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## THE APPLICABILITY OF THE CATALYTIC WET-OXIDATION TO CELSS

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### ABSTRACT

The wet-oxidation catalysis of Au, Pd, Pt, Rh or Ru on a ceramic honeycomb carrier was traced in detail by 16 to 20 repetitive batch tests each. As a result, Pt or Pd on a honeycomb carrier was shown to catalyze complete nitrogen gasification as  $N_2$ . Though the catalysts which realize both complete nitrogen gasification and complete oxidation could not be found, the Ru+Rh catalyst was found to be most promising. Ru honeycomb catalyzed both nitrification and nitrogen gasification.

### PREFACE

Wet-oxidation is the reaction in which soluble or suspended organic materials are oxidized in a pressure vessel at a temperature of 120 to 374°C and a residence time of several minutes to hours in the presence of oxygen and liquid water. The reaction can be carried out both in a batch system and in a continuous system.

The main advantage of wet-oxidation, when applied to the waste management system for CELSS (closed-ecological-life-support-system) in a spaceship, is in that, as a type of oxidation reactions, it can produce carbon dioxide, which is essential to plant photosynthesis, from the raw material of organic waste. In a wider sense, as it is a mineralization reaction, it can also play a part as a re-distribution center of elements to each unit of the CELSS. The other advantages of wet-oxidation are (1) no biomass reproduction, (2) the stability of the reaction, (3) the stoichiometrically required amount of oxygen to be introduced, (4) short retention time and small insulation space, (5) no additives, (6) no bacteria or virus, (7) heat recovery and so on. Among these advantages, the first point is the most important and the 4th point is also important in the initial development stage of CELSS.

But wet-oxidation has also disadvantages. In a previous report /1/, the author showed that:

(1) In wet-oxidation without catalysts, non-oxidizable acetic acid is inevitably produced as a by-product and complete oxidation cannot be carried out. This prevents the wet-oxidation system from playing a part as the re-distribution center of  $CO_2$  and elements in CELSS.

(2) In wet-oxidation, the organic nitrogen in raw material is transformed exclusively to ammonia and not to nitrogen gas ( $N_2$ ) or nitrate form, both of which are the main chemical forms of nitrogen needed for CELSS.

In addition, the authors showed the possibility that these disadvantages may be overcome by the use of catalysts.

In the application of wet-oxidation as a waste management system for CELSS, complete oxidation and chemical form control of nitrogen are necessary. From this point of view, the authors will show in this paper the wet-oxidation catalysis of Au, Pd, Pt, Rh or Ru on a ceramic honeycomb carrier, which were proven to be useful as catalysts in the preliminary experiment /2/.

### EXPERIMENTAL METHOD

**Reactor and raw material:** Each experiment was carried out as a batch test using an autoclave with a volume of 580 ml. The filtrate of wet-oxidized-sewage-sludge obtained from the wet-oxidation facility of Yokohama-City-Northside-Sewage-Treatment-Plant was used as the raw material. The reason why soluble raw material was used instead of suspended material is that suspended materials generally poison the active points on the surface of a catalyst, and that it appeared to make it easier to select the best catalysts.

After the raw material was introduced to the autoclave, it was heated up. The temperature

reached the designated value in 30 min. The reaction times indicated hereinafter refer to the time at the designated temperature and do not include the time needed for heating. At the end of the desired reaction time, the autoclave was drenched in water to stop the reaction.

**Experiment 1:** The catalytic properties of Au, Pd, Pt, Rh and Ru, each of which is supported on the ceramic honeycomb, were examined and the changes of the properties with repetition of batch tests were traced. 20 batch tests were carried out with each catalyst. In each test, fresh raw material was introduced to the reactor. By using carriers, the surface area of each compound is increased and thus the number of active sites on it increases. In addition, the separation of the reactor output from the catalyst is also made easier. Moreover, the catalysts can be used repeatedly and the effusion of catalyst from the reactor is minimized.

A Pt catalyst with a cell number of  $32.5/\text{cm}^2$ , a cross-section area of  $5 \times 5$  cm and a height of 4 cm was used. The quantity of the Pt carried was 1.5 g per liter of the apparent volume of a honeycomb. When tested, it was laid on the bottom of the reactor. For catalysts except Pt, the cell number was  $28.4/\text{cm}^2$  and their shape was cylindrical with a diameter of 60 mm and a height of 50 mm. The quantity of the noble metal carried was about 2 g/l of the apparent volume of the honeycomb. It had a hole with a diameter of 8 mm at the cross-sectional center. The vertical shaft of the stirrer without a propeller was used for suspending the catalyst through the 8 mm hole mentioned above. The stirrer shaft was not moved in the experiments.

