

THERMAL DECOMPOSITION OF SO₃

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Abstract

The iodine-sulfur and the Westinghouse method are recognised as thermochemical methods for producing hydrogen from water. Thermal decomposition of SO₃ is an important process in both methods. This study evaluated the decomposition rate of SO₃ using a flow type apparatus. The decomposition rate of SO₃ was evaluated by the temperature dependence of oxygen concentration using a chemical kinetic model. The decomposition of SO₃ was assumed to be homogeneous reaction of first order. The decomposition rate without catalyst was estimated to be $3.99 \times 10^{11} \exp(-33,096/T) \text{ s}^{-1}$. When hematite was used as the catalyst, the decomposition rate constant increased drastically to $1.31 \times 10^{15} \exp(-36,299/T) \text{ s}^{-1}$. The decomposition ratio for cases with the catalyst was found to approach 1.0 within 2 seconds at 1173K by the chemical dynamics calculation. This indicated that the decomposition of SO₃ was efficient at 1173K.

Introduction

Hydrogen is a promising fuel for the next-generation energy systems. Nuclear energy can provide heat and electricity to produce hydrogen. Thermochemical decomposition of water using nuclear heat has been studied for hydrogen production. Iodine-sulfur (IS) and Westinghouse (WH) method are recognised as high efficient thermochemical methods of producing hydrogen from water [1]. Thermal decomposition of sulfur trioxide (SO_3) is an important process in both the IS and WH method. Although thermochemical data of SO_3 is available, the decomposition rate of SO_3 is not established.

This study evaluated the decomposition rate of SO_3 using a flow type experimental apparatus. Using the obtained decomposition rate, time dependence of the SO_3 concentration was calculated by the chemical kinetic model to find a suitable temperature for the decomposition of SO_3 .

