

Preparation of a Monolith-Supported Au/TiO₂ Catalyst Active for CO Oxidation

François Moreau¹, Geoffrey C Bond^{1*}, Ronald Hughes¹, Jacob A Moulijn², Michiel Makkee², Kamasamudram Krishna², and Bozena Aejijelts Averink Silberova²

¹ Institute for Materials Research, University of Salford, Salford, Greater Manchester M5 4WT, UK

² DelftChem Tech, Catalysis Engineering, Faculty of Applied Sciences, Delft University of Technology, Julianlaan 136, NL 2628 BL, The Netherlands

* Corresponding author, e-mail address
Geoffrey10bond@aol.com

Abstract

The development of a method for making an adherent coating of Au/TiO₂ on a cordierite monolith is described. The optimum method entails first forming a wash-coat of TiO₂ by combining a colloidal dispersion of TiO₂ with Degussa P-25 TiO₂ that has been washed, dried and crushed. Subsequent deposition of gold from HAuCl₄ solution at pH 9 resulted in a catalyst that was less active for the oxidation of carbon monoxide than a similar preparation using only P-25, but reproducible values of T₅₀ of about 250 K were obtained.

Keywords

cordierite monolith, gold on titania, CO oxidation

Introduction

The discovery that supported gold catalysts can have high activity for the oxidation of CO has stimulated extensive research on them [1]. It is now evident that this activity is directly linked to two main factors: (i) small particle size, and (ii) the use as support of an oxide of a transition metal able to assist the reaction [2,3]. The most widely-used preparative method is the so-called deposition-precipitation, first employed by M. Haruta and his associates [4]; careful control of the pH especially during the final stages of the preparation has enabled the activity of Au/TiO₂ catalysts to be maximised [5].

The largest application of ceramic monoliths as catalyst supports is in the automotive industry, for the control of gaseous and particulate emissions from gasoline and diesel-fuelled engines; all automobiles are now fitted with either ceramic or metallic honeycomb-supported catalysts, which have now replaced packed-bed reactors [6]. The channels permeating the monolith allow high flow-rates with only a low pressure-drop. Cordierite (Al₃Mg₂Si₅AlO₁₈), selected because of its commercial availability, has a low thermal expansion coefficient, high mechanical strength and excellent thermal stability, and is therefore often used as a material for monoliths. Its main disadvantage is its low surface area (0.7 m²g⁻¹), but this can be increased by deposition of a 'wash coat' of a high-area oxide. Typically alumina is introduced inside the channels by a 'dip and drain' technique; the coated monolith is then calcined. The noble metals platinum and palladium, which are able to resist high temperature and are relatively sulfur tolerant, can be impregnated as their salts during a second stage or directly added in the washcoat to impart the necessary catalytic activity [7]. Gold catalysts, suitably prepared, have a much higher activity for CO oxidation than either palladium or platinum [4], and its ability to resist sulphur poisoning has been briefly discussed [1]. Gold could therefore be of potential interest for the control of gaseous emissions.

The preparation and testing of monolithic catalysts is of interest to many research groups [7-10]. Many different techniques for putting a wash-coat on the monolithic body have been used; for example, colloid, sol-gel, slurry and polymer coating [7]. Lee and Gavrilidis [11] have reported a high catalytic activity for Au/γ-Al₂O₃/cordierite monoliths for CO oxidation, although alumina is not generally recognised as being the first choice of support for gold catalysts [1]; their work will be considered further below.

The purpose of the present work was to develop a procedure for coating pieces of cordierite monolith with an Au/TiO₂ catalyst that would be active for the oxidation of CO. We previously listed some of the variables in the preparation of powder Au/TiO₂(P-25) catalysts, any of which could affect their performance in CO oxidation [5,12,13], and we reported in particular on the influence on pH control in determining the gold particle size and activity. Those different studies have been used in order to propose a suitable

method of preparation of Au/monolith catalyst active for CO oxidation.

Experimental Procedures, Preparation Methods, Results and Discussion

It is convenient to present the results obtained by each method used immediately after its description. The procedure for the catalytic testing is therefore described first; certain of the monolith preparations used a pre-formed Au/TiO₂ catalyst [5], the preparation of which is then outlined.

Oxidation of Carbon Monoxide

This was carried out in a plug-flow reactor, the gas flow (0.50 vol% CO) in synthetic air being introduced through a mass flow controller [5]. The standard test used a 55 cm³ min⁻¹ reactant flow and 50 mg of catalyst powder (space velocity 17,000 h⁻¹). Analysis was performed on-line by means of a Varian 3300 GC using a manual sampling valve, CTRI column (Alltech), TCD, and helium carrier gas. The experiments were carried out between 183-373 K, sub-ambient temperatures being achieved by mixing methanol with Cardice or liquid nitrogen; higher temperatures were obtained by heating the reactor in a furnace. CO conversion was measured as a function of temperature. Activity was first tested at room temperature after three hours, the reactor was then placed in a Dewar flask, and the temperature lowered, after which it was allowed to rise stepwise. Various pieces of treated monolith were tested under the same conditions (see Table 1); each piece was wrapped in Teflon tape to minimise gas flow between it and the reactor wall. The test used a 55 cm³ min⁻¹ reactant flow and 160 - 530 mg monolith pieces (space velocity 3,700 - 12,250 h⁻¹).

