Non-Thermal Plasma Decomposition of Dilute Trichloroethylene in Air - Catalyst Effect

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1 Abstract:

High pressure non-thermal plasma decomposition performance for low density, typically 250 ppm, volatile organic compounds (VOCs), mostly trichloroethylene, in synthesized air was examined for various conditions. In order to improve the VOCs decomposition energy efficiency of the plasma reactor, new manganese-dioxide supported alumina spheres were examined, where that catalyst works well to decompose the plasma-produced ozone even at the room temperature. At that ozone decomposition process in the catalyst, the trichloroethylene (TCE) was also oxidized very well. Although the specific energy density (SED: input discharge energy, Joule per 1 litter gas) was rather small, the TCE decomposition efficiency was more than 99 % at some conditions. Still now, the optimal amount of the catalyst was not yet determined. Increasing effect of the catalyst amount was examined concerned with the byproduct behaviour.

2 Introduction

The non-thermal plasma is very effective technique in decomposing toxic gaseous contaminants in the air, in the combustion flue gas, in the waste gas from the industrial factories or breeding farms and so on. Already many researchers have reported various test results. Prof. Ohtsuka and his Hitachi Group researchers reported that NO oxidation process was observed in the combustion flue gas, if the ESP operation current was large enough, much higher than the normal current [1]. As the power efficiency was so bad, that technique was not studied any more. In 1970'~1980', late Prof. Masuda developed pulsed technique (from microseconds to nanoseconds pulse) for ESP and also found NOx oxidation by that pulse[2]. His follower, Prof. Mizuno introduced that pulse technology to Florida State University and also succeeded in reducing NOx in the flue gas[3]. A little bit earlier, Ebara Co. and JAERI(Japan Atomic Energy Research Institute: now changed to Japan Atomic Energy Agency: JAEA) investigated high energy electron (MeV) beam irradiation effect on De-NOx, De-SOx in the flue gas[4]. At that stage, many researchers in various field, have strong interest that plasma in atmospheric pressure. Some results are reviewed by late Prof. J.S.Chang and others [5]. Some members of the Institute of Electrostatics Japan reported NOx removal in the flue gas conditions [6-8]. Shimizu et al and Yoshioka group used AC discharge[7,8] but Ohkubo, Chang et al still used DC high voltage with chemical reagent injection just the in the plasma region. They named that as corona radical ion shower[6]. That non-thermal plasma is also applied to decompose toxic volatile organic compounds (VOCs) in the air [9-13]. For example, Prof. Yamamoto and his group in RTI reported VOCs including CFC-113 (which is famous for the ozone layer destruction in the stratosphere) decomposition by the plasma in the batch process [9]. The authors also succeeded in decomposing wide range CFC-113 (10,000 ppm to 100 ppm) in the continuous process (flowing state)[10]. AIST group also reported various VOCs decomposition by packed-bed type or barrier discharge reactors [11]. Einaga and his group reported the ozone effect on the decomposition [12]. Urashima and Chang group at McMaster University also tried to decompose various VOCs by the similar modulated plasma reactor [13]. The authors still continued to enhance the VOCs decomposition concerning with the ozone decomposition. Especially TCE (trichloroethylene) decomposition performance was experimentally examined for several years. The authors group learned how to make the manganese-dioxide supported alumina catalyst from Ogata and Kim and tested their performance. At some amounts of the catalyst at the room temperature condition, still the ozone remains in the processed air by the plasma and the catalyst. The optimization of the catalyst amount was tested and that results are described in this paper.