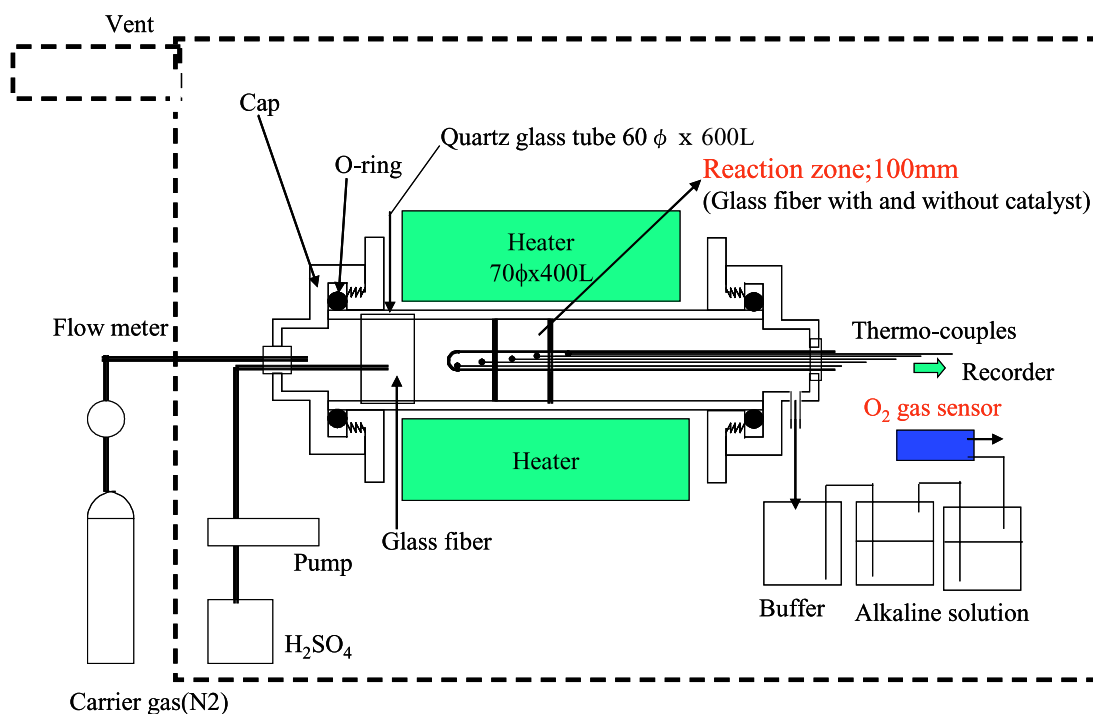
Experimental

The experimental apparatus consisted of an electric heater, a glass tube and gas bubblers as shown in Figure 1. The apparatus was set in a ventilator due to high toxicity of sulfur dioxide (SO_2). The glass tube was set inside the heater. Nitrogen was used as a carrier gas. Sulfuric acid (H_2SO_4) decomposed into SO_3 and water in the inlet part of the glass tube. Then SO_3 decomposed into SO_2 and oxygen in near the center of the glass tube, where a temperature was the highest in the glass tube. After the gases were passing through water in the gas bubblers, the concentration of oxygen was measured.

The flow rate of nitrogen was changed from 0.2 to 0.4 L/min. H_2SO_4 was fed to the glass tube at a rate of about 0.05 cc/min. The temperature inside the glass tube was heated up to 1323K. Temperature distribution in the glass tube was measured by 5 thermocouples. The temperature increase rate was changed from 5 to 20 K/min. The decomposition rate of SO_3 was estimated by the temperature dependence of oxygen concentration using a chemical kinetic model.

Glass fiber with and without a catalyst was used to examine effect of the catalyst on the decomposition of SO_3 . Although a suitable catalyst for the SO_3 decomposition is not known well, a catalyst such as the salts of vanadium and silver, ferric oxide, chromium oxide, and some of rare earths is used by industry for production of H_2SO_4 . The catalyst used for the decomposition of SO_3 was ferric oxide or hematite due to its availability.

Figure 1. Experimental apparatus



Decomposition Rate of SO_3

Chemical Kinetic Model

H_2SO_4 decomposes thermally as follows;



The first reaction occurs at a temperature of around 773K. So H_2SO_4 was expected to decompose at the inlet of the glass tube. The decomposition rate constant of the reaction 2, k , can express in an Arrhenius' formula,

$$k = A \exp(-B/T) \quad (3)$$

where A is pre-exponential factor, B is constant equals E/R , E is activation energy, R is gas constant, and T is temperature. The decomposition ratio, X , was defined as follows,

$$\begin{aligned} X &= [\text{SO}_2] / [\text{SO}_3]_0 \\ &= 2 [\text{O}_2] / [\text{H}_2\text{SO}_4] \end{aligned} \quad (4)$$

where [A] represented molar concentration of A species and 0 showed the initial state. Here the initial concentration of SO₃ was equal to the feeding concentration of H₂SO₄ assuming complete decomposition of H₂SO₄. The oxygen concentration corresponded to half of SO₂ concentration according to the reaction 2. When the decomposition of SO₃ was assumed to be homogeneous reaction of first order, the thermal decomposition rate was expressed as follows,

$$\begin{aligned} d[\text{SO}_2] / dt &= k [\text{SO}_3] \\ d([\text{SO}_2]/[\text{SO}_3]_0) / dt &= k ([\text{SO}_3]_0 - [\text{SO}_2]) / [\text{SO}_3]_0 \\ dX / dt &= k (1 - X) \end{aligned} \quad (5)$$

The following equation could be obtained by integrating the equation 5 [2].

$$\ln\{-\ln(1 - X) / T^2\} = \ln(A / \phi B) - B / T \quad (6)$$

where ϕ is temperature increase rate. If the term of $\ln\{-\ln(1 - X) / T^2\}$ was plotted against $1/T$, the decomposition rate constant could be obtained from the slope and intercept.

