RESEARCH NOTE

One-Step Flame Synthesis of an Active Pt/TiO₂ Catalyst for SO₂ Oxidation—A Possible Alternative to Traditional Methods for Parallel Screening

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Flame synthesis as a route for production of composite metal oxides has been employed for the one-step synthesis of a supported noble metal catalyst, i.e., a Pt/TiO₂ catalyst, by simultaneous combustion of Ti-isopropoxide and platinum acetylacetonate in a quench-cooled flame reactor. The average size of the platinum particles supported on aggregated nanoparticles of TiO₂ is approximately 2 nm. The high SO₂ oxidation activity of the catalyst proves that platinum is not "hidden" in the titania matrix. The flame-produced catalyst showed catalytic activity similar to that of samples prepared by wet platinum impregnation of pure titania. ©️ 2002 Elsevier Science

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INTRODUCTION

Flame synthesis of materials is widely used in the production of materials such as carbon black, fumed silica, and TiO₂ (1, 2). In recent years, research efforts have been more focused on the synthesis of multicomponent materials in the flames (3, 4). In a few cases only, catalytic materials were prepared using the gas-phase flame aerosol method. The latest example is the work of Stark *et al*. (5), who produced V₂O₅/TiO₂ composite particles in a flame reactor, which were shown to have excellent catalytic properties and selectivity for the catalytic reduction of NO with NH₃. Previous work by Katz and Miquel (3) also produced the same composite material in a counter-diffusion flame, but did not report catalytic activity measurements.

In general, the flame synthesis method is suitable for producing composite materials. Using this method, Jensen *et al*. (4) produced a high-surface-area ZnAl₂O₄ spinel by introducing volatile Zn and Al precursors (acetylacetonate compounds) into a premixed flame zone followed by rapid

quench-cooling. The intimate mixing of the precursors on the molecular level in the gas phase prior to the formation of the metal–oxide "monomers" enables the formation of a high-surface-area spinel phase within a few milliseconds of residence time in the high-temperature zone. The traditional wet synthesis methods are limited by the calcination step, which is necessary to transform the precipitated material to the mixed oxide spinel phase, and normally this step is followed by a loss of surface area. Jensen (6) applied the premixed flame to produce the ternary mixture of CuO/ZnO/Al₂O₃ as an alternative method for production of the methanol synthesis catalyst.

Here, we have extended the flame synthesis route to one-step synthesis of a supported noble metal catalyst, i.e., a Pt/TiO₂ catalyst. The flame reactor, with optional quench-cooling, was developed in earlier work (7) and it has proved very efficient for controlled synthesis of nanoparticles by combustion of volatile metal precursors. For the present study, we added a unit for delivering a titanium precursor. The catalyst is characterized for BET surface area (N₂ adsorption), by transmission electron microscope (TEM) images, and the catalytic activity for the oxidation of SO₂ is measured. The flame-produced catalyst is compared to two other catalysts prepared by wet impregnation of (i) pure flame-produced TiO₂ and (ii) commercial G5-TiO₂ titania (Millennium, type TIONA-G5, 340 m²/g). The main goal is to extend the flame synthesis route to the synthesis of supported noble metals and to show that active samples can be prepared.

EXPERIMENTAL

The principle of the flame synthesis setup is shown in Fig. 1. The burner is identical to that developed by Hansen *et al*. (7) and Johannessen (8). There is a circular (4 cm in diameter) premixed flame zone (methane and air) with a central jet for the injection of the metal precursors with

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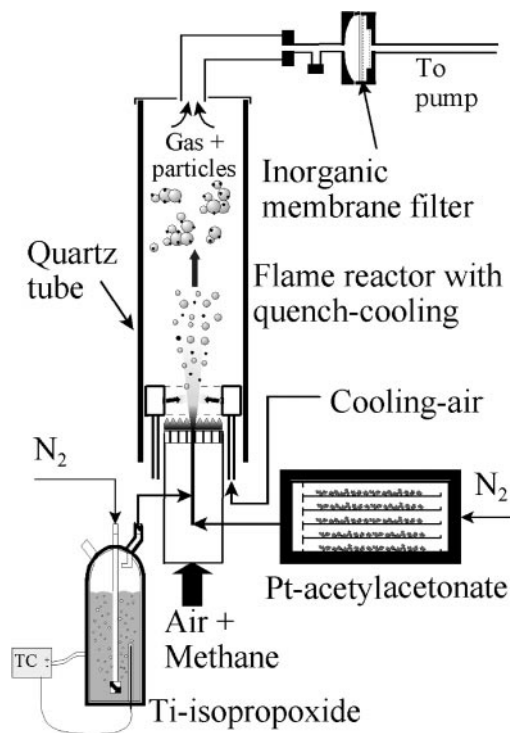[1] To whom correspondence should be addressed. E-mail: tj@kt.dtu.dk.

