Charge Transfer Auto Oxidation-Reduction Type Semiconductor Catalyst: Application to MINOYAKI Tiles and it's Effects Shoji ICHIMURA and Keiichiro ICHIMURA

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We have developed a new semiconductor catalyst based transition metals oxide that has a higher function of auto oxidation-reduction. The new catalyst is called "CT catalyst".

The catalyst is manufactured by ordering synthesis several kinds of substances having an electron donor and acceptor, electron carrier, oxidate and reductant reagent. The catalyst is a high purity, easy-to-sinter and white fine ceramics powder.

When the new catalyst is used in a tiles industry, the catalyst is dispensed into a glaze and then can use in conventional procedure. The tiles added catalyst has new functions of self-cleaning surface, antifuntgal and antimicrobial.

Key Wards:

Charge Transfer, Auto-Redox Semiconductor Catalyst, Self clean surface, CT catalyst

1. INTRODUCTION

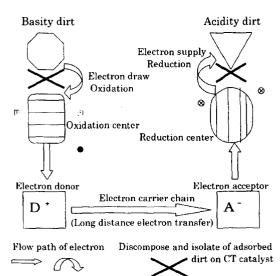
During the last hundred years, with the development of building construction technology, there were many tall building used tiles. But, with the advent of tall buildings, washing tiles wall of buildings has become downright dangerous and expensive. Recently, the need to decrease the maintenance cost of tall buildings with tiles wall have become important. Therefore, a great has been made to settle this problem. It is known that materials coated with of photo catalyst (TiO₂) exhibit self-cleaning and anti-fouling properties as a result of the decomposition of organic dusts and super-hydro philycation. However, there are some difficulties when this technology applies to tiles industry. The first is the temperature condition of photo catalyst properties : an equilibrium phase of photo catalyst TiO₂ must to keep under 700°C, while tiles producing processes need the more higher temperature than 700 $^{\circ}$ C to hold the mechanical strength, stable chemical properties and other manufacture properties of tiles.

Therefore, the production process of tiles to applying of photo catalyst TiO_2 needs two more process than general production of tiles. This becomes cost up of tiles. The second is that the condition of photo catalysis reaction of TiO_2 need UV light and water. This is difficult over of large areas of various shapes of building. To solve these problems, we have synthesized new catalyst – charge transfer auto-oxidation-reduction semiconductor (CT catalyst) and have developed durable surface coating technology at tiles manufacture.

2. EXPERIMENTAL

2.1 Synthesis of CT catalyst

As shown in Figure 1, the principle of CT catalyst is the base composition form of organized arrangement with electron donor and acceptor pair, electron carrier chain, oxidation center and reduction center. In the complex compound crystals of CT catalyst, there are the other activators.



Driving forces of CT catalysis reaction are thermal energy from solar or entourage.

Fig. 1 Action image of CT catalyst

We have synthesized CT catalyst test sample from mixing the oxides of MnO(D+), CoO(A-) and $TiO_2(E \text{ carrier})$ in Pt and Pd complex powder. After sintering at 1350°C, we got a fine white powder of complex oxide solid.

In Figure 2, we show the elements arrangement in CT catalyst crystal by analyzing the data of X ray diffraction pattern. The upper figure shows the coordination position of electron donor, acceptor and electron carrier. This mono-crystal structure is a perovskite form in one layer. The down figure shows the complex structure of CT catalyst compound involved reduction and oxidation centers and the other activators.

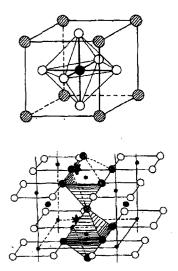


Fig. 2 Crystal structure of CT catalyst

2.2. Thermoelectric power of CT catalyst.

To confirm the semiconductive character of CT catalyst, we have measured the temperature dependency of thermoelectric power of CT catalyst. As shown in Figure 3, the experimental results show that CT catalyst has a typical semiconductive property. Therefore, we may suggest that this CT catalyst is a mixed crystal semiconductor involved five elements.

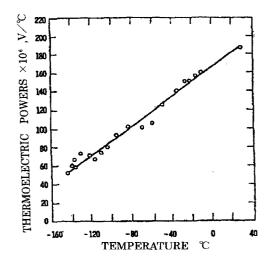


Fig. 3 Thermoelectric power of CT catalyst

We offer our suggestive model of an electron energy level diagram and an activation scheme of CT catalysis reaction.

From our analysis, in a thermally activated diffusion process of electron pointing to jumps of charge carriers activated by normal lattice vibrations or phonons, a general equation for the mobility is

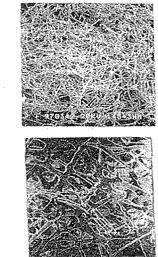
$$\mu = \frac{a^2 e \nu_0 e^{-q/kT}}{kT}$$

where a is jump length , $v \circ is$ frequency of jump, and q is activation energy for jump. This will be discussed further in other paper. Shoji Ichimura et al.

