

An Electrodeposited Copper Zeolite Catalyst for the Removal of the Pollutant, Nitric Oxide, from Combustion Gases

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A novel catalyst containing copper zeolite has been prepared by electrodeposition techniques and tested for its ability to remove nitric oxide, the pollutant produced in combustion gases. The catalyst was prepared on a copper substrate by codepositing inert zeolite particles into a copper matrix. The effect of pH, current density, temperature, and zeolite concentration on the surface coverage of zeolite on the copper has been investigated. The final copper zeolite catalyst was then tested for its ability to decompose nitric oxide to its constituents, nitrogen and oxygen, in the temperature range 300 to 800°C (572 to 1472°F).

Nitrogen oxides (NO and NO₂) are present in small concentrations in the exhaust gases of internal combustion engines, furnaces and other combustion equipment. These oxides cause a wide range of environmental problems, such as the formation of acid rain. They are also regarded as being damaging to human health.¹ As a result, legislation on emissions of nitrogen oxides is becoming increasingly more stringent. One method of reducing nitric oxide involves reduction reactions with hydrocarbons and carbon monoxide in the exhaust gases.² An alternative and preferred method is by the catalytic decomposition of nitric oxide to nitrogen and oxygen.³

Although nitric oxide is thermodynamically unstable, the decomposition reaction is inhibited by a high activation energy of 364 kJ/mol (86.9 kcal/mol). However, zeolites such as CuZSM5 and HZSM5 are both known to be effective for both reduction and decomposition of nitric oxide.⁴ This is because of the high total surface area and the well-defined pore system of zeolites, which have been used in pellet or bead form. However, the use of pellets or beads is usually associated with a high pressure drop, which, in the case of internal combustion engines, can cause a loss of power and an increase in fuel consumption.

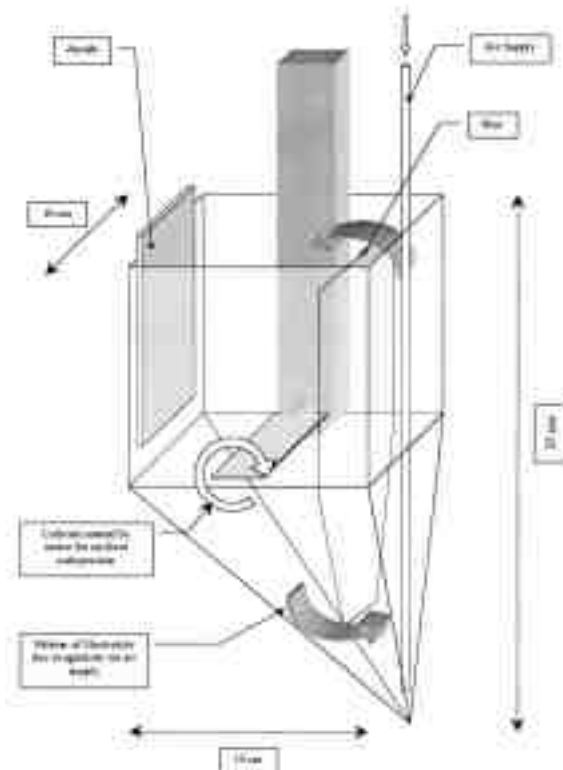


Fig. 1—Electroplating bath used for the preparation of codeposited catalysts.



Fig. 2—Section of codeposited catalyst.

Nuts & Bolts: What This Paper Means to You

This paper deals with an application rather than a process. The search continues for an effective automotive catalyst from handling nitric oxides. Using the old principles of codepositing particles with metals, the authors have developed a catalyst by coplating zeolite particles, with plenty of surface area, in copper. They studied how well the zeolite goes into the deposit by varying current density, temperature and particle zeolite concentration. Then they determined whether it worked or not. (It did, at the lower temperatures of 570 to 750°F.)

