

品川化成株式会社「オゾン分解剤の開発」

Shinagawa Chemicals Co., Ltd. “Development of Ozone Decomposition Catalyst”

若 杉 勝 廣^{*1}

Katsuhiko WAKASUGI

南 園 広 志^{*3}

Hiroshi MINAMIZONO

三 星 敏 雄^{*2}

Toshio MITSUBOSHI

平 井 猛 行^{*4}

Takeyuki HIRAI

Abstract

Ozone is used to disinfect water and decompose volatile organic compounds because of its strong oxidizing ability, although it is bad for human health and also the global environment. It is necessary to decompose the ozone in gas before exhausting to the atmosphere. Our company has supplied SEKADO-KR as a decomposing catalyst since 1974. Recently we have developed new types of catalysts to meet the demand for strong catalysts utilizing the newest ozone technology. Development is reported on in this paper.

1. はじめに

オゾンは強い酸化能力を有することから上水や下水の消毒、清浄化或いは有機ガスの分解、繊維の漂白など幅広く利用されている。一方、こうした積極的な利用のほかに、紫外線、プラズマ、コロナ放電といったエネルギーを使用した際に付加的に発生してしまうものもある。オゾンは強い殺菌能力を有することから毒性も強く、人体に害を及ぼすものである。また近年、南極上空の成層圏におけるオゾン・ホール拡大が問題になっているが、対流圏においては増加傾向にあり、地球温暖化や、酸性雨の原因のひとつになっている。¹⁾ それゆえオゾンを含むガスは無害化後に大気放出することが地球環境を守る上で重要である。弊社は昭和49年にオゾン分解剤KRを開発し、市場に供給してきたが²⁾近年オゾンの活用が盛んになるのに伴いオゾン分解剤に対する性能向上の要請も強くなってきた。今回、触媒特性の再検討により、新しい分解剤を開発できたので報告する。

1. Introduction

Because of strong oxidizability, ozone is used for disinfection and purification of water, decomposition of organic gas, and bleaching of textiles. On the other hand, it is additionally generated in ultraviolet rays, plasma, and corona discharge. Since it has strong oxidizability, toxicity is also strong. Ozone is harmful to the human body. In addition, recently, enlargement of the ozone hole in the stratosphere of the South Pole sky has become a problem, but there has been an increase in the amount of ozone in the troposphere. This is one of the causes for global warming and acid rain.¹⁾ Consequently, in order to protect the global environment, gases which include ozone must be exhausted after detoxification. Our company developed the ozone decomposition catalyst KR in 1974, and supplied it to the market.²⁾ Recently, requests for the efficiency improvement of ozone

*1 大石橋市品川栄源連鑄耐火材料有限公司 副董事長 Executive Vice President, Shinagawa Rongyuan Refractories Co., Ltd.

*2 品川化成株式会社 真岡工場 取締役工場長 Director Works Manager, Mooka Works, Shinagawa Chemicals Co., Ltd.

*3 品川化成株式会社 真岡工場 技術室長 Manager, Technical Section, Mooka Works, Shinagawa Chemicals Co., Ltd.

*4 品川化成株式会社 真岡工場 Mooka Works, Shinagawa Chemicals Co., Ltd.

Table 1 Composition of Samples (wt%)

	No.1	No.2	No.3	No.4	No.5	KR
SiO ₂	30	20	20	23	36	44
Al ₂ O ₃	27	16	16	21	31	38
Fe ₃ O ₄	42	-	-	-	-	-
FeO	-	63	-	-	-	-
Fe-Si	-	-	63	-	-	-
MnO ₂	-	-	-	55	16	-
C	-	-	-	-	16	18
Packing density (g/cm ³)	1.15	1.40	1.40	1.10	0.75	0.65
Bulk density (g/cm ³)	1.6	2.0	2.0	1.6	1.1	1.0

2. 実験方法

1) 分解剤の作製

試作品はアルミナ・シリカ・ゲルと特殊活性炭からなるKRの配合において、活性炭部分（容積含有率21%）を他の触媒材料で置換し作成した。その組成をTable 1に重量比で示す。