Preparation of 1% Au/TiO₂ (Degussa P-25) powder catalyst

Deposition-precipitation (DP) is a seemingly simple procedure of catalyst preparation, capable however of numerous variations, some of which have been described in the literature [1], but all too often the published accounts omit details that might be important or even critical. We have previously listed some of the variables in the preparation of Au/TiO₂(P-25) catalysts, any of which could affect their performance in CO oxidation [5,12,13], and have reported in particular on the influence on pH control in determining the gold particle size and activity with gold loadings of less than 2%. A procedure was formulated in which the optimum pH for high activity was shown to be ~9.

A reference powder catalyst was prepared by this method: the pH of an aqueous HAuCl₄ solution (10⁻⁴ M) was first raised to 10 using 0.1 M NaOH solution. TiO₂ (1g per 50ml solution, Degussa P-25, as received) was then added with stirring at room temperature; there was an immediate decrease in pH, which was then raised and held at 9 by further addition of 0.1 M NaOH as necessary. The resulting suspension was stirred for 1 hour at 343 K. After cooling it was filtered and the solid washed thoroughly and then vacuum-dried at

room temperature. The catalyst was not calcined. The actual gold content was determined by Atomic Absorption Spectroscopy [5].

Preparation of coated monoliths

The cordierite monolith pieces supplied by Corning were cylindrical, 4 cm long and 0.6 cm diameter; the wall thickness was ~0.16 mm, and the cell dimension corresponded to 62 cells cm⁻², (i.e. 400 cpsi). Each piece weighed about 0.5 g.

In order to ensure adherence of the catalyst or its support to the walls of the monolith's channels, a colloidal dispersion of the supporting oxide is commonly used as a binder [6]. A TiO₂ colloid was therefore first prepared by slowly adding 0.3 mole of Ti(O⁻C₃H₇)₄ to 1 l of distilled water at 343 K; the speed of addition was 1 ml min⁻¹. The alkoxide was hydrolysed by adding 0.15 mole of HNO₃ dropwise, and the hydrolysis was continued at 353 K for 16 h with vigorous stirring; the final pH of the suspension was 1.6.

Scanning electron microscopy

The surface morphology of the coated monoliths was studied using a Phillips XL20 Scanning Electron Microscope; the samples were first sputtered with a thin layer of gold to avoid charging.

First method

As it is important to limit the number of steps in a catalyst preparation, a procedure known as 'slurry coating' was first attempted using the pre-formed Au/TiO₂, to avoid having to carry out a further impregnation to introduce the metal. The Au/TiO₂ was added to the colloid, and as large particles of the catalyst were then present with the much smaller (x 10²) colloidal particles of TiO₂, the slurry was ball-milled (Fritsch type 00.001, model 523) to lower the size of the catalyst particles below 5 μm, so that they were comparable to the size of the larger macropores of the cordierite. They were therefore able to enter these pores, and therefore a stronger binding of the catalyst was obtained. The monolith was first dried at 393 K for 24 h, and after cooling it was placed in the slurry for 2 min; it was then withdrawn, shaken to remove the excess slurry and warm air was blown into the channels from sequentially altered directions to clear the channels further. It was then placed in an oven, the temperature of which was raised (0.2 K min⁻¹) to 393 K, where it remained for 24 h.

Despite the good quality of the coating, the monolith failed to exhibit any activity for CO oxidation below 423 K, the main reason being that the final pH of the preparation (1.5) was too low; previous work [12] has shown that at this pH previously formed gold particles can dissolve and be re-deposited as precursors to much larger particles.

Second method

In order to avoid this problem, the pH of the TiO₂ colloid was first raised to 9 by adding 0.1 M NaOH, but this caused it to coagulate; nevertheless the catalyst was added, and the

Table 1

Activity of Au/TiO₂ supported on cordierite monolith prepared by method 4 for oxidation of CO

Wt. Catalyst/g	Wt. Au/mg	T ₅₀ /K	r _{sp} ^a	E _a /kJ mol ⁻¹
0.53	1.8	265	0.1	25
0.50	2.75	255	0.35	22
0.16	1.1	259	0.4	35
0.30	2.1	245	0.4	35

^a In mol_{CO} s⁻¹ g_{Au}⁻¹ at 243 K

monolith dipped in the resulting slurry: no ball-milling was performed. There was some increase in catalytic activity, but the coagulation caused the coating to be thick and irregular. This method was deemed unsatisfactory.