To overcome this problem, it was decided to examine the use of a codeposited catalyst on a metallic substrate. This type of catalyst should combine the benefits of a low pressure drop with a high specific catalytic activity. Previous work by motor manufacturers⁵ has shown that a lower pressure drop can be achieved with a metallic catalyst supporting noble metals than with a conventional type catalyst. Also, it is known that zeolites can be grown *in situ* on a wire gauze and have a high catalytic activity toward nitric oxide decomposition.⁶ For these reasons, it was decided to examine the factors that influence the preparation of a codeposited catalyst, and to test the catalyst in

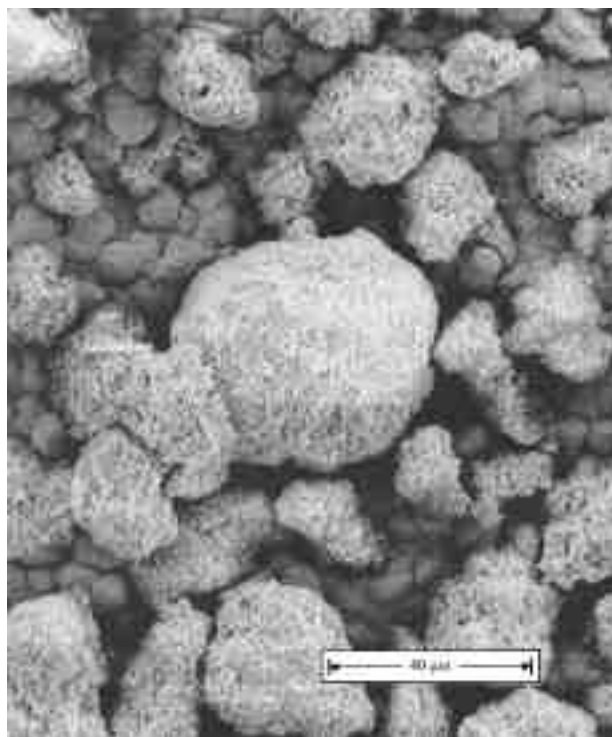


Fig. 3—Electron microscope image of the codeposited copper zeolite.

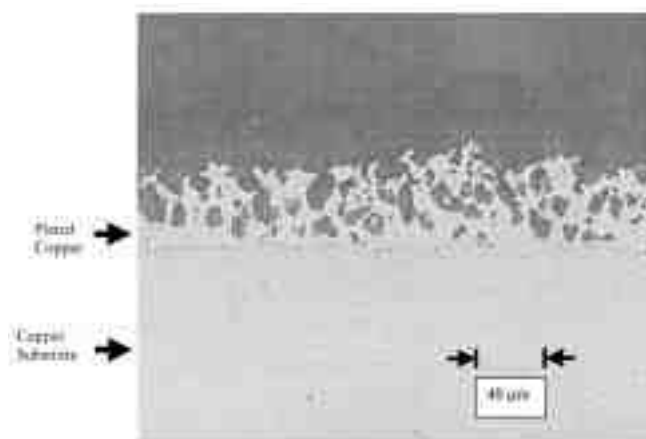


Fig. 4—Photomicrograph of the codeposited copper zeolite catalyst.

an atmosphere of nitric oxide at selected temperatures. For comparison, a pure copper catalyst was also tested.

Experimental Procedure

Preparation of the Zeolite Powder

The copper zeolite that was required for codeposition was prepared from sodium zeolite powder, NaZSM5 using the following procedure.⁷ The particles were first washed in distilled water, filtered and dried at 110°C (230°F). They were then immersed in 0.01M copper acetate solution to ion exchange the sodium for copper. To ensure full completion of the ion exchange process, the particles were stirred and left for 24 hours. After this time, the zeolite particles were filtered, dried and, after being weighed, were transferred to the plating bath. The zeolite had a general formula $\text{Cu}(\text{AlO}_2)_x(\text{SiO}_2)_y \cdot z\text{H}_2\text{O}$ with a Si/Al ratio of 20. In the plating bath, copper sulphate solution at a concentration of 200 g/L (26.7 oz/gal) had previously been prepared.

Table 1
Effect of pH on Particle Coverage

pH of Electroplating Bath	Surface Covered by Zeolite Particles
2.0	4%
2.5	6%
3.0	59%
3.5	59%

Table 2
Effect of Catalyst in Reducing Nitric Oxide

Catalyst Temperature, °C	%Reduction of Nitric Oxide (by volume)	
	Copper Zeolite	Copper
300	95%	
400	77%	0%
500	16%	15%
600	27%	17%
700		37%
800		61%

Details of the Plating Bath

The electroplating bath used for the preparation of codeposited catalysts is shown in Fig. 1. It was designed to enable the insoluble zeolite to be kept in suspension in the plating solution by agitation. This was achieved by flowing air at a rate of 1.0 L/min (0.035 ft³/min) through a 3-mm internal diameter stainless steel pipe submerged in the plating solution. The position of the pipe and the weir enabled the particles of zeolite to pass vertically up and over the top of the weir, as shown in Fig. 1. The metallic substrate to be coated was positioned to one side of the weir where the particles flowed vertically downwards. Previous studies using flow-visualization techniques enabled the optimum position of the weir to be found for different particle sizes in the bath.