まず添加原料の触媒効果を比較するため、No.1からNo.4を試作し、その後No.5を追加試作した。これらの配合はKRと同様に混練、造粒、乾燥、解砕の工程を経て、回転式打錠機により $\phi 5.75 \times 5.25$ mmの錠剤に成型した。錠剤は170℃で4時間乾燥した後、オゾン分解装置による性能評価試験に供した。

decomposition catalyst have become strong with active utilization of ozone. A new ozone decomposition catalyst was developed by reexamining catalytic characterization of some materials. It is reported on below.

2. Experiment

1) Production of ozone decomposition catalyst

The KR samples consisted of alumina-silica gel and activated carbon (volume content 21%). Carbon was replaced with other substitute catalyst material. First, in order to compare the catalyst effect of materials, samples No.1 to No.4 were produced and No.5 was added later. These compositions were molded into $\phi 5.75 \times 5.25$ mm tablets with a rotation type tableting machine through the process of mixing, granulation, drying, and grinding in the same manner as KR. The Ozone decomposition ability of the samples was investigated by ozone decomposition equipment after drying at 170 degrees C for 4 hours.

2) Ozone decomposition examination

An evaluating examination was performed with the test equipment shown in Figs. 1 and 2.

An Ozonizer and ozone monitor which were

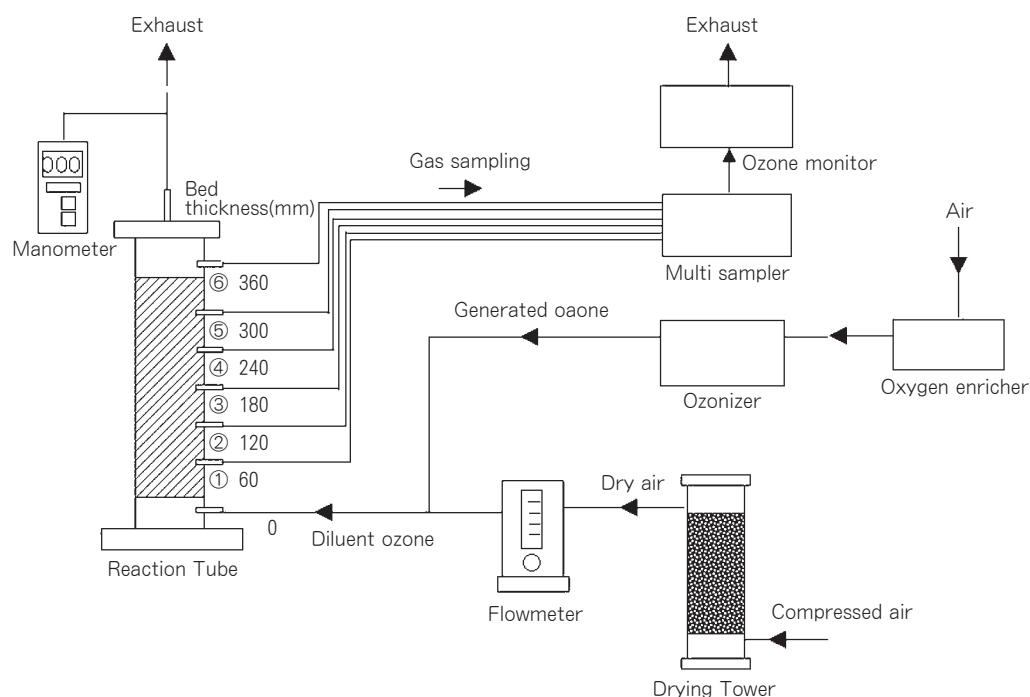


Fig. 1 Gas flow chart.



Fig. 2 Appearance of ozone decomposition evaluation equipment.