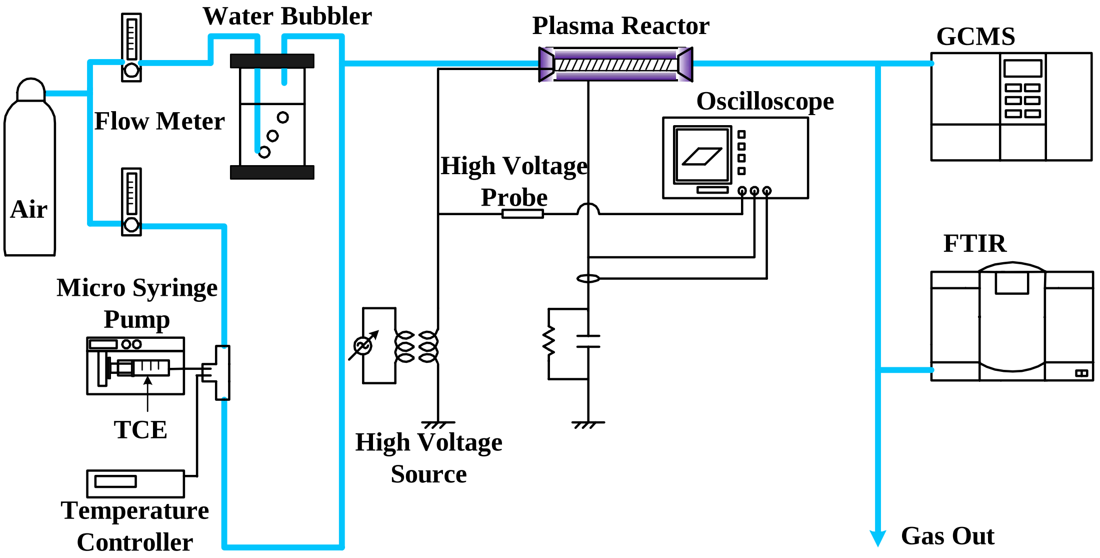

Fig.3-1 TCE decomposition experimental system

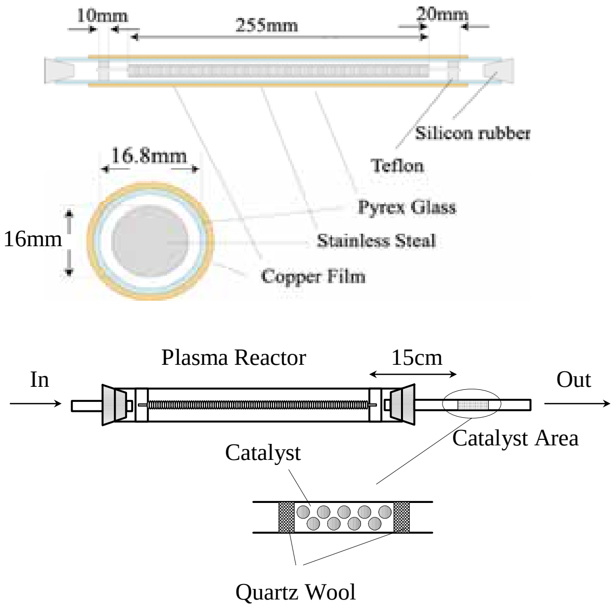

Fig.3-2 Plasma reactorgeometry try and thecatalyst

3 Experimental

3.1 Experimental system

The basic construction of the experimental system is the same as the former one [16] which is shown in Fig.3-1. Several AC power source has been used for tests. One is 50 Hz commercial power voltage-boosted by the transformer. High voltage AC power amplifier is also tested for wave-form examination. After the plasma process, the plasma-processed gas passes through the catalyst tube which is not shown in Fig.3-1. All experiments reported here were done at the room temperature. The ozone decomposition catalyst is also at the room temperature. Details of the size of the plasma reactor (about 30 cm long with the discharge gap of 0.4 mm) and the position of the catalyst are also shown in Fig.3-2. The residual contaminant-components after the plasma-process, such as the ozone and TCE, are observed by the standard FTIR (Fast Fourier Transform Infra-Red Spectrometer Shimadzu: IR-Prestige-21) with a multi-reflection long path absorption cell. The ozone concentration is calibrated by the comparison with the JIS method (Iodine method). For by-product analysis after the process, the gas-chromatograph-mass-spectrometer, GCMS, (Shimadzu: GCMA-QP5050A) with an automatic gas-sampling unit, is used where that operates automatically with some time interval.

3.2 Gas and Catalysts

Humidity of the sample gas (if not shown in the data, the sample gas is dry) is controlled by water bubbling at thermo-bath and the TCE concentration is adjusted with the motor-controlled low injection syringe as shown in the figure. After TCE liquid injection, that liquid is vaporized by the heated metal mesh because of low vapour pressure of TCE. The air in the bombe is synthesized air of 4nitrogen and 1oxygen. In this experiment, the synthesized air flow rate is 1.0 l/min and the TCE concentration is adjusted to 250 ppm. The catalyst tube shown in Fig.3-2 is filled with the manganese-dioxide supported alumina spheres of 3 mm in diameter. That catalyst is hand-made. That manufacturing process was under guidance by AIST group (Drs. Ogata and Kim). The total amounts of tested catalysts (MgO_2-supported alumina spheres) were 100, 300, 500, 800, 1,000, 2,000, or 3,000 mg individually.

