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# Catalytic reduction of $N_2O$ with $CH_4$ over various Cu-SBA-15 catalysts

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**ABSTRACT** – The $N_2O$ 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 N2O with methane were carried out in a flow reactor system at atmospheric pressure with 100 mL/min total flow was used. For the $N_2O$:$CH_4$ ratio effect, suggested that $N_2O$ reacts with $CH_4$ is represented by $4N_2O + CH_4 \rightarrow 4N_2 + CO_2 + 2H_2O$. 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.

## 1. INTRODUCTION

Due to the increasing concern over environmental issues, studies on $N_2O$ 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 $N_2O$ decomposition [1-2]. Catalytic reduction is an alternative to catalytic decomposition with the potential to lower the temperature for effective $N_2O$ removal by addition of a reducing agent. Therefore, the use of hydrocarbons as reducing agent is widely and easily available, such as $CH_4$, $C_3H_6$ or $C_3H_8$ required to meet commercial feasibility [3]. Previous report, the Cu/SBA-15 samples prepared by pH adjustment method shows higher activity on $N_2O$ 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, $CH_4$ 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 $N_2O$ by $CH_4$ is applied to simultaneous removal of $N_2O$ and $CH_4$ in the emission gases by various Cu- SBA-15.

## 2. METHODOLOGY

### 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.

### 2.2 $N_2O$ decomposition and reduction with $CH_4$

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 on-line gas chromatograph 7680A (Agilent) equipped with two columns in series (molecular sieve 5A and Heyasep Q) and TCD detector. For $N_2O$ decomposition, the reaction gas composed of 1.0% $N_2O$ in He at a total flow rate of 100 mL/min. Meanwhile for $N_2O$ reduction with $CH_4$, reaction gas mixture was composed of 1.0 % $N_2O$ and 0.1%,0.25% and 1% $CH_4$ in He at a total flow rate of 100 mL/min, respectively to $N_2O$:$CH_4$ ratio of 10:1, 4:1 and 1:1.

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of different $N_2O$:$CH_4$ ratio

The effect of catalytic activity in the differences $N_2O$:$CH_4$ volume ratio on $N_2O$ reduction reaction on Cu/SBA-15 (1:30) prepared by pH adjustment sample have been done. Figure 1 shows catalytic activity of $N_2O$ reduction by $CH_4$ at different $N_2O$:$CH_4$ ratio compared to $N_2O$ decomposition in the absence of $CH_4$. The catalytic activity of $N_2O$ decomposition on Cu/SBA-15 catalyst was significantly promoted by the presence of $CH_4$. The conversions of $CH_4$ in different $N_2O$:$CH_4$ volume ratio reactions were compared in Figure 2, $CH_4$ conversion increased with the reaction temperature and with $N_2O$:$CH_4$ ratio. Meanwhile, Figure 3 shows the plotting graph $N_2$ and $O_2$ formation verses $N_2O$ conversion at different $N_2O$:$CH_4$ ratio. The slope of the $N_2O$ decomposition to $CH_4$ conversion is 4.0, 1.0 and 0.33, for $N_2O$:$CH_4$ ratio of 1:1, 4:1 and 10:1 respectively. Based on relationship of volume and mole of gases in Avogadgo Law, suggested that $N_2O$ reacts with $CH_4$ is represented by $4N_2O + CH_4 \rightarrow 4N_2 + CO_2 + 2H_2O$. Simultaneous presence of $N_2O$ with $CH_4$ is essential for the high selective catalytic reduction (SCR) activity of $N_2O$ with $CH_4$. This is related to the high initial rate of $CH_4$ in $N_2O$ + $CH_4$ reaction on Cu/SBA-15. The $CH_4$ plays an important role in the $N_2O$ reduction, because the catalytic activities in $N_2O$ conversion were drastically enhanced by the presence of $CH_4$. According to Nobukawa and Sugawara, nascent oxygen transients (O*) from $N_2O$ dissociation before accommodation on stable adsorption sites can play an important role in activation and oxidation of $CH_4$. Thus, it seems that methane effectively reduced oxidized active sites (O*) and therefore increased the rate of the $N_2O$ conversion [5].

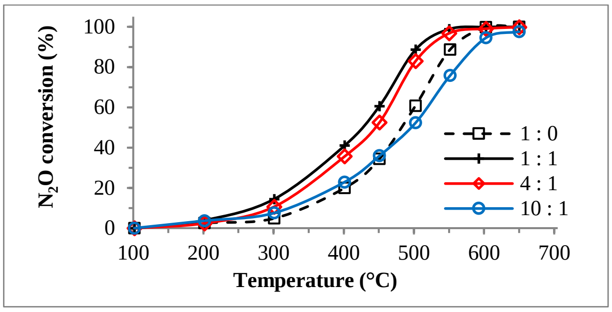


Figure 1 The catalytic activity of $N_2O$ reduction by $CH_4$ on Cu/SBA-15 at different $N_2O$:$CH_4$ ratio.

