Catalytic reduction of N\textsubscript{2}O with CH\textsubscript{4} over various Cu-SBA-15 catalysts

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\textbf{ABSTRACT} – The N\textsubscript{2}O catalytic reduction by methane over Cu-SBA-15 molar ratio (1:30) was studied based on physical mixture, impregnation method and pH adjustment method preparation. All catalytic reduction of N\textsubscript{2}O with methane were carried out in a flow reactor system at atmospheric pressure with 100 mL/min total flow was used. For the N\textsubscript{2}O:CH\textsubscript{4} ratio effect, suggested that N\textsubscript{2}O reacts with CH\textsubscript{4} is represented by 4N\textsubscript{2}O + CH\textsubscript{4} \→ 4N\textsubscript{2} + CO\textsubscript{2} + 2H\textsubscript{2}O. The Cu/SBA-15 prepared by pH adjustment method has highest activity compared to Cu-SBA-15 prepared by impregnation method and physical mixture of CuO and SBA-15.

\section{1. INTRODUCTION}

Due to the increasing concern over environmental issues, studies on N\textsubscript{2}O have oriented towards the development of catalytic systems for its elimination. Various types of catalysts have been reported to be active for the decomposition of nitrous oxide. Cu-SBA-15 is one of those materials showing better prospects for application as catalyst for N\textsubscript{2}O decomposition [1-2]. Catalytic reduction is an alternative to catalytic decomposition with the potential to lower the temperature for effective N\textsubscript{2}O removal by addition of a reducing agent. Therefore, the use of hydrocarbons as reducing agent is widely and easily available, such as CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6} or C\textsubscript{3}H\textsubscript{8} needed to meet commercial feasibility [3]. Previous report, the Cu/SBA-15 samples prepared by pH adjustment method shows higher activity on N\textsubscript{2}O decomposition due to copper atom was substituted in the framework of the SBA-15 with better dispersion of copper species on mesoporous silica and easily reduced copper-silica support interaction CuO to Cu due to the weakening of copper - silica support interaction [2,4]. Known that, CH\textsubscript{4} is strong greenhouse-effect gases with a global warming potential (GWP) per molecule of about 20 times that of carbon dioxide. Therefore, it is interesting studies that a selective catalytic reduction (SCR) of N\textsubscript{2}O by CH\textsubscript{4} is applied to simultaneous removal of N\textsubscript{2}O and CH\textsubscript{4} in the emission gases by various Cu-SBA-15.

\section{2. METHODOLOGY}

\subsection{2.1 Cu on SBA-15 preparation}

For Cu on SBA-15 molar ratio (1:30) by the pH adjustment and impregnation samples was prepared based on previous report [2]. Meanwhile, physical mixture of copper oxide in SBA-15 samples was prepared by the required amount of powder form copper oxide was mixed together in one (1) gram of prepared SBA-15 to obtain Si:M molar ratios of 30:1.

\subsection{2.2 N\textsubscript{2}O decomposition and reduction with CH\textsubscript{4}}

The catalytic experiments were carried out in an alumina tube (4.76 mm i.d.) micro-reactor. Amount of 500.0 mg sample was filled into the tube to form a catalyst bed. The reaction temperature was monitored by a K-type thermocouple inserted inside the catalyst bed. The reaction unit was equipped with mass flow controllers and product analysis was performed with online gas chromatograph 7680A (Agilent) equipped with two columns in series (molecular sieve 5A and Heyasep Q) and TCD detector. For N\textsubscript{2}O decomposition, the reaction gas composed of 1.0% N\textsubscript{2}O in He at a total flow rate of 100 mL/min. Meanwhile for N\textsubscript{2}O reduction with CH\textsubscript{4}, reaction gas mixture was composed of 1.0 % N\textsubscript{2}O and 0.1%,0.25% and 1% CH\textsubscript{4} in He at a total flow rate of 100 mL/min, respectively to N\textsubscript{2}O:CH\textsubscript{4} ratio of 10:1, 4:1 and 1:1.

\section{3. RESULTS AND DISCUSSION}

\subsection{3.1 Effect of different N\textsubscript{2}O:CH\textsubscript{4} ratio}

The effect of catalytic activity in the differences N\textsubscript{2}O:CH\textsubscript{4} volume ratio on N\textsubscript{2}O reduction reaction on Cu/SBA-15 (1:30) prepared by pH adjustment sample have been done. Figure 1 shows catalytic activity of N\textsubscript{2}O reduction by CH\textsubscript{4} at different N\textsubscript{2}O:CH\textsubscript{4} ratio compared to N\textsubscript{2}O decomposition in the absence of CH\textsubscript{4}. The catalytic activity of N\textsubscript{2}O decomposition on Cu/SBA-15 catalyst was significantly promoted by the presence of CH\textsubscript{4}. The conversions of CH\textsubscript{4} in different N\textsubscript{2}O:CH\textsubscript{4} volume ratio reactions were compared in Figure 2. CH\textsubscript{4} conversion increased with the reaction temperature and with N\textsubscript{2}O:CH\textsubscript{4} ratio. Meanwhile, Figure 3 shows the following graph N\textsubscript{2} and O\textsubscript{2} formation verses N\textsubscript{2}O conversion at different N\textsubscript{2}O:CH\textsubscript{4} ratio. The slope of the N\textsubscript{2}O decomposition to CH\textsubscript{4} conversion is 4.0, 1.0 and 0.33, for N\textsubscript{2}O:CH\textsubscript{4} ratio of 1:1, 4:1 and 10:1 respectively. Based on relationship of volume and mole of gases in Avogadgo Law, suggested that N\textsubscript{2}O reacts with CH\textsubscript{4} is represented by 4N\textsubscript{2}O + CH\textsubscript{4} \→ 4N\textsubscript{2} + CO\textsubscript{2} + 2H\textsubscript{2}O. Simultaneous presence of N\textsubscript{2}O with CH\textsubscript{4} is essential for the high
selective catalytic reduction (SCR) activity of N₂O with CH₄. This is related to the high initial rate of CH₄ in N₂O + CH₄ reaction on Cu/SBA-15. The CH₄ plays an important role in the N₂O reduction, because the catalytic activities in N₂O conversion were drastically enhanced by the presence of CH₄. According to Nobukawa and Sugawara, nascent oxygen transients (O*) from N₂O dissociation before accommodation on stable adsorption sites can play an important role in activation and oxidation of CH₄. Thus, it seems that methane effectively reduced oxidized active sites (O*) and therefore increased the rate of the N₂O conversion [5].

was shifted to the left from SBA-15 pure sample. Both catalysts sample reached 100% conversion of N₂O at 600°C. Meanwhile, Cu/SBA-15 pH adjustment sample was much higher than other samples N₂O reduction by CH₄.

4. CONCLUSIONS
This paper has successfully demonstrated that the Cu/SBA-15 prepared by pH adjustment has highest activity compared to Cu-SBA-15 prepared by impregnation method and to physical mixture of CuO. Suggestion that N₂O reacts with CH₄ in this study is represented by 4N₂O + CH₄ → 4N₂ + CO₂ + 2H₂O.

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