Rotation of the substrate was possible using a 12V permanent magnet DC motor positioned above the bath. Pieces of copper foil substrate of dimensions 2 cm x 6 cm x 0.1 mm (thick) (~0.8 in. x ~2.4 in. x ~4 mils) were held in a rotating fixture and submerged in the plating solution. During electroplating, the copper foil was rotated at a speed of 6 RPM. The temperature of the plating solution could be adjusted using a mineral-insulated stainless steel sheathed heater with PID control. The pH of the solution was measured before and after each test using a glass pH sensor. Current to the electrodes was provided by a stabilized voltage supply, and constant current was applied in all tests.

Details of the Catalyst

The copper zeolite was codeposited onto copper foil strips described above. The substrates were pretreated by first scrubbing with α -alumina particles and then rinsing with distilled water. The copper foil was placed in 10 percent nitric acid for one minute, rinsed with distilled water again and transferred to the electroplating bath. After plating, the strips were taken out of the bath, rinsed with distilled water and dried in an oven. A total of four strips were codeposited and half of these were crimped, as shown in Fig. 2. The catalyst strips that were crimped showed no apparent spalling of the deposit from the substrate. These catalyst strips were then

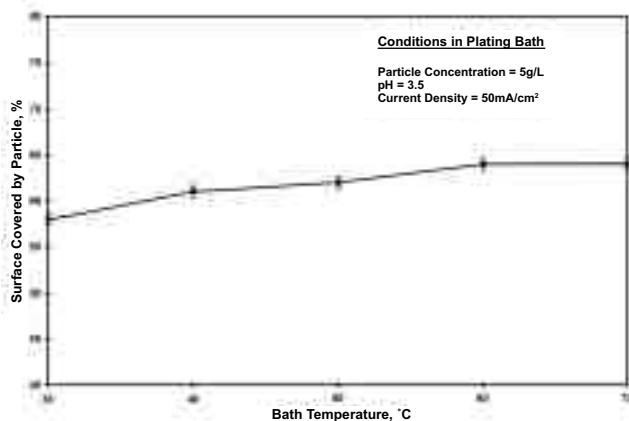


Fig. 5—Effect of plating bath temperature on particle coverage.

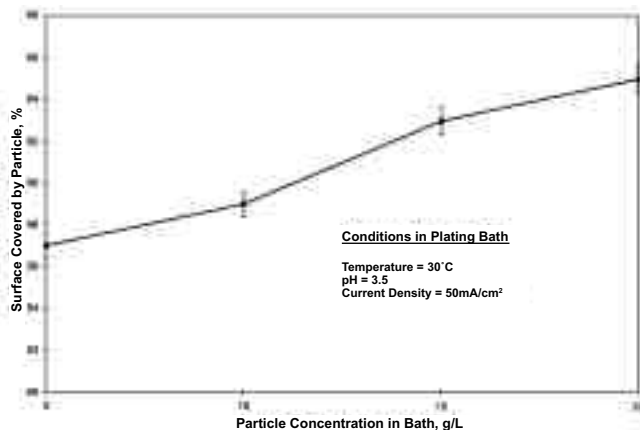


Fig. 6—Effect of particle concentration on particle coverage.

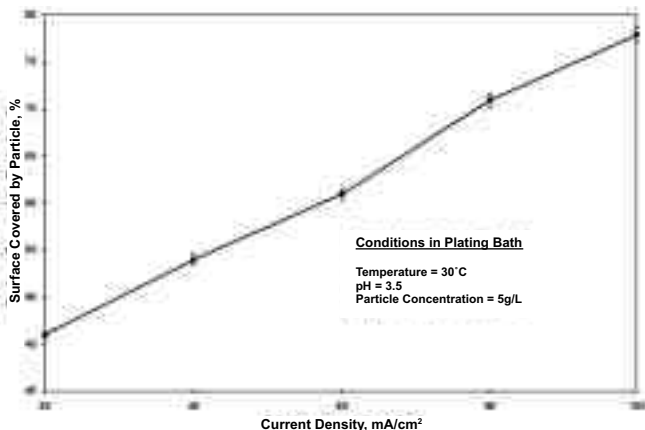


Fig. 7—Effect of current density on particle coverage.

packed into the catalyst holder of dimensions 0.5 cm x 1 cm x 4 cm (~0.2 in. x ~0.4 in. x ~1.6 in.). Finally, the assembly was either heat treated in oxygen-free nitrogen or transferred directly to the furnace for final testing. The copper catalyst used for comparison purposes had the same dimensions as the codeposited zeolite catalyst, and was pretreated by an identical procedure.