Determination of Decomposition Rate Constant

Figure 2 shows plots of $\ln\{-\ln(1 - X) / T^2\}$ as a function of $1/T$ for cases without the catalyst. The slopes should be the same for the cases with different temperature increase rates. The temperature increase rates were 5, 10, and 20 K/min. After the experiment, there was yellowish residual near the outlet of the glass tube. If it was sulfur, further decomposition of SO₃ might occur. In that case, the slopes were not the same for the three cases since the decomposition mechanism was different from the above reactions.

If the decomposition of SO₃ assumed to follow the reaction 2, the average decomposition rate constant without the catalyst was evaluated to be $3.99 \times 10^{11} \exp(-33,096/T) \text{ s}^{-1}$ from the slopes and intercepts shown in Figure 2.

Figure 3 shows plots of $\ln\{-\ln(1 - X) / T^2\}$ as a function of $1/T$ for cases with the catalyst. The slopes were the same for cases with different temperature increase rates. The temperature increase rates were 5, 10, and 20 K/min. The average decomposition rate constant with the catalyst was evaluated to be $1.31 \times 10^{15} \exp(-36,299/T) \text{ s}^{-1}$. The decomposition rate constant increased drastically when the catalyst was used.

Figure 2. Decomposition rate without the catalyst

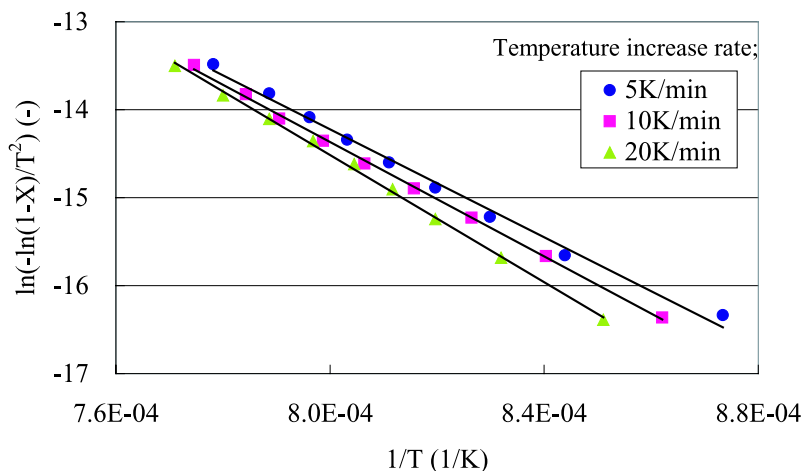
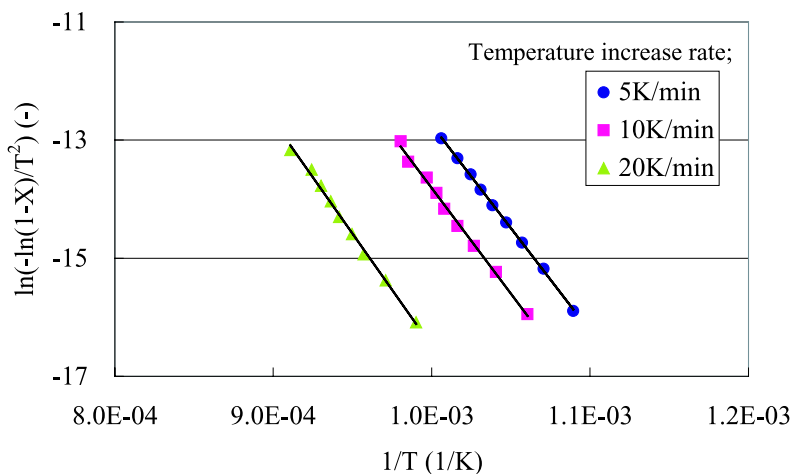


Figure 3. Decomposition rate with the catalyst



Temperature Dependence of Decomposition Ratio

Although the reaction 2 was assumed to be the decomposition reaction, the actual decomposition mechanism of SO_3 was written as follows,