2) オゾン分解評価試験

評価試験はFig. 1 及びFig. 2 に示した試験設備によって行った。オゾン発生器及びオゾン含有率測定機は荏原実業社製を使用し、反応塔及び配管については自社で作成した。反応塔は6層に分けてサンプリングができるように配慮した。オゾンの打ち込み条件は濃度を5,200 ppmで流量を10.6L/min.に設定し、破過濃度は0.1ppmとした。このとき空間速度は各層当り3000/hrで、塔全体では500/hrとなる。

3. 実験結果

1) 試験後外観

KRとNo.5は表面が試験前に黒色を呈していたが、試験後には灰色に変わっており、活性炭の酸化したことが推察できる。他の材料については外観に大きな変化は認められなかった。

2) 破過時間

各材料の破過時間を各層ごとにFig. 3 に示した。最も破過時間の長いものはNo.4, No.5であり、両者は測定時間が長くなりすぎるため4層目（層厚240mm）が破過した時点で測定を中止した。No.3は破過時間が2時間と最短であった。No.1, No.2及びKRは中間的な結果であり、100時間弱で破過した。すなわちこれらの触媒の中で効果の最も高いものは MnO_2 単味と MnO_2 -活性炭であった。しかし MnO_2 単味は重量が重いため、重量当りの分解量で比較すると MnO_2 -活性炭系がベストである。

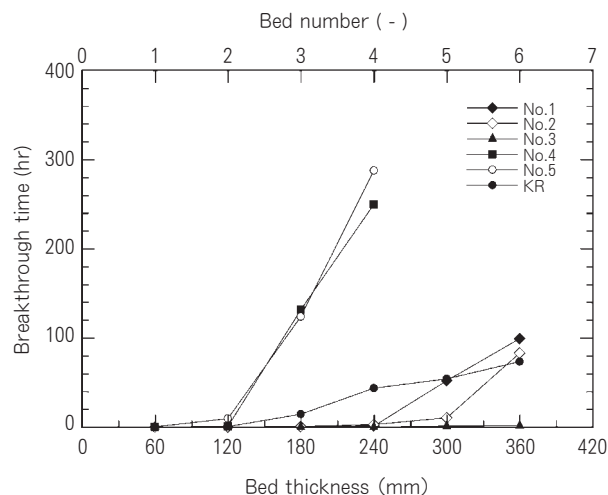


Fig. 3 Breakthrough time for each layer of each sample.

manufactured by Ebara Jitsugyo Corporation were used, and reaction tube and gas piping were made by us. The reaction tube was divided into 6 layers, so that each layer could be sampled. Test conditions were ozone concentration 5,200ppm, flow rate 10.6L/min and break through concentration 0.1ppm. Under these conditions, space velocity per each layer is 3000mm/hr, and it becomes 500mm/hr in entire tube.

3. Results and Discussion

1) Appearance of samples after examination

Although the surfaces of KR and No.5 were black before the examination, they changed to gray after the examination and we can guess that the activated carbon oxidized.

But, considerable change was not recognized in the appearance of the other materials.

2) Break through time

The Break through times for each material in each layer are shown in Fig.3.

The Break through times of No.4 and No.5 were longest. Because the measuring times for both samples were too long, when the 4th layer (bed thickness 240mm) broke through, measurements were stopped. The Break through time of No.3 was 2 hours, and was the shortest. The results for No.1, No.2 and KR were intermediate with a break through time of 100 hours or less. The material in

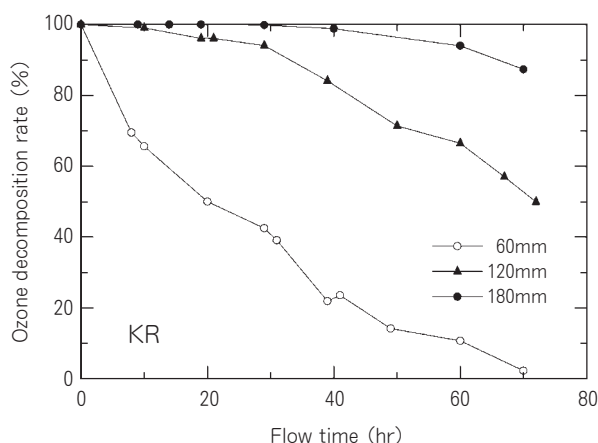


Fig. 4-a Change in Decomposing Rate on KR.