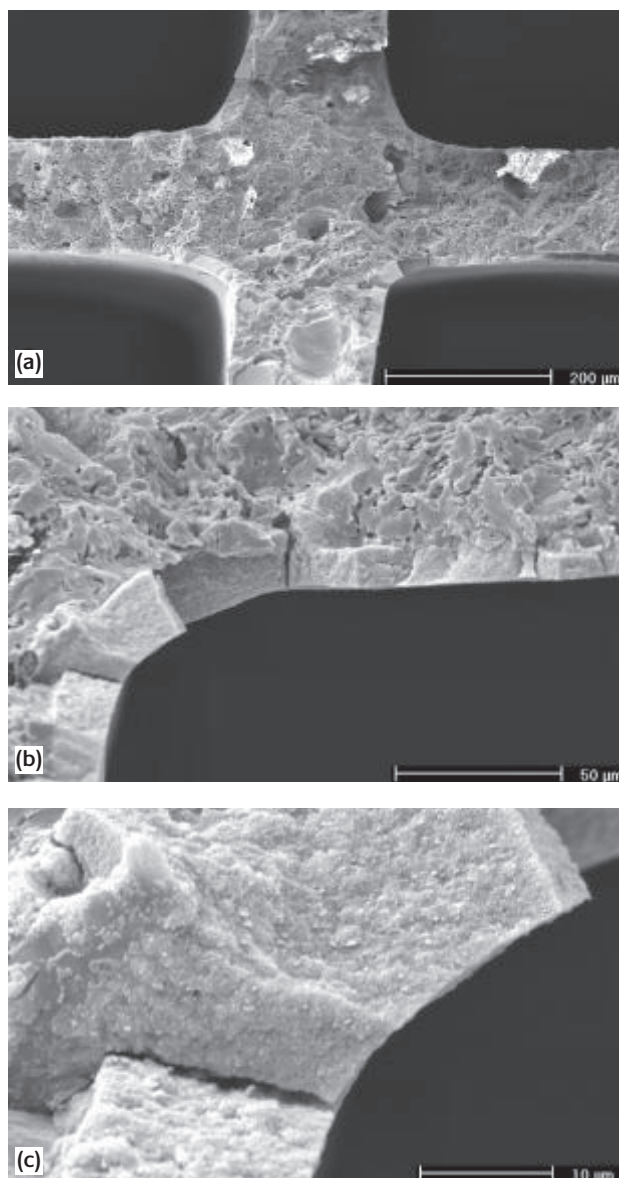
Third method

An attempt was then made to deposit a freshly prepared Au/TiO₂ catalyst onto the monolith without the assistance of the TiO₂ colloid. The catalyst powder was carefully milled and then mixed with deionised water; the slurry was ball-milled, and the pH raised to 9 by NaOH addition. The monolith was dipped into this, and processed as before. Although it showed activity for CO oxidation, visual inspection showed that the quality of the coating was not satisfactory, and a properly attached layer could not be obtained in the absence of the colloid.

Fourth method

It was then decided to resort to first forming a TiO₂ coating on the monolith, and then depositing gold on it from HAuCl₄ solution. In a first attempt the monolith was dipped into a slurry of P-25 TiO₂ (10 g) with the TiO₂ colloid (50 g) without ball-milling, but after processing it was seen that a very poor coating had been produced. It was then discovered that first washing, drying and crushing the P-25 before combining it with the colloid led to a good quality coating, on which the gold could then be deposited. 1g of TiO₂ P-25 was suspended in 50 ml deionised water and stirred for 1 h at 343 K; it was then filtered, washed thoroughly and vacuum-dried at 373 K. 10 g of the washed and dried TiO₂ was crushed before being added to 50 g of the TiO₂ colloid, and the suspension vigorously stirred; it was then used to coat the monolith by the method described above.

The coated monolith pieces were held in place in a beaker by means of plastic-coated wires that kept them along the wall at the bottom of the beaker, and then immersed in a solution of HAuCl₄ raised to pH 9 by NaOH. This solution was then agitated by a magnetic stirrer in order to ensure passage of the solution through the channels of the monolith, the direction of flow through the channels being changed periodically to obtain a better distribution of metal along their length. After draining, and drying at 373

**Figure 1**

Scanning electron micrographs of the Au/TiO₂ monolith catalysts prepared by the fourth method

K, the monolith was tested for CO oxidation, and a much higher activity was found. Four monolith pieces were prepared in an identical manner, and showed excellent reproducibility (see Table 1). A long-term test was performed at room temperature on one of the monoliths, and after a slight decrease in conversion during the first 25 h (0.15% conversion h⁻¹), the catalyst was quasi-stable during the following 50 h (Figure 2).