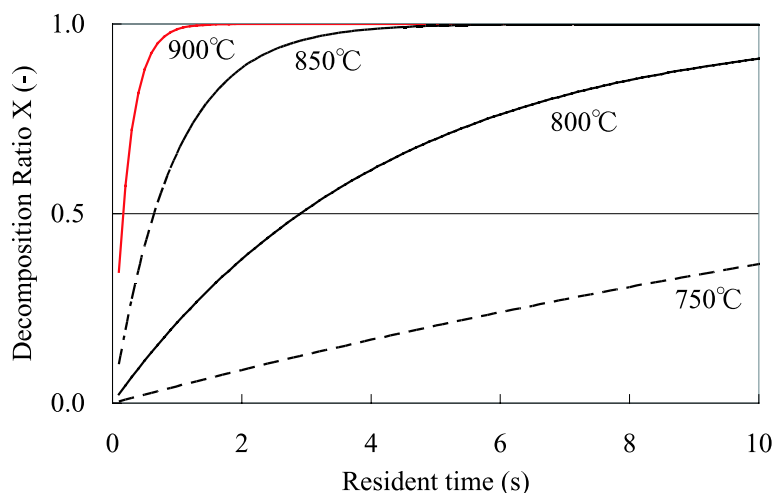


where k is rate constant and M is third species such as water and nitrogen gas in this case. The concentrations of species were calculated by the chemical dynamics calculation. In the calculation, the rate constants were assumed based on the above data and the references [3, 4]. Figure 4 shows the time

dependence of the decomposition ratio for cases with the catalyst. The time needed to reach the decomposition ratio of 1.0 corresponded to resident time in a decomposer of SO_3 . The resident time decreased with increase of a temperature. This indicated that the thermal efficiency was improved with increase of a temperature. The resident time was about 2 seconds at 1 173K. At this temperature, the size of the decomposer could be reduced with the high thermal efficiency.

The decomposition ratio was approaching 1.0 as shown in Figure 4. The decomposition ratio calculated by a thermal equilibrium calculation was about 0.9 at 1 173K. This indicated that the back reaction rate was slower than that expected by the equilibrium calculation. The rate constant of the reaction 9 corresponding to the back reaction was smaller by a factor of 3 than that of the reaction 8 corresponding to the forward reaction. Therefore, the decomposition ratio became nearly 1.0.

Figure 4. Time dependence of decomposition ratio



Summary

The iodine-sulfur (IS) and the Westinghouse (WH) method are recognized as thermochemical methods for producing hydrogen from water. Thermal decomposition of SO_3 is an important process in both the IS and WH method. This study evaluated the decomposition rate of SO_3 using a flow type apparatus. The time dependence of oxygen concentration was measured with a constant temperature increase rate. The decomposition rate of SO_3 was estimated by the temperature dependence of oxygen concentration using a chemical kinetic model. The followings were clarified.

(1) The decomposition of SO_3 was assumed to be homogeneous reaction of first order. The decomposition rate without catalyst was estimated to be $3.99 \times 10^{11} \exp(-33,096/T) \text{ s}^{-1}$. When hematite was used as the catalyst, the decomposition rate constant increased drastically to $1.31 \times 10^{15} \exp(-36,299/T) \text{ s}^{-1}$.

(2) The concentration of chemical species was evaluated by the chemical dynamics calculation. The decomposition ratio for cases with the catalyst approached 1.0 within 2 seconds at 1 173K.

(3) The size of the decomposer of SO_3 could be reduced if the decomposition temperature increased to 1 173K. The thermal efficiency of the decomposition was evaluated to be almost 1.0 at 1 173K.