4 Experimental Results

4.1 TCE Decomposition Efficiency and Residual Ozone

Figure 4-1 shows trichloroethylene (TCE) decomposition efficiency versus applied discharge energy which is named as Specific Energy Density (SED) for different amount of catalyst. SED is the input discharge energy for 1 *l* processed gas and calculated by the following equation.

$$SED \quad [J/L] = \frac{Power[J/s]}{FlowRate[L/s]}$$

TCE decomposition efficiency is also calculated as

{1-Processed TCE /original TCE }*100%

observed by FTIR absorption signal. A small amount of the catalyst, 100mg, TCE decomposition efficiency increases about 20 % at SED of about 10 J/l. When the catalyst amount is more than 1,000 mg, TCE decomposition efficiency is roughly 100 % only at SED of 10 J/L. However, the residual ozone concentration after passing through the ozone decomposition catalyst is still high as shown in Fig. 4-2. In this figure, the ozone generation by the plasma process for 250 ppm TCE contaminated dry air is shown in no catalyst line. That is about 1,000 ppm at SED of 20 J/L which is very high. When the amount of the catalyst is 2,000 mg, still high residual ozone of 100 ppm is detected at SED of 20 J/L. That ozone should be removed, especially in the living room by the regulation. At the amount of 3000 mg catalyst, that penetrated ozone concentration is roughly zero in this input power level which will be shown in near future by other student.

4.2 Byproducts Analysis

In the TCE decomposition process, various kinds of byproducsts are observed, such as chlorine (Cl_2), phosgene ($COCl_2$), tetra-chloro-methane (CCl_4), trichloro-acet-aldehide (TCAA CCl_3COH), dichloro-acetylchloride (DCAC CCl_2HCOCl) and so on. The latter two are the same molecular weight of 147.4 where only the positions of chlorine and hydrogen atoms are different. Figure 4-3 shows the production of phosgene versus injected energy for different amounts of catalyst. In any case of the SED, the phosgene generation is the largest without the catalyst, but the catalyst amount dependency is not so simple. At SED of about 20 J/L, phosgene generation is plotted for the input discharge energy (SED) as shown in Fig.4-4. Although the phosgene generation without the ozone-decomposition catalyst is far larger than any other case, the phosgene signal becomes peak at the catalyst amount of 800 mg. Still now, the authors do not explain that summit mechanism, but can say

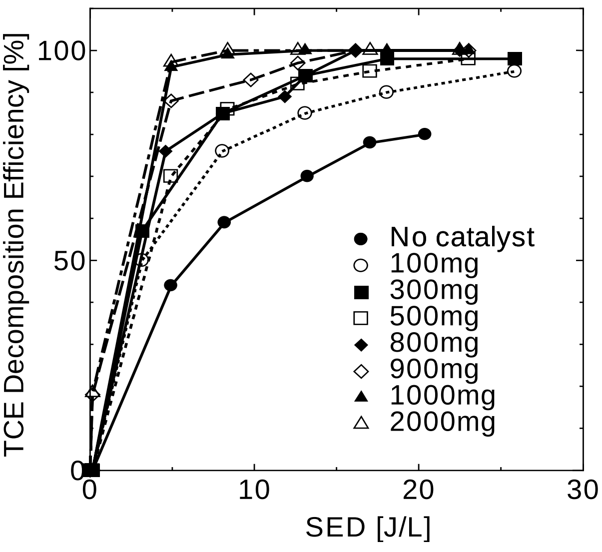

Fig.4-1 TCE decomposition efficiency for applied discharge energy (SED)

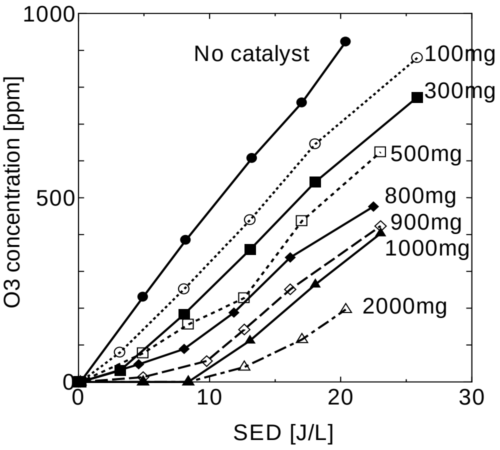

Fig.4-2 Ozone generation by the plasma discharge energy for different amount of ozone-decomposiotion catalyst.