3. APPLICATION OF CT CATALYST TO MINOYAKI TILES.

3.1 Manufacturing of MINOYAKI tiles coated with CT catalyst.

After mixing of CT catalyst powder to ordinary glaze of tiles, we have made MINOYAKI tiles sample by the general manufacturing technology of MINOYAKI producing processes. We have sintered the tiles coated with the glaze involved different concentration of CT catalyst powder at usual temperature which produce MINOYAKI tiles(1120 $^\circ\!\mathrm{C}\,{\sim}\,1250\,^\circ\!\mathrm{C}$). The glaze involved CT catalyst powder was sprayed onto the fresh surface of row tiles before setting into a tunnel furnace. These technology and processes are no kinds of change to the anv ordinary manufacturing technology and processes of MINOYAKI tiles. In Figure 4, we show the SEM picture of the surface of CT tiles. We can see the net work structure of CT catalyst glaze in the surface layer of MINOYAKI tiles.



imes 20 of upper

20KV

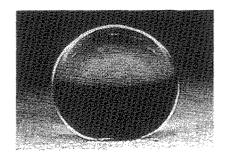
15,000

Fig. 4 SEM photo micrographs of surface of CT tiles. The samples were observed with SEM (JSM-6400Fs; JEOL, Ltd.,) operated at 20KV voltage.

The physical, chemical and mechanical properties of CT tiles are no any change to an ordinary MINOYAKI tiles and the CT tiles has more good durability.

3.2. The other properties of CT tiles.

CT catalyst is so-called solid electrolyte involved positive and negative charge point at different position in crystal lattice. Therefore, we may expect CT catalyst two different of hydrophobic characters. We have observed the contact angle between water and surface of CT tiles. At same time, we also have observed the contact angle between oil and CT tiles (Fig.5).



Water drop on CT tiles



Oil drop on CT tiles Fig.5 Photographs of contact angle between water , oil and CT tiles.

These results show that CT tiles, at first step of stain, can protect to both dirt with aqueous or oily dust. This property can not be observed in photo catalyst TiO₂.

We have also examined the antifuntgal and antimicrobial characters of CT tiles surface. These effects were observed by the cover glass method using in the antifuntgal test. We tested the CT antimicrobial action using live V tiles alginolyticus and the results are shown in the photograph of fluorescent microscope (Fig.6). On the CT tiles surface, the V. alginolyticus were killed in about five hours, even in the room temperature condition. These effects were many times repeatable.

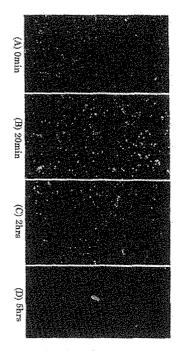


Fig.6 Photograph of fluorescent microscope Antimicrobial action of CT tiles Test bacteria; V. alginolyticus

4. PROTECTION TO AIR POLLUTION BY CT TILES.

Environmental pollution has been a large social problem. Air pollution, especially NOx, aldehyde and sulfide from the combustion of hydrocarbons fuel, is particularly serious problem. Automotive exhaust gas, especially, is much worse in large cities and the surrounding area of high way. To solve this problem, we have observed the capability of removing NOx and Formaldehyde on the surface of CT tiles. As shown in Figure 7 and 8, we have confirmed that CT tiles can decompose NOx or Formaldehyde contaminants adsorbed on the surface. Based on this experimental result. CT tiles are very useful industrial and construction materials.

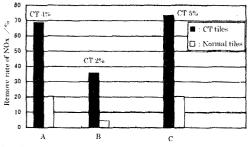


Fig. 7 Remove capability of NOx on the surface of CT tiles at 5 hours after flashing of NOx

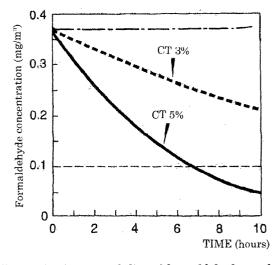


Fig. 8 Remove capability of formaldehyde on the surface of CT tiles

This capability has also been observed that sulfur dioxide can be similarly decompose and removed from CT tiles surface. The range of concentrations of air pollutants that can be efficiently removed is 0.01 ppm to 50 ppm. This is better method to remove pollutants from air.

5. CONCLUSION

- CT catalyst can apply to tiles manufacture, without any change of an ordinary technology of the existing facilities.
- (2) Tiles coated with CT catalyst have an anti microbial and self-cleaning effect.
- (3) CT tiles has the capability of decomposition of NOx and aldehyde compounds adsorbed on the surface of tiles.
- (4) CT tiles has enough durability as an exterior and interior building material.

6. ACKNOWLEDGEMENT

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Reference.

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