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TABLE OF CONTENTS

FOREWORD	3
OPENING SESSION	9
<i>Thierry Dujardin</i> Welcome address	11
<i>Osamu Oyamada</i> Opening Remark	13
SESSION I	
The prospects for Hydrogen in Future Energy Structures and Nuclear Power’s Role	15
<i>Chair: M.C. Petri</i>	
<i>M. Hori, M. Numata, T. Amaya, Y. Fujimura</i> Synergy of Fossil Fuels and Nuclear Energy for the Energy Future	17
<i>G. Rothwell, E. Bertel, K. Williams</i> Can Nuclear Power Complete in the Hydrogen Economy?	27
<i>S. Shiozawa, M. Ogawa, R. Hino</i> Future Plan on Environmentally Friendly Hydrogen Production by Nuclear Energy	43
SESSION II	
The Status of Nuclear Hydrogen Research and Development Efforts around the Globe	53
<i>Chair: M. Methnani, W.A. Summers</i>	
<i>M. Hori, S. Shiozawa</i> Research and Development For Nuclear Production of Hydrogen in Japan	55
<i>A.D. Henderson, A. Taylor</i> The U.S. Department of Energy Research and Development Programme on Hydrogen Production Using Nuclear Energy	73
<i>F. Le Naour</i> An Overview of the CEA Roadmap for Hydrogen Production.....	79
<i>Y. Sun, J. Xu, Z. Zhang</i> R&D Effort on Nuclear Hydrogen Production Technology in China	85

<i>A.I. Miller</i> An Update on Canadian Activities on Hydrogen.....	93
<i>Y-J. Shin, J-H. Kim, J. Chang, W-S. Park, J. Park</i> Nuclear Hydrogen Production Project in Korea.....	101
<i>K. Verfondern, W. von Lensa</i> Michelangelo Network Recommendations on Nuclear Hydrogen production	107
SESSION III Integrated Nuclear Hydrogen Production Systems	119
<i>Chairs: A. Miller, K. Verfondern</i>	
<i>X. Yan, K. Kunitomi, R. Hino and S. Shiozawa</i> GTHTTR300 Design Variants for Production of Electricity, Hydrogen or Both.....	121
<i>M. Richards, A. Shenoy, K. Schultz, L. Brown, E. Harvego, M. Mc Kellar, J.P. Coupey, S.M. Moshin Reza, F. Okamoto, N. Handa</i> H2-MHR Conceptual Designs Based on the SI Process and HTE	141
<i>P. Anzieu, P. Aujollet, D. Barbier, A. Bassi, F. Bertrand, A. Le Duigou, J. Leybros, G.Rodriguez</i> Coupling a Hydrogen Production Process to a Nuclear Reactor	155
<i>T. Iyoku, N. Sakaba, S. Nakagawa, Y. Tachibana, S. Kasahara, K. Kawasaki</i> HTTR Test Programme Towards Coupling with the IS Process.....	167
<i>H. Ohashi, Y. Inaba, T. Nishihara, T. Takeda, K. Hayashi Y. Inagaki</i> Current Status of Research and Development on System Integration Technology for Connection Between HTGR and Hydrogen Production System at JAEA	177
SESSION IV Nuclear Hydrogen Technologies and Design Concepts	187
<i>Chairs: K. Kunitomi, J.S. Herring, Y.S. Shin, T. Takeda</i>	
<i>K. Onuki, S. Kubo, A. Terada, N. Sakaba, R. Hino</i> Study on Thermochemical Iodine-Sulfur Process at JAEA	189
<i>S. Kubo, S. Shimizu, H. Nakajima, K. Onuki</i> Studies on Continuous and Closed Cycle Hydrogen Production by a Thermochemical Water-Splitting Iodine-Sulfur Process	197
<i>A. Terada, Y. Imai, H. Noguchi, H. Ota, A. Kanagawa, S. Ishikura, S. Kubo, J.Iwatsuki, K. Onuki, R. Hino</i> Experimental and Analytical Results on H ₂ SO ₄ and SO ₃ Decomposers for IS Process Pilot Plant.....	205