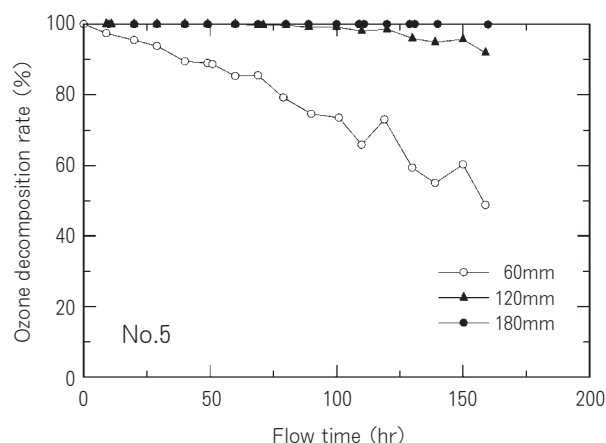


Fig. 4-b Change in Decomposing Rate on No.5.

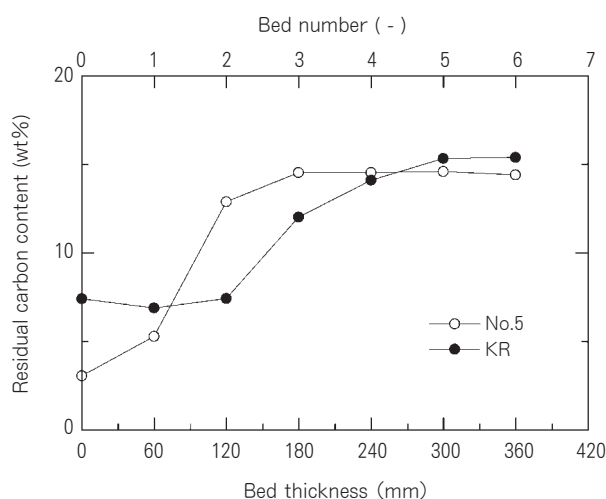


Fig. 5 Changes in Residual Carbon on KR and No.5.

3) オゾン分解性能

分解性能はオゾンの打ち込み濃度やガス流速などの条件により変化するため絶対的な数値として表わすことは難しい。そこで一般的には分解されたオゾン濃度を打ち込み濃度で除した値を分解率(%)と呼び、分解性能の目安にしている。KRとNo.5について分解率の経時変化をFig.4-aと4-bに示した。KRはNo.5に比べ、劣化速度が急激である。したがってNo.5はKRに比べ分解性能が高いと判断できる。

4. 考 察

No.5は配合から考えると、No.4とKRの中間的能力を示さなければならないが、実際にはNo.4に勝るとも劣

which the catalytic effect was highest among these catalysts was MnO_2 (single component) and mixture of MnO_2 and activated carbon.

When the amount of decomposition per weight is compared, a light weight MnO_2 -activated carbon system is the best.

3) Ozonolysis efficiency

Since ozonolysis efficiency changes with conditions such as ozone concentration and flow velocity, it is difficult to express as an absolute numerical value. Therefore, the value which divides decomposed ozone concentration by initial concentration is called decomposition rate (%). It is considered to be the standard of ozonolysis efficiency. The changes in the decomposition rate of KR and No.5 with time are shown in Fig.4-a and 4-b.

The decrease in the ozone decomposition rate of KR was rapid in comparison with No.5.

So it was recognized that ozonolysis efficiency of No.5 was higher than KR.

4. Results and Discussion

Although the composition of No.5 is estimated to be intermediate ability between No.4 and KR, ozonolysis efficiency of No.5 was as well or better than No.4. The reason is considered as follows.