The amount of zeolite on the surface of the catalyst was estimated from the percentage surface coverage using an optical research microscope, with a color video camera attached to a PC for image capture. The image was then analyzed using image analysis software. In this method, the captured image of the surface was converted to two colors representing the plated copper as one color (e.g., grey) and the zeolite particles as the other color (e.g., yellow). The image analysis software then calculated the percentage of

the surface covered by the zeolite particles. Three images of the same surface were examined and the results averaged. These results varied by $\pm 1\%$. Although the results were compared to standard gravimetric analysis, it was difficult to obtain consistent readings with gravimetric analysis because the coatings were quite thin.

A scanning electron microscope image of the codeposited catalyst is shown in Fig. 3. This shows the larger particles of copper zeolite surrounded by nodular copper that had been plated from solution. As can be seen from the figure, it appears that the copper zeolite was exposed at the surface and not plated over with copper.

The coatings of several samples were examined in cross section by mounting the sample in Bakelite®. A photomicrograph of one of these samples is shown in Fig. 4. Grinding the surface of the sample before microscopic examination removed the zeolite particles, but the photomicrograph shows where the zeolite particles resided, surrounded by plated copper. The volume-percent incorporated in this example is approximately 50 percent, and the mean diameter of the particles approximately 30 μm (1.18 mils).

As can be seen, the thickness of the coating in this example was quite thin (about 50 μm ; 2 mils), because the duration of plating was quite short. However, tests were not carried out to examine whether the percentage of the particle surface coverage changed with film thickness or duration of the plating time.

The Furnace & Nitric Oxide Measurement System

The furnace used to heat the catalyst was a radiant tube electric furnace. A gas mixture with a composition of nitrogen with 50 ppm of nitric oxide was passed over the catalyst assembly at a flow rate of 40 cm^3/min (2.44 $\text{in.}^3/\text{min}$). The concentration at the inlet and the outlet of the catalyst holder was monitored using a portable gas analyzer.

Results & Discussion

The two main areas investigated were: (1) the conditions in the plating bath that affected the preparation of the catalyst, and (2) the effectiveness of the catalyst for the reduction of nitric oxide.

The Effect of Plating Bath Conditions On Particle Coverage

The effect of temperature, pH, particle concentration, and current density on the particle coverage of copper zeolite on the substrate was examined. The percentage particle coverage was estimated from surface images obtained from the optical microscope. The influence of particle size of the zeolite, the speed of rotation of the cathode, and the influence of additives on the codeposition process were not covered in this paper.

Variation of pH in the Plating Bath

Initial attempts to codeposit copper zeolite onto a copper substrate were not successful because of the low pH of the solution in the plating bath. As mentioned previously, the contents of the plating bath were copper zeolite ZSM5 and copper sulphate solution at a concentration of 200 g/L (26.7 oz/gal). As shown in Table 1, at low values of pH, the zeolite particles did not adhere well to the surface of the copper.

By increasing the pH to 3.0, the surface coverage of zeolite particles on the surface of the copper substrate increased. It was decided not to exceed a value of pH 3.5 to prevent formation of hydroxides.

The results found here are in broad agreement to those obtained from other studies using a wide range of metal matrix composites.⁸⁻¹⁰ From these studies, it had been found that the rate of incorporation of particles into the metal matrix either remained the

same or increased when the pH was lowered until it reached a critical value of about 2.0. At pH values lower than the critical value, the rate of incorporation decreased with a decrease in pH.

In the current system, as the pH was lowered, some ion exchange between copper and hydrogen ions in the zeolite itself would have occurred to some extent. Therefore, to prevent a loss of surface coverage of the zeolite and also to minimize ion exchange, all codeposition runs were carried out at a pH of 3.5.