<i>M.A. Lewis, M.C. Petri, J.G. Masin</i> A Scoping Flowsheet Methodology for Evaluating Alternative Thermochemical Cycles	219
<i>S. Suppiah, J. Li, R. Sadhankar, K.J. Kutchcoskie, M. Lewis</i> Study of the Hybrid Cu-Cl Cycle for Nuclear Hydrogen Production.....	231
<i>M. Arif Khan, Y. Chen,</i> Preliminary Process Analysis and Simulation of the Copper-Chlorine Thermochemical Cycle for Hydrogen Generation	239
<i>W.A. Summers, J.L. Steimke</i> Development of the Hybrid Sulfur Thermochemical Cycle	249
<i>P. Anzieu, P. Carles, A. Le Duigou, X. Vitart, F. Lemort</i> The Sulfur-Iodine and Others Thermochemical Processes Studies at CEA	259
<i>K-K. Bae, K-S. Kang, S-D. Hong, C-S. Park, C-H. Kim, S-H. Lee, G-J. Hwang</i> A Study on Hydrogen Production by Thermochemical Water-splitting IS (Iodine-Sulfur) Process	269
<i>P. Zhang, B. Yu, L. Zhang, J. Chen, J. Xu</i> Present Research Status and Development Plan of Nuclear Hydrogen Production Programme in INET	277
<i>T. Nakagiri, T. Kase, S. Kato, K. Aoto</i> Development of the Thermochemical and Electrolytic Hybrid Hydrogen Production Process for Sodium Cooled FBR.....	287
<i>J.S. Herring, J.E. O'Brien, C.M. Stoots, G.L. Hawkes, P. Lessing, W. Windes, D. Wendt, M. Mc Kellar, M. Sohal, J.J. Hartvigsen</i> Progress in High-temperature Electrolysis for Hydrogen Production.....	297
<i>Y. Kato</i> Possibility of a Chemical Hydrogen Carrier System Based on Nuclear Power	309

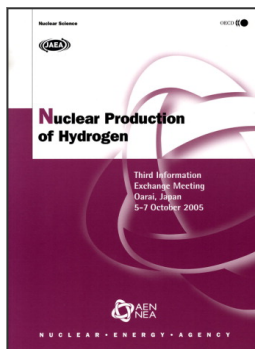
SESSION V

Basic and Applied Science in Support of Nuclear Hydrogen Production

Chairs: Y. Kato, P. Anzieu, Y. Sun

<i>C-H. Kim, B-K. Kim, K-S. Kang, C-S. Park, S-H. Lee, S-D. Hong, G-J. Hwang, K-K. Bae</i> A Study on the HI Concentration by Polymer Electrolyte Membrane Electrodialysis.....	321
<i>H-S. Choi, G-J. Hwang, C-S. Park, H-J. Kim, K-K. Bae</i> The Preparation Characteristics of Hydrogen Permselective Membrane for Higher Performance in IS Process of Nuclear Hydrogen Production	329
<i>H. Karasawa, A. Sasahira, K. Hoshino</i> Thermal Decomposition of SO ₃	337

<i>S. Fukada, S. Suemori, K. Onoda</i> Direct Energy Conversion by Proton-conducting Ceramic Fuel Cell Supplied with CH ₄ and H ₂ O at 600-800°C	345
<i>M. Ozawa, R. Fujita, T. Suzuki, Y. Fujii</i> Separation and Utilisation of Rare Metal Fission Products in Nuclear Fuel Cycle as for Hydrogen Production Catalysts?.....	355
<i>H. Kawamura, M. Mori, S-Z. Chu, M. Uotani</i> Electrical Conductive Perovskite Anodes in Sulfur-based Hybrid Cycle	365
<i>Y. Izumizaki, K-C. Park, Y. Tachibana, H. Tomiyasu, Y. Fujii</i> Generation of H ₂ by Decomposition of Pulp in Supercritical Water with Ruthenium (IV) Oxide Catalyst.....	381
SESSION SUMMARIES	389
RECOMMENDATIONS	391
<i>Annex A: List of Participants</i>	393
<i>Annex B: Meeting Organisation</i>	411
<i>Annex C: Additional Presentations to the Second HTTR Workshop</i>	413



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