Catalytic reduction of N₂O with CH₄ over various Cu-SBA-15 catalysts

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ABSTRACT – The N₂O 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 N₂O:CH₄ ratio effect, suggested that N₂O reacts with CH₄ is represented by 4N₂O + CH₄ → 4N₂ + CO₂ + 2H₂O. 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 N₂O 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 N₂O decomposition [1-2]. Catalytic reduction is an alternative to catalytic decomposition with the potential to lower the temperature for effective N₂O removal by addition of a reducing agent. Therefore, the use of hydrocarbons as reducing agent is widely and easily available, such as CH₄, C₂H₆ or C₃H₈ required to meet commercial feasibility [3]. Previous report, the Cu/SBA-15 samples prepared by pH adjustment method shows higher activity on N₂O 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, CH₄ 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 N₂O by CH₄ is applied to simultaneous removal of N₂O and CH₄ 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 N₂O decomposition and reduction with CH₄

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 N₂O decomposition, the reaction gas composed of 1.0% N₂O in He at a total flow rate of 100 mL/min. Meanwhile for N₂O reduction with CH₄, reaction gas mixture was composed of 1.0% N₂O and 0.1%,0.25% and 1% CH₄ in He at a total flow rate of 100 mL/min, respectively to N₂O:CH₄ ratio of 10:1, 4:1 and 1:1.

3. RESULTS AND DISCUSSION

3.1 Effect of different N₂O:CH₄ ratio

The effect of catalytic activity in the differences N₂O:CH₄ volume ratio on N₂O reduction reaction on Cu/SBA-15 (1:30) prepared by pH adjustment sample have been done. Figure 1 shows catalytic activity of N₂O reduction by CH₄ at different N₂O:CH₄ ratio compared to N₂O decomposition in the absence of CH₄. The catalytic activity of N₂O decomposition on Cu/SBA-15 catalyst was significantly promoted by the presence of CH₄. The conversions of CH₄ in different N₂O:CH₄ volume ratio reactions were compared in Figure 2, CH₄ conversion increased with the reaction temperature and with N₂O:CH₄ ratio. Meanwhile, Figure 3 shows the plotting graph N₂ and O₂ formation verses N₂O conversion at different N₂O:CH₄ ratio. The slope of the N₂O decomposition to CH₄ conversion is 4.0, 1.0 and 0.33, for N₂O:CH₄ ratio of 1:1, 4:1 and 10:1 respectively. Based on relationship of volume and mole of gases in Avogadro Law, suggested that N₂O reacts with CH₄ is represented by 4N₂O + CH₄ → 4N₂ + CO₂ + 2H₂O. Simultaneous presence of N₂O with CH₄ 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](image1.png)

**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](image2.png)

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

![Figure 3](image3.png)

**Figure 3** Plotting N_2O conversion versus 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](image4.png)

**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 impregnation, and (d) Cu/SBA-15(1:30) prepared by pH modification.

![Figure 5](image5.png)

**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 → 4N_2 + CO_2 + 2H_2O.

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