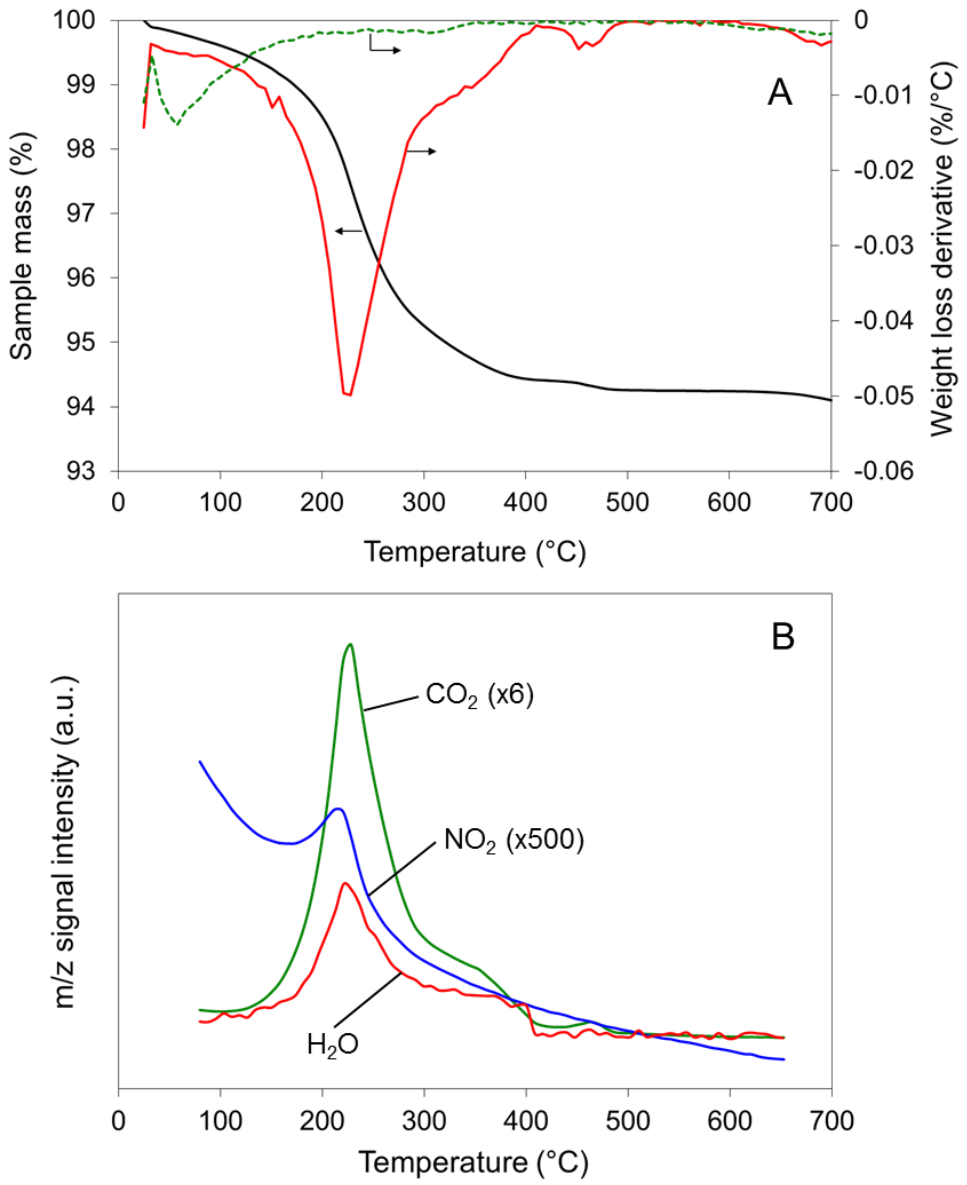



**Fig. 3**: TGA-MS experiments on OAgVT-0.25. (A) Thermogravimetric analysis (TGA) and derivative TGA of the catalysts. Arrows indicate the ordinate axis. The dotted line is the derivative TGA obtained with $TiO_2$ or VT catalyst. (B) $CO_2$ (m/z = 44), $H_2O$ (m/z = 18) and $NO_2$ (m/z = 46) evolvement measured from Ag-promoted catalysts during TGA by online MS (signal magnification is indicated in brackets).