The residual carbons of each layer of KR after 80hr testing and No.5 after 130hr testing is shown respectively in Fig.5. As shown in Fig.4a, it was guessed that the decomposition capability of the 1st

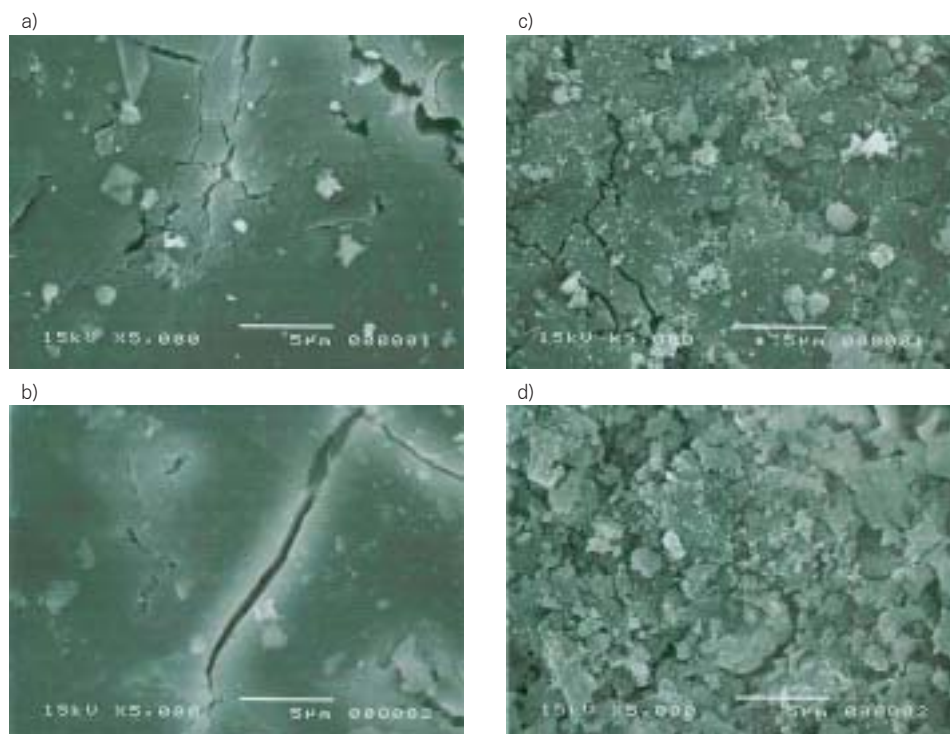


Fig. 6 SEM Image of KR and No.5 before and after Test.
a) Surface of KR before test c) Surface of No.5 before test
b) Surface of KR after test d) Surface of No.5 after test

らない性能を発揮した。この理由について考察を加えない。

Fig. 5 にKRは80時間試験後、No.5は130時間時点における各層のサンプルについて残留炭素量を示した。KRはFig.4-aにおいて1層目がすでに分解能力が失われているにもかかわらず、底部から2層目は7～8%の炭素を残している。これは当初配合量の約40%に当たる。これに対してNo.5はまだ分解能力を保持している1層目でも残存量が5%まで減少し、当初配合量の30%まで低下している。したがって仮にさらに測定を続けた場合、No.5の1層目の残存量は更に低下すると考えられる。

このメカニズムを調査するために試験前後のKRとNo.5について走査型電子顕微鏡による観察を行った。

KRは炭素の消費により組織の多孔化が進行すると予測していたが、結果は試験前後で際立った違いはなく、むしろ逆に試験後に緻密化していることが覗える。それに対してNo.5は粗い組織が試験後により粗くなり、気孔が増加している様子が観察できる。このことからMnO₂の添加が材料組織と触媒性能に違いをもたらしたと考えられる。すなわち金属酸化物であるMnO₂はオゾンの還元触媒であると同時に炭素の酸化触媒として働く

layer of KR was lost. However, 7 to 8wt% of carbon remained from the bottom to the 2nd layer. This is equal approximately to 40wt% of the carbon content which is combined.

On the other hand, although the decomposition capability of the 1st layer of No.5 remained, the amount of residual carbon decreased to 5wt%, and is approximately 30wt% of the carbon content which is combined.

When measurement continued further, it is thought that the amount of carbon of the 1st layer of No.5 decreases more. In order to investigate this mechanism, observation of raw and post test samples of KR and No.5 by SEM was performed.