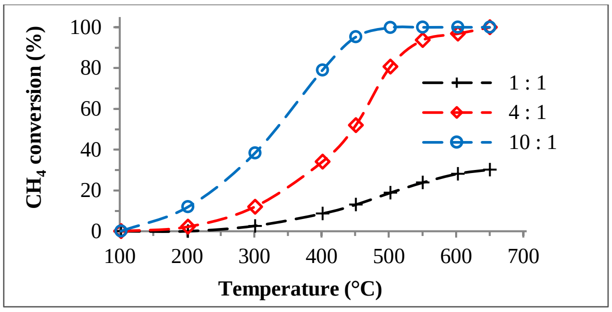


Figure 2 $CH_4$ conversion against Reaction temperature on different $N_2O$:$CH_4$ ratio.

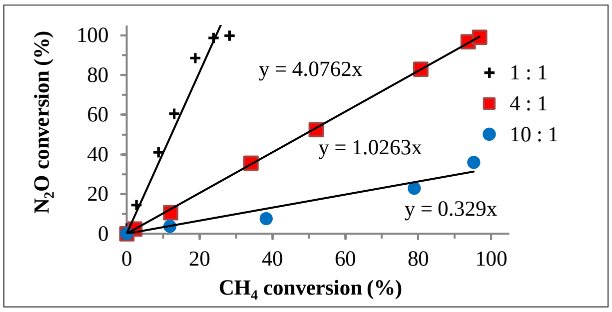


Figure 3 Plotting $N_2O$ conversion verses $CH_4$ conversion on different $N_2O$:$CH_4$ ratio.

### 3.2. Catalytic activity of $N_2O$ conversion

Figure 4 present $N_2O$ decomposition on various copper on SBA-15. Cu/SBA-15 prepared through pH modification sample highest activity causing 80 % conversion at 550 °C. Cu on SBA-15 prepared by impregnation method and physical mixture samples show reached 80 % conversion at 650 °C.

Meanwhile, catalytic activity of $N_2O$ reduction by $CH_4$ on various copper on SBA-15 was shows as in Figure 5. For Cu-SBA-15 impregnated, and CuO-SBA-15 physical mixture sample, the $N_2O$ conversion curve was shifted to the left from SBA-15 pure sample. Both catalysts sample reached 100% conversion of $N_2O$ at 600°C. Meanwhile, Cu/SBA-15 pH adjustment sample was much higher than other samples $N_2O$ reduction by $CH_4$.

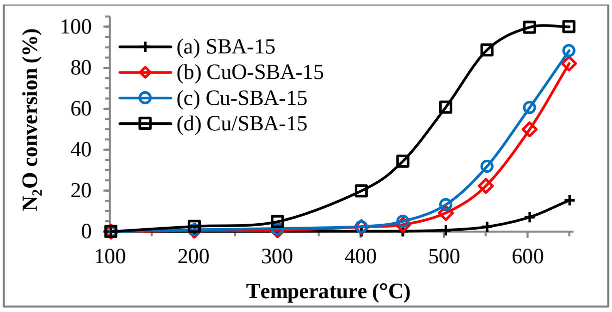


Figure 4 The catalytic activity of $N_2O$ decomposition on (a) SBA-15, (b) CuO-SBA-15 (1:30) physical mixture, (c) Cu-SBA-15 (1:30) prepared by impregnated, and (d) Cu/SBA-15(1:30) prepared by pH modification.

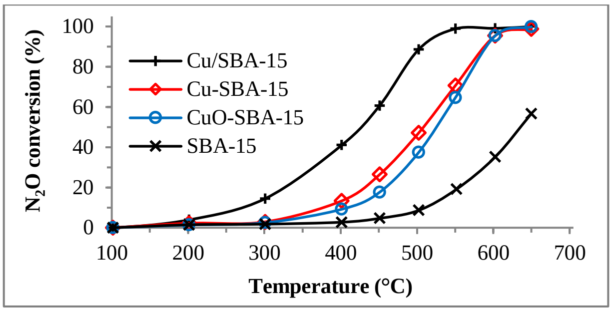


Figure 5 The catalytic activity of $N_2O$ reduction by $CH_4$ at $N_2O$:$CH_4$ (1:1) volume ratio on various copper condition of (a) Cu/SBA-15 pH adjustment, (b) Cu-SBA-15 impregnated, (c), CuO-SBA-15 physical mixture and (d) SBA-15.

## 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 $N_2O$ reacts with $CH_4$ in this study is represented by $4N_2O + CH_4 \rightarrow 4N_2 + CO_2 + 2H_2O$.

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