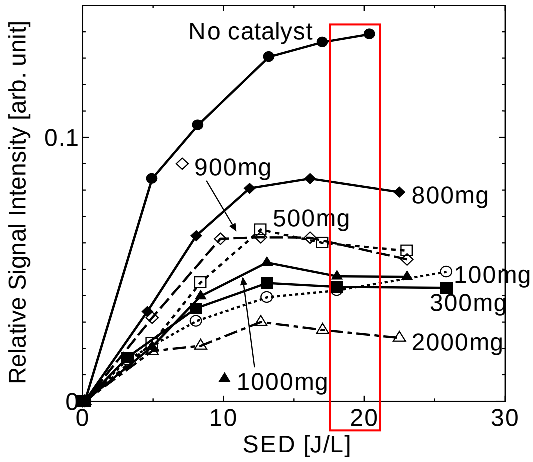

Fig.4-3 Phosgene generation versus specific energy density for different amounts of the catalyst.

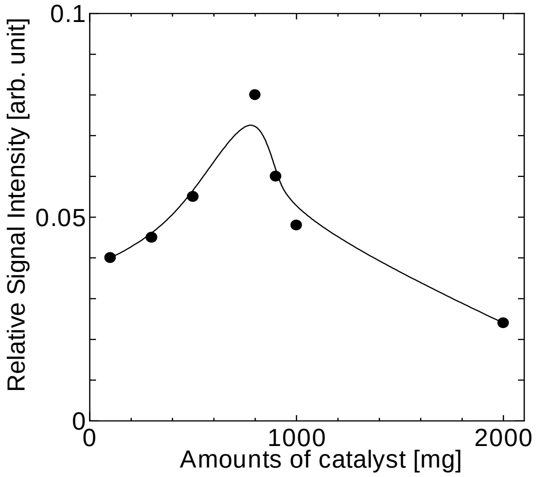

Fig.4-4 Phosgene production related with the catalyst at SED of 20J/l.

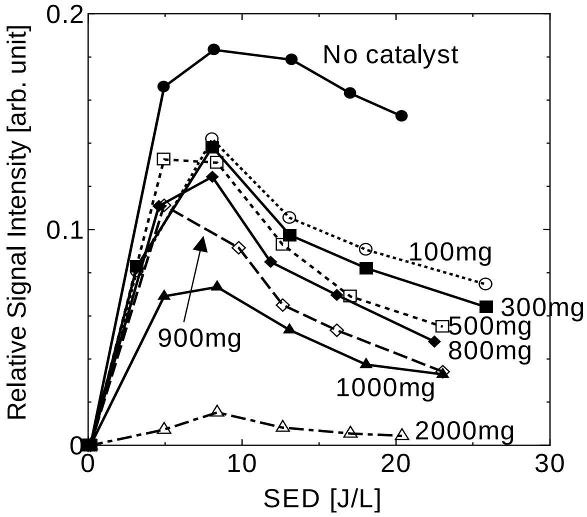

Fig.4-5 TCAA generation versus the input discharge power (SED) for different amount of the catalyst.