It was estimated that the structure of KR becomes porous, depending upon the consumption of carbon. There is no considerable difference after ozone decomposition test. After testing, the structure of rather dense KR was observed. On the one hand, the surface of No.5 was rougher after testing, and an increase in the number of pores was observed. It is guessed that the addition of MnO₂

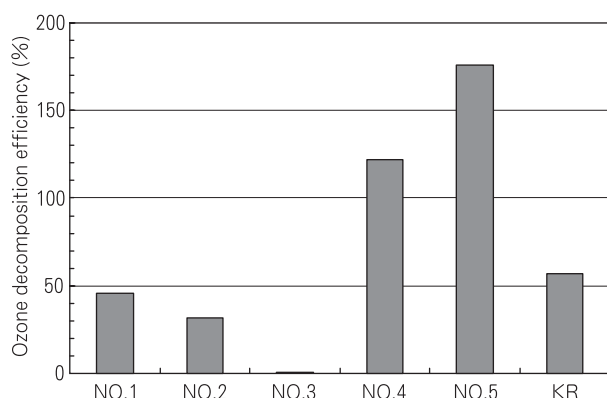


Fig. 7 Amount of ozone decomposition by sample weight.

ことにより全体のオゾン分解性能を向上せしめていると結論付けられる。

5. まとめ

これまで当社は、アルミナ・シリカ・ゲルと活性炭からなるオゾン分解剤SEKADO-KRを供給してきた。KRの分解性能向上を目的に触媒材料を再検討し、アルミナ・シリカ・ゲル-MnO₂系 (No.4) の効果が高いことを確認した。しかし、MnO₂を添加した系は重量が重く、経済的でないため一部を活性炭に置換したNo.5を試作した。

No.5はMnO₂と活性炭を重量比で1:1にした配合であるが、No.4と同等以上の分解性能を示した。この理由は遷移元素であるMnO₂がオゾンの還元触媒として働く一方、炭素の酸化触媒として働くためと推定される。No.5の充填重量はNo.4の70%であるため、Fig. 7に示すように分解性能は1.4倍であり、今回実験した中で最も性能が高いと評価できる。

ところで、MnO₂は特定化学物質であり、生産現場や材料の廃棄において、今後使用が困難になる可能性がある。

本実験で遷移金属が酸化触媒効果も発揮することが確認できたことから、今後は環境にやさしい例えば鉄系、チタン系などの原料と活性炭の組み合わせを検討していきたい。

created the difference in structure of materials and catalyst efficiency.

The MnO₂ is metallic oxide simultaneously operated as a reduction catalyst for ozone and an oxidation catalyst for carbon and a total improvement in ozonolysis efficiency was consequently obtained.

5. Summary

Until now, our corporation supplied ozonolysis material SEKADO-KR which consists of the alumina silica gel and the active carbon. As a result of re-investigating some materials with the aim of improving the ozonolysis efficiency of KR, The high efficiency of alumina silica gel-MnO₂ system (No.4) was verified.

The system with MnO₂ is heavy, and is not economical. In order to make No.4 light, a part of MnO₂ was replaced by activated carbon and No.5 was produced.

The composition of No.5 was 1:1 by weight for MnO₂ and activated carbon, but ozonolysis efficiency was better than No.4.

The reason is presumed to be that MnO₂, which is a transition element, acts as a reduction catalyst for ozone and also as a carbonaceous oxidation catalyst.

Therefore the filling weight of No.5 is 70% that of No.4, with on ozone decomposition efficiency is 1.4 times that of No.4 as shown in Fig.7. No.5 showed the highest ozone decomposition efficiency during these experiments.

MnO₂ is a specific chemical substance. When it is considered that abandonment of the manganese material influences environment, one should avoid use of MnO₂.

Since transition metal showed an oxidization catalyst effect for carbon in this experiment, we would like to examine various combinations of materials, such as environment-friendly iron oxide-carbon system and titanium oxide-carbon system.

References

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