In order to see whether the activity shown by the monolith was affected by the process of forming the coating and by the way in which the gold was deposited, the material formed by drying the slurry of the washed P-25 plus the colloid was used as support in a conventional preparation. This was carried out by depositing a gold precursor at pH 9 and room temperature.

The gold content was only 0.34%, but the resulting catalytic activity (0.4 × 10⁻⁴ mol_{CO} s⁻¹ g_{Au}⁻¹ at 243 K) was the same as that shown by the best monolith pieces

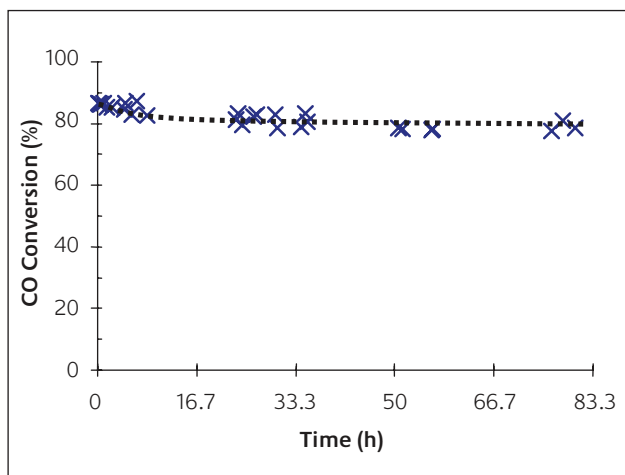


Figure 2

Long term stability test at room temperature on an Au/monolith sample; (190 mg catalyst, 55 ml min⁻¹ 0.5 vol. % CO (balance air))

(see Table 1); this was however somewhat smaller than that shown by a 0.5% Au/TiO₂ catalyst ($3.7 \times 10^{-4} \text{ mol}_{\text{CO}} \text{ s}^{-1} \text{ g}_{\text{Au}}^{-1}$ at 243 K). A possible reason for this is that some of the metal may have been encapsulated by the colloid during the preparation.

Examination of coated monoliths by SEM

Extensive examination of the products of each method of preparation was conducted by scanning electron microscopy (SEM), and the qualitative observations on the degree of success reported above are based on this technique. Using monoliths made by the fourth method, SEM images were obtained of the top of the monolith, on a cut about 5 mm below the top, and on a cut made at about the middle. Perpendicular views of the coated layer in inner and outer channels as well as cross-sections of the coating were taken. The presence of coating material inside the cordierite structure was also probed.

The monolith was seen to be almost homogeneously coated by TiO₂; the thickness of the layer varied slightly from channel to channel, and along the length of the channel. On the top and bottom the coated layer was slightly thicker than in the middle. The average thickness near the middle was about 20 μm in the corners of the channels, and about 10 μm along the walls, this causing the channels to become more circular in appearance. The coating consisted of particles of less than 1 μm in size. Figures 1 to 3 illustrate the quality of the coating as it existed 5 mm from the top of the piece.

Comparison with other work

Lee and Gavriilidis [11] have applied an aqueous solution of HAuCl₄ held at pH 9 for 4 h to a cordierite monolith already coated with γ-Al₂O₃; after hot-water washing and drying in air at 393 K, it was calcined at 573 K for 4 h. It weighed 1.5 g and its gold loading was 0.082%; using 1% CO and a total flow of 50 ml min⁻¹ at 297 K, the conversion after 150 min was ~85%. This corresponds to a rate of about

$0.1 \text{ mol}_{\text{CO}} \text{ s}^{-1} \text{ g}_{\text{Au}}^{-1}$, but quantitative comparison with our activities is impossible due to the large difference in temperature.

Conclusions

Construction of a coherent uniform wash-coat of TiO₂ on cordierite monolith appears to depend critically on the use of a TiO₂ colloidal binder, and on prior washing of the P-25 before its admixture with the colloid. It is unclear what the physical consequences of the washing, drying and crushing the P-25 are; this will require further work.

The specific activity of the Au/TiO₂ on the monolith, and of the powder form of the catalyst containing the colloid, was somewhat less active than a typical 1% Au/TiO₂ catalyst, but optimisation of the parameters of the preparation should enable this difference to be removed.

About the corresponding author



Geoffrey Bond held academic posts at the Universities of Leeds and Hull before joining Johnson Matthey plc as Head of Catalysis Research in 1962. In 1970 he was appointed Professor of Applied Chemistry at Brunel University; he retired in 1992 and is now Emeritus Professor.

Acknowledgement

We gratefully acknowledge financial support from the European Commission's FP5 programme through the AURICAT Training Network HPRN-CT-2002-00174.

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