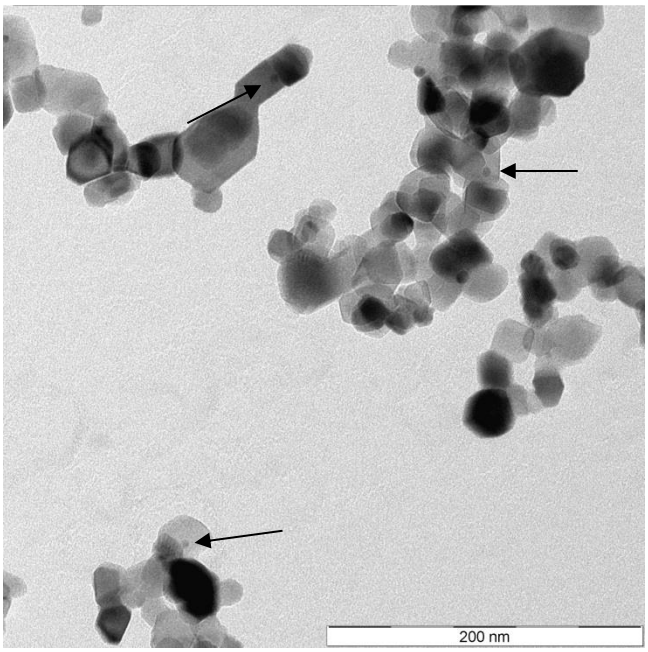



**Fig. 4:** TEM picture of an OAgVT-0.5 catalyst; the arrows indicate silver nanoparticles.

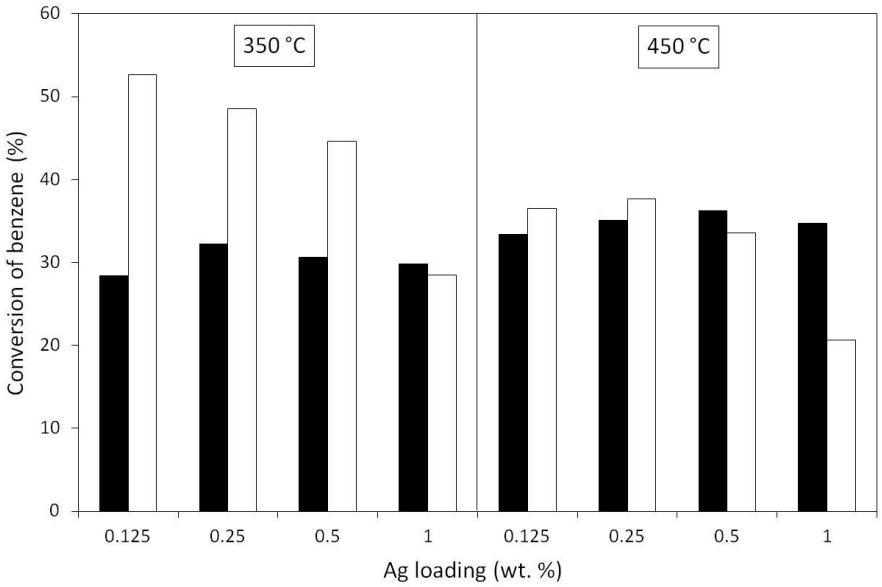



**Fig. 5:** Catalytic performances at 250 °C of VT + OAgT (expected) (■) and OAgVT (□) catalysts in the total oxidation of benzene.