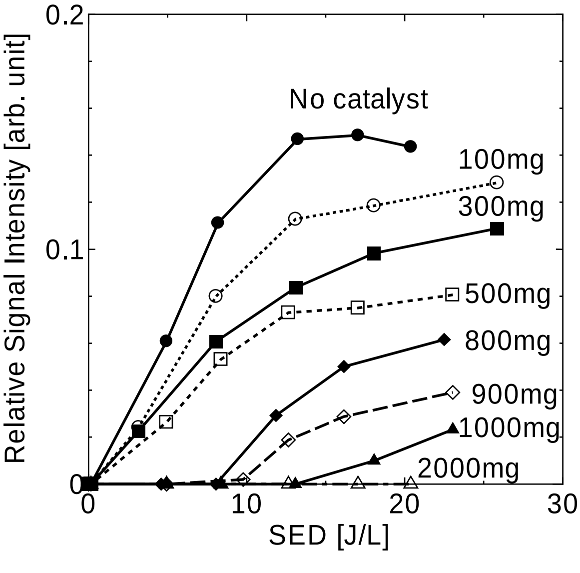

Fig.4-6 DCAC generation versus the input discharge power (SED) for different amount of the catalyst.

that the sufficient amount of the catalyst indicating that the generation of phosgene is much reduced with the oxidation of phosgene which occurs with the generation of atomic oxygen at the ozone decomposition, maybe.

The generation of TCAA and DCAC are also interesting as shown in Figs.4-5and 4-6. As main byproducts after the plasma process, the generation of both TCAA and DCAC are much larger than other cases (with the catalyst). At low SED, TCE is changed to TCAA (maybe oxidation effect by the plasma). That tendency increases with the input power (SED) At SED of more than 10 J/L, TCAA generation decreases with the increase of SED. This tendency is common for any other cases where the ozone decomposition catalyst exists although the generation of TCAA is much suppressed. If the catalyst is 2,000 mg, TCAA is only a little it generated at any conditions. For DCAC production, the catalyst also decreases the production of the DCAC in general. If the amount of the catalyst is 2,000 mg, the DCAC generation is not observed at any range of SED. Without the catalyst, DCAC maximum is at the 13 J/L which is a little bit larger than the maximum of TCAA generation. However, in the case of DCAC generation, with a slight use of the catalyst, that generation maximum is not observed but the DCAC signal increases with the SED monotonically. Those data suggested several matters. At low SED, by the plasma, TCE changes to TCAA in the plasma region. The produced ozone in the plasma region is decomposed by the catalyst and the atomic oxygen may be produced. If the catalyst is enough and all ozone made in the plasma reactor is decomposed, plasma generated TCAA and residual TCE may be oxidized to carbon oxide with the production of chlorine. No appearance of DCAC is interesting. At high SED of more than 10 J/L, the generation of TCAA is much suppressed. They are oxidized by the strong plasma and the atomic oxygen generated by the decomposition of the ozone. A little bit DCAC remains if the ozone decomposition is not enough (the atomic oxygen is also not sufficient). Another feature of the byproduct is the production of the chlorine. At high SED, especially with large amount of the catalyst, the chlorine production is very large. Maybe TCE can be oxidized to carbon oxide, water and chlorine, finally in this process. Therefore, the chlorine must be trapped finally by other method.

4.3 Humidity Effects

As well known, the ozone generation in the air is much suppressed by the humidity. Those effects are also examined for TCE decomposition by the plasma where the catalyst is not used for simplicity. The ozone generation according with the input power (SED) in the 250 ppm TCE contaminated synthesized air is shown in Fig.4-7 where RH=0 is not means perfect dry (ultra-dry) but without artificial humidification where RH means relative

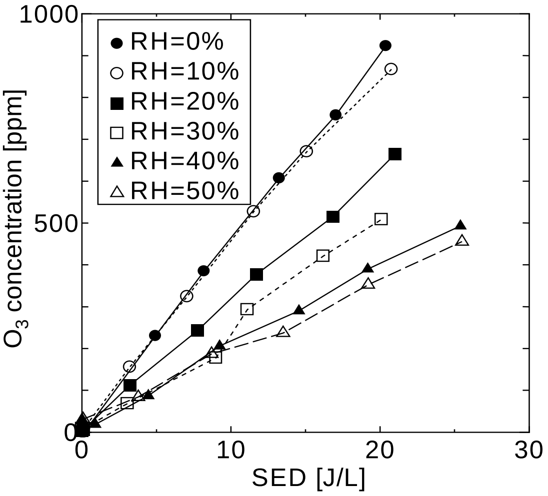

Fig.4-7 The ozone generation in theTCE contaminated air with the input discharge energy (SED) for different humidity.