FIG. 1. An outline of the flame synthesis equipment consisting of flow controllers (not shown), saturators for the liquid Ti-isopropoxide and the solid Pt-acetylacetonate, a burner, a quench-cooling unit, and a filter unit. Metal precursors are fed to the premixed flame in a central jet.

nitrogen as carrier gas. Precursors of liquid Ti-isopropoxide and solid Pt-acetylacetonate are delivered from a thermostated bubble bottle and a sublimation unit, respectively. The sublimator is the design of Jensen *et al*. (4). A well-defined quench-cooling of the flame is obtained by a special arrangement of the nozzles, i.e., an upward and tangential direction, which stabilizes the flow pattern (7). This creates a flame zone with a short residence time at high temperature and an otherwise slowly cooling flame when quenching is not applied (Table 1). Feed gases are delivered from pressure bottles through calibrated rotameters. Product particles are collected on filters.

The specific surface area of the several titania samples was determined by nitrogen adsorption using the triple-point BET adsorption isotherm (9). All samples were outgassed overnight at $120°C$. The composition of the catalyst

was determined by chemical analysis (atomic absorption spectrophotometric method).

For the catalytic activity tests, the conversion of SO_2 was measured in a fixed-bed reactor system operated over a temperature range between 250 and $700°C$ at atmospheric pressure. The catalyst was fixed in a small U-shaped Pyrex-glass tube between two plugs of quartz wool and inserted into a furnace. All tests were performed with a feed gas flow of 30 ml/min (measured at 298 K, 1 atm) using a gas flow controller (Brooks, 5810). The inlet concentration was 10% O_2 and 11% SO_2 balanced with N_2. To keep conversions below 60%, the catalyst loading was 0.5 mg in all cases. The weighing procedure consisted of (i) drying the sample in an oven, (ii) weighing the empty reactor, (iii) loading the reactor with the sample from a desiccator, (iv) weighing the loaded reactor until the desired catalyst mass was reached, (v) heating the loaded reactor in an oven at $150°C$, and (vi) repeated measuring of the weight until constancy in weight was reached.

The concentration of SO_2 was monitored by a spectrophotometer by the UV absorption peak at 300.4 nm. The SO_2 conversion, which was kept under 60%, was determined from the depletion in the gas mixture before and after it passed the reactor. All gases, before and after the reactor, were dried through P_2O_5 columns. When the conversion was higher than 40%, condensation was observed in the outlet. After a 1-h stabilization of the catalytic performance at each temperature, the outlet was connected to a P_2O_5 filter, after which the gas was cleaned with condensed liquid oleum. This was verified by the clean cuvette after the completion of each series of measurements. The filter was changed after each measurement.

RESULTS AND DISCUSSION

The Flame Reactor

Particle nuclei are formed by thermal decomposition and oxidation of the metal precursors. Real particles are then formed by nucleation and grown by the continuous enlargement of mass per particle due to the coagulation of particles. Coalescence of crystallites, or primary particle growth, results in larger particles. The particle formation process can be "interrupted" by quench-cooling the product gases after a short residence time in the flame. As a result, one can

TABLE 1

Flame Operating Conditions[a]

	Methane	Air	Q-flow	Ti saturator	Quench height
With quench	0.62 L/min	9.8 L/min	9 L/min	70 (low) or 80 (high) °C	1.5 cm
No quench	0.62 L/min	9.8 L/min	—	70 (low) or 85 (high) °C	—

[a] All flow rates are measured at 298 K, 1 atm.

maintain a certain level of specific surface area by freezing the sintering of collide primary particles. From that point, additional collisions will merely result in larger agglomerates of primary particles. Figure 2 shows the flame reactor in operation, with and without quench-cooling, for the synthesis of pure TiO_2. Decomposition of the precursor takes place immediately above the central jet. Subsequently, the formation of TiO_2 particles is evident from the white plume of particles rising from the center of the reactor. The effect of quench-cooling can be seen from the breakup, i.e., dilution and cooling, of the particle jet. Previous measurements on this flame reactor (7) showed a rapid drop of more than 400°C at the level of quench-cooling. The freezing of the coalescence process is the primary tuning parameter for obtaining a higher specific surface area of the TiO_2 particles.