Variation of Temperature in the Plating Bath

The effect of temperature in the plating bath on the particle coverage is shown in Fig. 5. There was a very slight increase in the amount of zeolite that had been adsorbed onto the copper substrate as the temperature increased from 30 to 60°C (86 to 140°F). Above this temperature, no further improvement could be seen.

This result seems to be consistent with other studies on the effect of bath temperature. For example, Sautter¹¹ found little influence of temperature in the range from 20 to 80°C (68 to 176°F) on the percentage of Al₂O₃ deposited for Ni/Al₂O₃ baths. Also, for Cu/Al₂O₃ baths, White and Foster¹² found that as the temperature increased, the rate of particle adsorption increased. At higher temperatures, particles could more easily approach the electrode, allowing more rapid interaction with the electrode surface. Also at the higher temperatures, the viscosity of the water would be lower, thereby slightly changing the thickness of the boundary layer.

Effect of Particle Concentration in the Plating Bath

The effect of particle concentration on percent surface coverage is shown in Fig. 6. At a temperature of 30°C (86°F) and pH 3.5, the particle coverage increased by 8 percent as the concentration of zeolite in the bath increased from 5 to 20 g/L (0.67 to 2.67 oz/gal).

It was thought that below about 5 g/L (0.67 oz/gal), the surface coverage would decrease rapidly. This is because it had been found previously⁸ that the volume fraction of particles in the codeposited surface varied either linearly or logarithmically with particle concentration in the bath. Over the measured range (Fig. 6), an increase in the particle concentration in the electrolyte would increase the number of particles reaching the electrode, and thereby increase the surface coverage. At higher concentrations, collision between the zeolite particles inhibited the entrapment of more particles and the effect of concentration would reach a plateau.

Variation of Particle Coverage with Current Density

Current density had the most significant effect on the coverage of zeolite particles on the copper. As shown in Fig. 7, as the direct current density increased from 2.0 to 10.0 A/dm² (~18.6 to 92.9 A/ft²), the percentage of the surface covered by particles increased from 46% to 78% at a temperature of 30°C (86°F) and pH 3.5. At the higher current density of 10.0 A/dm² (92.9 A/ft²), there was no evidence of hydrogen evolution or pitting of the surface.

It was found from previous studies that for most particle/electrolyte systems, the current density had a significant and complex effect on the percent-volume of codeposited particles. At low current densities, the percent-volume of codeposited particles increased with current density to a maximum, and then decreased with increasing current density. It was therefore decided to fix the current voltage at the mid-value of 5.0 A/dm² (~46.4 A/ft²) for all runs involving the preparation of the zeolite catalyst.

Reduction of Nitric Oxide

Both the copper zeolite (CuZSM5) and the pure copper catalysts were examined for their ability to reduce nitric oxide at different

temperatures. This was achieved by passing a gas mixture of nitrogen with 50 ppm of nitric oxide over each catalyst and measuring the percent reduction of nitric oxide. The temperature was increased after each set of measurements, and results are shown in Table 2.

It can be seen that the zeolite was very effective at the lower temperatures (300 to 400 °C; 572 to 752°F) but became less effective at higher temperatures. This would be expected because copper zeolite has been found to have a high catalytic activity at lower temperatures, but much lower catalytic activity at intermediate and higher temperatures. The pure copper, on the other hand, is not active at low temperatures (around 400°C; 752°F), but started to become effective at the higher temperatures (above 700°C; 1292°F).

Conclusions

Copper zeolite (CuZSM5) has been successfully codeposited onto a copper substrate using an electroplating bath containing copper sulphate solution and copper zeolite particles. The electroplating bath enabled the particles of copper zeolite to be kept in suspension during plating by air agitation.

It was found experimentally that the following factors improved the codeposition process:

1. Increasing the bath temperature from 30 to 70°C (86 to 158°F);
2. Increasing the current density from 2.0 to 10.0 A/dm² (~18.6 to 92.9 A/ft²);
3. Increasing the particle concentration from 5 to 20 g/L (0.67 to 2.67 oz/gal) and
4. Maintaining the pH between 3.0 and 3.5.

It was also found that the codeposited zeolite reduced nitric oxide very effectively at the lower temperatures (300 to 400°C; 572 to 752°F), but became less effective at the higher temperatures. Conversely, the copper catalyst did not reduce nitric oxide at the lower temperatures, but started to become effective at temperatures above 700°C (1292°F).

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