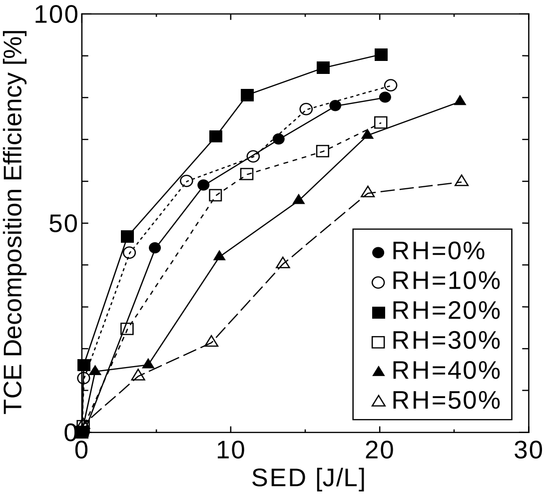

Fig.4-8 TCE decomposition efficiency change with the input energy density (SED) for different humidity conditions.

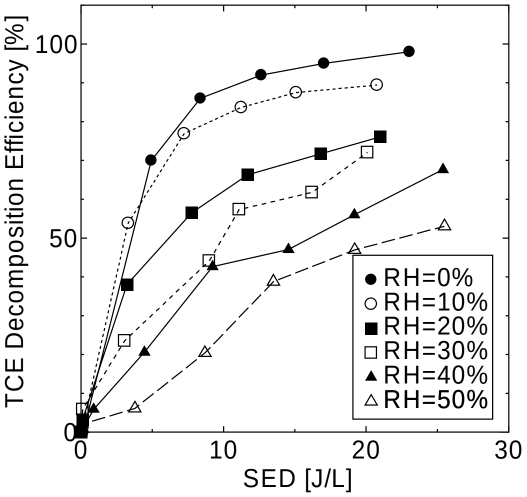

Fig.4-9 TCE decomposition efficiency versus the discharge input power (SED) for different humidity where the amount of the catalyst is 500 mg.

humidity. Humidity from 10 % to 50 % is adjusted by the bubbling water temperature. In the case of pure air, the generation of the ozone in super dry condition is much higher than the data shown in Fig.4-7 because of the existence of TCE which also suppresses the ozone generation pretty large. At the same condition, TCE decomposition efficiency change with the input power (SED) for different humidity is also shown in Fig.4-8 where the TCE decomposition efficiency is the largest at the humidity of 20 %. Chemical researchers reported that the OH radical has very strong oxidation ability and the decomposition of .aromatic compounds is enhanced by the water addition. In the case of chain hydrocarbon decomposition, the decomposition efficiency is not so good in total. In fact, for the non-thermal plasma process of dilute TCE with the catalyst as shown in the previous section in this paper, the dry condition is better because of that the rich generation of the ozone in dry condition enhances the catalyst-assisted TCE decomposition as shown in Fig.4-9 where the amount of the catalyst is 500 mg. In Figs.4-7 and 4-8, the similarity of the data at RH=0 and RH=10%, may be due to the back ground water vapour effect which is not well controlled in this experiment.

One attempt to explain why the OH radical has so much strong oxidation effect is experimentally investigated now. We observed the OH radical rotational temperature change after the discharge by using the LIF technique with multi-spectra. OH temperature becomes large just after the discharge when the humidity is high. At high temperature, the chemical reaction is much enhanced. The details of that will be presented in near future.

5 Summary

The dilute trichloroethylene decomposition in the atmospheric pressure (synthesized) air by using the non-thermal plasma process is much enhanced by the post catalyst process where the catalyst works as the ozone decomposer and TCE also oxidized by the atomic oxygen as the ozone decomposition product. If the amount of the catalyst is sufficient, 2 or 3,000 mg for gas flow rate of 1l/min in our case, TCE decomposition is very high, close to 100% at SED of 5 J/L but for better oxidation (no toxic by-products) SED should be 20 J/L. In this case, main by-products are carbon-oxide, water, chlorine but still a little bit amount of phosgene is also detected.

Humidity effects are also examined and the generation of OH radicals by the discharge enhances the OH temperature and the chemical reaction is increased. However, for TCE decomposition, the decrease of the ozone generation with the humidity suppresses the total decomposition and the dry condition is much better in total.

Precise oxidation mechanism of dilute TCE in the plasma and in the catalyst are not yet known but some tendency is shown in this paper.

6 Acknowledgement

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7 Literature

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