Computer simulation studies on the particle formation process were performed by combining computational fluid dynamics (CFD) with models for particle dynamics. The CFD simulations were carried out similarly to the work presented in (7, 10, 11). The two small inserted contour plots in Fig. 2 show the simulated particle mass fractions of the two flame configurations. The breakup pattern is accurately captured by the three-dimensional simulation of the upward, swirling flow of cooling air. This is a valuable tool in the design phase of such a flame reactor.

TABLE 2

Specific Surface Area (BET) Measurements of Pure TiO_2 Produced under Different Operating Conditions

Ti-saturator temperature (°C)	No quench (m^2/g)	With quench (m^2/g)
70	38	95
85	29	94

Specific Surface Area of TiO_2

Table 2 summarizes the specific surface area measurements under different operating conditions. Two different levels of production rates of the support, TiO_2, were applied by setting the temperature of the Ti-isopropoxide bubble bottle to 70 and 85°C, respectively. Without quench-cooling, powders with a surface area in the range of 30–40 m^2/g were produced. When quench-cooling was applied, the surface area increased to approximately 100 m^2/g for both saturator temperatures, i.e., high and low production rate.

Catalyst Production

The quenched flame with the highest production rate of TiO_2 (85°C) was chosen for the synthesis of the Pt/TiO_2 catalyst. The determination of the sublimation pressure of
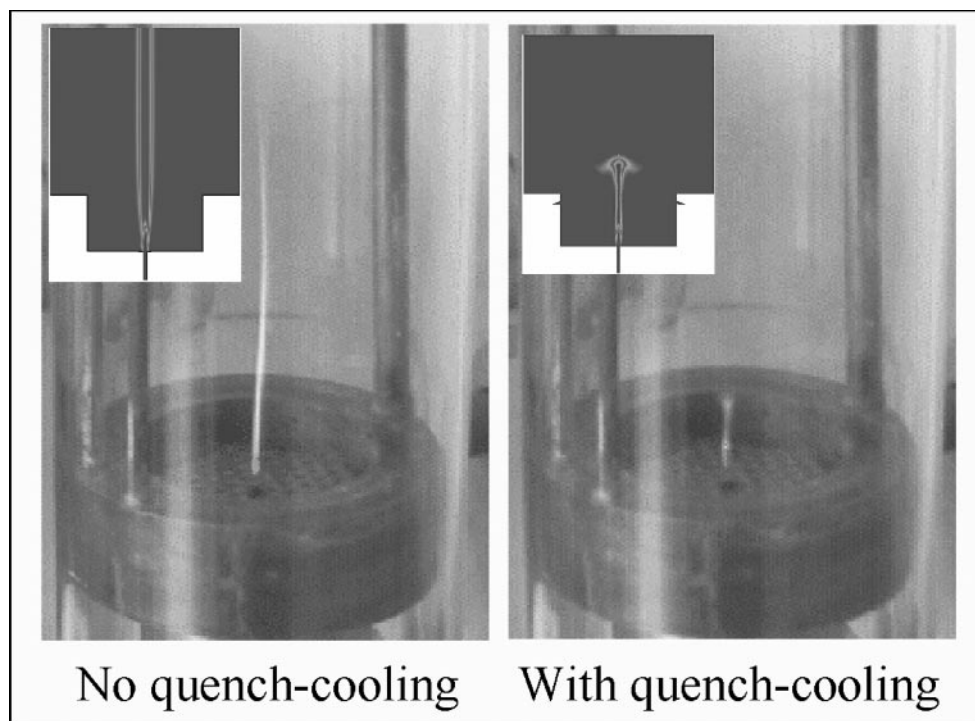

FIG. 2. Photographs of the burner during particle production (without/with quench-cooling). Quench-cooling results in a well-defined (and short) residence time at elevated temperature, after which the particle jet is broken up, cooled, and diluted. TiO_2 particles can be seen as white plumes. The insets show simulated (CFD) contours of the particle mass fraction.