Each batch test was carried out at a temperature of  $260^\circ\text{C}$ , a pressure of  $75 \text{ kgf}/\text{cm}^2$  (7.35 MP) and a time of 60 min. The stoichiometrically required amount of oxygen was added to the reactor in case of the Pt catalyst and 1.5 times of its amount was introduced in the case of the other catalysts.

**Experiment 2:** The combined effects of elements were examined using the Ru and Rh catalysts. Their shape were the same as those of Ru, Rh, Pt and Pd in Experiment 1. The total quantity of Ru and Rh carried was 3 g/l of the volume of catalysts. The weight ratio of Ru to Rh was 1 to 3, 1 to 1 and 3 to 1. 16 batch tests were carried out. The reactor temperature, pressure and time were also the same as those in Experiment 1. 1.5 times the amount of oxygen to oxidize raw material completely was added to the reactor.

## RESULTS

**Experiment 1:** Figures 1 and 2 show the relation between the repetition times and COD in the reactor output when Ru, Rh, Pd or Pt on a honeycomb carrier was used. COD of the raw material was 14.4 g/l and COD of the reactor output without catalyst (control) was 5.87 g/l.

In case of Au, it was entirely released from the honeycomb carrier during the first batch test. COD and Kjeldahl nitrogen in the reactor output was shown to be the same as those of the control. The bare ceramic honeycomb without Au was put in the reactor with the same raw material as in Experiment 1 and wet-oxidized under the same experimental conditions. As a result, it was discovered that the ceramic carrier itself will not catalyze either oxidation or chemical form transformation of nitrogen.

In the case of Rh, COD of the reactor output was almost constant regardless of the number of times repeated and showed a value about half that of the control, that is, about 3 g/l. As COD of the raw sewage sludge treated in the wet-oxidation facility of Yokohama City was about 40 g/l, this value of 3 g/l accounts for 7.5% of the COD of the raw sewage sludge of Yokohama City. In the case of Ru, COD is the smallest at first among the 4 catalysts, then increases gradually with repetition and approaches the control. In the case of Pd, COD is secondarily the smallest at first and then increases with repetition and COD approaches a constant value, approximately about 3/4 of the control. In the case

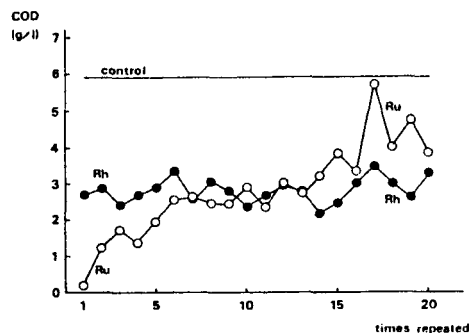


Fig. 1. The effects of the Rh or the Ru catalyst on the COD reduction

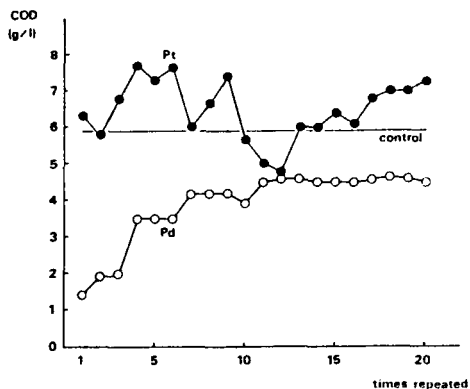


Fig. 2. The effects of the Pt or the Pd catalyst on the COD reduction

of Pt, COD repeats the increases and decreases with the repetition of the batch tests, but its change occurs near the value of the control. Therefore, it was proven that Pt honeycomb, in this experiment, does not catalyze oxidation.