Pt(acac)$_2$, i.e., calibration by measuring weight loss, was difficult due to that of the low loading of the expensive Pt(acac)$_2$ compound in the sublimator unit. Using 190°C as the sublimation temperature resulted in Pt loading, which was comparable to that of the wet-impregnated samples. The low content of platinum in the powder did not affect the overall specific surface area of the TiO$_2$ support, which in the resulting catalyst was approximately 100 m^2/g.

For comparison to a traditional method, impregnation of flame-produced pure TiO$_2$ and a so-called G5-TiO$_2$ was carried out with a platinum acetylacetonate solution. The platinum loading on the final product was 2 wt%, the same as that in the flame-impregnated sample.

Transmission Electron Microscope Images

The morphology of the catalyst was studied in a Phillips 300-kV TEM. Two different magnifications of the Pt/TiO$_2$ catalyst are shown in Fig. 3. The low magnification reveals the dendritic, open structure of the agglomerated primary particles of TiO$_2$. At high magnification, one can directly observe platinum particles nicely dispersed as small particles (average 2 nm; some indicated by arrows) on the entire TiO$_2$ particle network. In transmission images, it is difficult
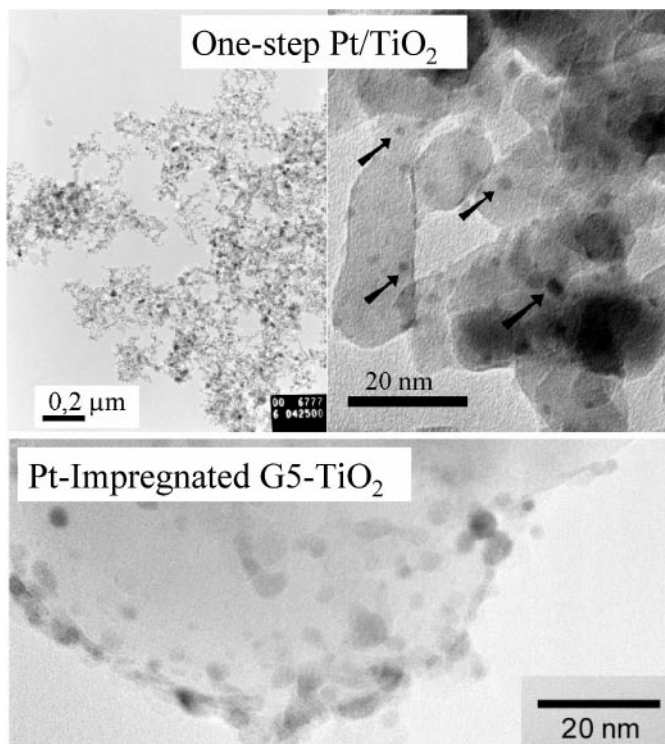

FIG. 4. SO$_2$ oxidation activity measurements of three different catalysts: (a) Pt-impregnated flame-produced TiO$_2$ (100 m^2/g), (b) Pt-impregnated G5-TiO$_2$ (340 m^2/g), and (c) Pt/TiO$_2$ (100 m^2/g) from one-step flame synthesis.

to distinguish between embedded particles and particles located on the TiO$_2$ surface. However, as derived from the activity measurements, the platinum is indeed exposed to the gas phase. Large, dark areas on the TEM image are due to multiple layers or Bragg orientation of TiO$_2$ particles. For comparison, a TEM image of the impregnated G5-TiO$_2$ is shown at the bottom of Fig. 3.

SO$_2$ Oxidation Activity

The activities of the three catalyst samples shown in Fig. 4 are identified as follows: (i) wet impregnation of flame-produced TiO$_2$ (100 m^2/g), (ii) wet impregnation of a commercial G5-TiO$_2$ powder (340 m^2/g), and (iii) one-step flame synthesis of Pt/TiO$_2$ (100 m^2/g).

The graph shows the catalyst activity based on the total amount of platinum in the catalyst as a function of the temperature. All three catalysts have a maximum in activity close to 525°C. The most interesting aspect of the results is that the one-step prepared sample is just as active as either the impregnated pure flame-produced TiO$_2$ powder or the impregnated G5-titania. The nice distribution of platinum on the titania support can be explained qualitatively by aerosol dynamics. Platinum oxides have a low melting point and a tendency to decompose at low temperature; e.g., PtO decomposes at 550°C (10). Since titania is a much more stable material, the following steps outline the formation process.

1. Ti and Pt precursors decompose shortly after entering the jet in the flame environment.

2. The more stable TiO$_2$ forms nuclei, which grow to give TiO$_2$ particles by collision and coalescence.

3. At lower temperature downstream (higher) in the flame, the onset of nucleation results in the formation of

FIG. 3. Upper part: TEM images of the one-step prepared Pt/TiO$_2$ catalyst. Top left: Low magnification of the dendritic aggregate structure of the TiO$_2$ support. Top right: Close-up of the highly dispersed Pt particles, which are distributed homogeneously on the TiO$_2$ aggregates (some Pt particles indicated by arrows). Lower part: TEM image of Pt-impregnated G5-TiO$_2$.
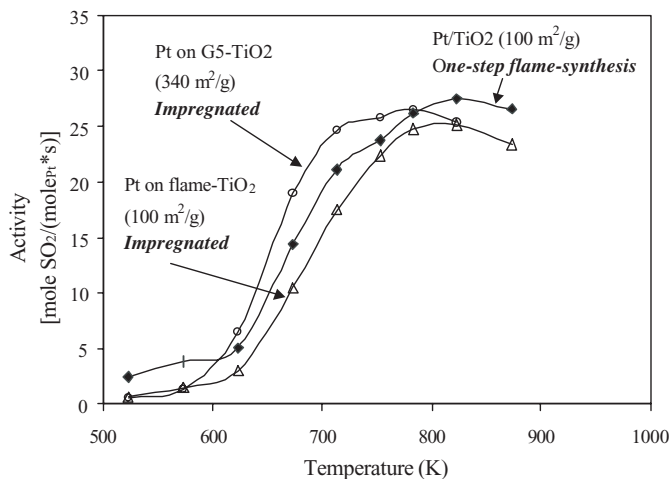
platinum metal particles after decomposition of the respective oxide. These may start to nucleate as separate particles or condensate on the surface of existing TiO_2 particles. The latter process, i.e., heterogeneous nucleation, is thermodynamically favored over the homogeneous nucleation of the individual platinum particles. This is also known as consecutive nucleation, as explained in Jensen *et al*. (4) This also sets the limit of the flame process: the second phase condenses on the support phase only if the support phase is more thermally stable. However, in many heterogeneous catalysts, the support material is more stable and inert e.g., titania, alumina, zirconia. Therefore, the flame method presented here can be extended to a large range of catalytic systems.

CONCLUSIONS

We have presented the first results of a synthesis route by which one can produce active supported noble metal catalysts in one step. TEM images revealed that the noble metal, platinum, was dispersed in small particles (approximately 2 nm) on larger, dendritic aggregates of the titania support. In addition, SO_2 oxidation measurements showed that the one-step sample was just as active as the Pt-impregnated flame-produced TiO_2 under otherwise identical flame synthesis conditions. Comparison to the Pt impregnation of G5-TiO_2 (340 m^2/h) revealed that the one-step catalyst was just as active.

In summary, we have shown that active catalysts can be produced in flame processes. We do not claim that more active catalysts are produced by the flame technique than by conventional methods. However, the catalyst can be produced in one step, and in this manner, by modification of traditional industrial flame-produced TiO_2 production units, production on a large scale would be, in principle, easier.

In addition, the future prospect of this method on a laboratory scale is a setup with an array of precursor delivery units for the production of small amounts of new materials with large variations in composition. By such a screening method, promising candidates can be tested for activity and characterized by, e.g., TEM and various spectroscopic methods. This would be advantageous in a screening process as opposed to parallel screening setups with evaporation of various metals on small spots, where postreaction analysis is difficult.

The ongoing research will focus on the possibilities for catalyst screening and on the optimization of flame operating conditions for enhancing the properties for the catalyst.

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