Figures 3 and 4 show the nitrogen quantity in the liquid of the reactor output when Rh or Ru honeycomb was used, respectively. The total nitrogen of the control was 1480 mg/l. In the case of Rh, the quantity of nitrate nitrogen is constant and small, regardless of the repetition number. On the other hand, the quantity of Kjeldahl nitrogen was very small at first, then increases and approaches a constant value after being repeated five times. The constant value occupied about a half of the control. The difference between the control and the sum of Kjeldahl and nitrate nitrogen is considered to be gasified as nitrogen gas ( $N_2$ ). In the case of Ru, Kjeldahl nitrogen is very small in quantity and nitrate nitrogen is very large in quantity. Though nitrate nitrogen was so small in quantity during the first batch test, but increased suddenly after being repeated two times, and thereafter, maintained a value of about half of the control. In the case of Pd, the quantity of Kjeldahl nitrogen in the liquid ranged from 1.8 to 35.3 mg/l and that of nitrate nitrogen ranged from 13.8 to 88.5 mg/l. On the other hand, in the case of Pt, Kjeldahl nitrogen ranged between 29.0 and 192 mg/l in quantity and nitrate nitrogen was not detected. In both cases, nitrogen in the raw material was transformed into nitrogen gas ( $N_2$ ).

**Experiment 2:** Figure 5 show the relation between COD in the liquid of the reactor output and repetition number when the weight ratio of Ru to Rh is 1 to 1. COD of the raw material and the control are both the same as those in Experiment 1. In any honeycomb catalyst of this experiment, CODs behave alike. The small COD during the first batch test, followed by the sudden increase after that, is similar to the case of the Ru catalyst in Experiment 1. The consistency of COD after 3 or 4 repetitions is similar to the case of the Rh catalyst in Experiment 1.

Figure 6 shows the changes in the nitrogen quantity in the liquid of the reactor output with repetition. In this figure, the results when Ru/Rh is 1/1 are shown. Contrary to the case in which Ru or Rh was separately supported on a ceramic honeycomb, both Kjeldahl nitrogen and nitrate nitrogen were very small in quantity. Most of the nitrogen in the raw material was detected in the gas as  $N_2$ . When Ru/Rh is 1/3, the Kjeldahl nitrogen ranged from 0.3 to 26.2 mg/l and nitrate nitrogen ranged from 112 to 211 mg/l. When Ru/Rh is 3/1, the Kjeldahl nitrogen ranged from 0.3 to 21.8 mg/l and nitrate nitrogen ranged from 246 to 391 mg/l. In any case, the Kjeldahl nitrogen was very small compared to total nitrogen. The larger the ratio of Ru to Rh, the larger the nitrate nitrogen quantity became.

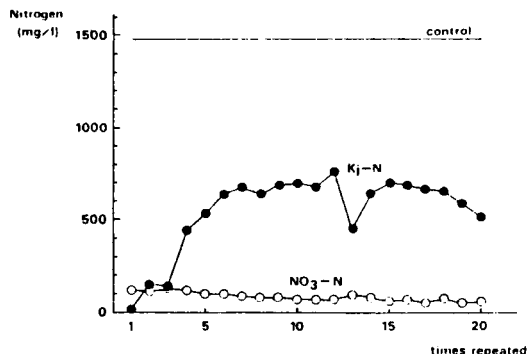


Fig. 3. The effects of the Rh catalyst on the chemical form of nitrogen

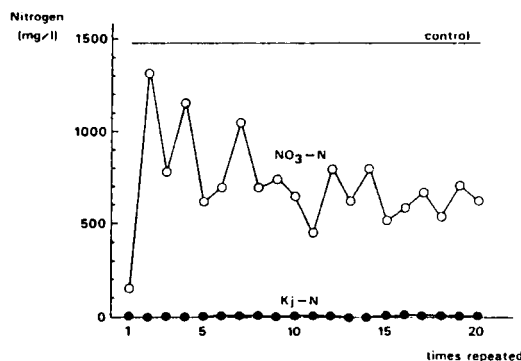


Fig. 4. The effects of the Ru catalyst on the chemical form of nitrogen

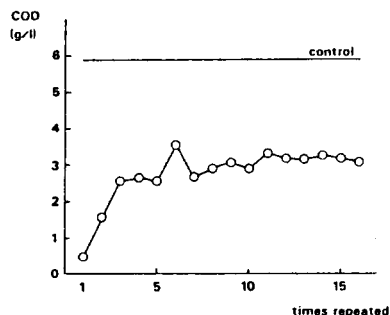


Fig. 5. The effects of Rh+Ru catalyst on the COD reduction (Ru/Rh = 1/1)

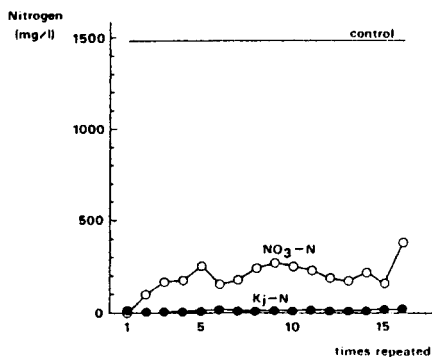


Fig. 6. The effects of Rh+Ru catalyst on the chemical form of nitrogen

Table 1 The Summary of the Experiments

	no catalyst	Rh	Ru	Pd	Pt	Ru+Rh
oxidation	-	+++	+	+	-	+++
nitrogen form	NH <sub>4</sub>	NH <sub>4</sub> <sup>+</sup> N <sub>2</sub>	NO <sub>3</sub> <sup>-</sup> N <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub> <sup>+</sup> NO <sub>3</sub>

## DISCUSSION

**Summary of the experiments :** Table 1 shows the summary of the experiments. It was discovered that complete nitrogen gasification as N<sub>2</sub>, which will be used as a component of air in a spaceship, is carried out by the use of Pt or Pd honeycomb catalysts, although in each case the COD reduction is low and/or unstable with repetition. A catalyst which would accomplish both nitrogen gasification and complete oxidation could not be found, but a promising one was found (Ru+Rh). If the main nitrogen form needed in CELSS is N<sub>2</sub>, then this catalyst is considered to be a good candidate for use in CELSS. COD reduction was higher and more stable than in the case of Pd or Pt. The transformable catalyst of the organic nitrogen to nitrate form, which plants in hydroponic solution utilize the most, could be found (Ru), but the nitrified nitrogen occupied about half of the control nitrogen and the rest was gasified as N<sub>2</sub>. In addition, a high rate and stable oxidation was not achieved.

If the wet-oxidation facility for CELSS is made under the present conditions, the two-step wet-oxidation will be adoptable. In the first step, wet-oxidation is carried out without catalyst. The organic substances in the raw material is oxidized to some extent, and the suspended matter which often poisons a catalyst is dissolved. In the second step, wet-oxidation is carried out with catalysts. The organic matter remaining at the first step is oxidized completely and the chemical form of nitrogen is controlled.

In the near future, the chemical form of nitrogen in the reactor output will be fully controlled by the use of noble metal catalysts. The largest problem to be overcome is that oxidation will not occur completely. To solve this problem in a short time span, countermeasures such as an increase in the catalyst quantity, reaction temperature, reaction time etc. will be taken, which will partially solve this difficulty. Generally speaking, the durability of a catalyst mainly depends on the solubilization or the release of catalytic compounds from its carrier and, on the other hand, the property of a catalytic reaction mainly depends on the combination of elements. Therefore, in a long time span, measures such as the exchange of carrier material to silica or titania, the addition of another element to Ru and Rh, the change of the combination of catalytic compounds and so on are to be researched hereafter.

**The subjects to be solved:** The subjects of wet-oxidation in the application to CELSS are as follows. The first is to find out the catalysts with which both complete oxidation occurs and the chemical form of nitrogen is controllable. The second subject is the correct measurement of the material balance. In addition to carbon and nitrogen, elements to be traced are P, K, Ca, Mg and S, which are macro nutrients of plants, Fe, Mn, B, Cu, Zn, Mo and Cl, which are micro nutrients of plants, and Al, Si, Cr, Ni, Hg, Pb, Cd and As, some of which are harmful to plants or the human body. The third is to examine and evaluate the quantity of the catalyst effused from the wet-oxidation system, though it is thought to be much smaller than in the case of copper compounds. The fourth is the measurement and evaluation of aldehyde, alcohol, carboxylic acids and other compounds with low molecular weights and low boiling points which are produced in wet-oxidation as end products in addition to acetic acid. If these compounds are produced in significant quantities, then the necessity to prevent these compounds from being produced or to remove them from the liquid or gas will be of importance.

On the other hand, research on making up a practical wet-oxidation facility for CELSS has been delayed. In its construction, it is noticed first that this system will be used under the condition of zero gravity. Problems such as leakage, elusion and wear will result from the high pressure and temperature and a more in-depth study is needed for the solution of these problems. As for the material of the reactor, for instance, the wet-oxidation facility on the earth first used SUS 316, then titanium was gradually adopted. The best material in space is still unknown. Examination of the effectiveness of such new materials as ceramics have yet to be fully tested. The investigation of the system composition of wet-oxidation in CELSS and of the materials and mechanisms to be chosen in each part needs to have a more intensified study carried out on it in the future. This study will be achieved with more effort than that on wet-oxidation reaction itself which the authors have been researching.

## REFERENCES

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