Kinetic and Stability Cu-SBA-15 catalysts in Reduction of N_2O with CH_4

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ABSTRACT – The kinetics of N_2O decomposition and reduction via CH_4 over Cu on SBA-15 molar ratio (1:30) was studied based on physical mixture, impregnation method and pH adjustment method preparation. All catalytic activities were carried out in a flow reactor system at atmospheric pressure with 100 mL/min total flow. The Cu/SBA-15 pH adjustment method has highest activity compared to another samples prepared. The activation energies become lower for N_2O decomposition with present of CH_4 and The sample of Cu/SBA-15 prepared by pH adjustment method was lowest activation energy, Ea (63 kJ/mol) compare to N_2O decomposition (92 kJ/mol) at 550 ºC and demonstrated a good stability.

1. INTRODUCTION

Nitrous oxide (N_2O) pollution abatement is an important environmental problem due to the high greenhouse potential of N_2O [1]. 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 [2]. N_2O and CH_4 are strong greenhouse-effect gases with a global warming potential (GWP) per molecule of about 300 and 30 times that of carbon dioxide, respectively [3]. SBA-15 is a mesoporous silica molecular sieves with large surface area, uniform hexagonal channels and higher hydrothermal stability, these are advantageous characteristics of a catalytic support. Previous report, the Cu on SBA-15 was prepared with better dispersion of Cu species on mesoporous silica and easily reduced copper-silica support interaction CuO to Cu due to the weakening of copper - silica support interaction [4]. Therefore, it is interesting to investigate of the kinetics of N_2O decomposition and reduction via CH_4 over selected catalysts Cu on SBA-15 different prepared condition.

2. METHODOLOGY

2.1. The various Cu on SBA-15 Preparation

For pH adjustment and impregnation method of Cu on SBA-15 molar ratio (1:30) samples was prepared based on previous report [4]. Meanwhile, physical mixture of copper oxide in SBA-15 samples was prepared by the mixed amount of CuO powder form together in 1.0 gram of prepared SBA-15 to obtain Si:M molar ratios of 30.

2.2. Kinetic studies

The procedure for the kinetics experiments performed in this study was adopted from Shen et al. [5]. The first-order rate constant (k), and the activation energy (E_a) were calculated based on the first-order reaction assumption for N_2O decomposition, the rate of N_2O decomposition can be represented as (Eq. 1),

$$r = k\, P_{N_2O} = A\, e^{-Ea}/RT\, P_{N_2O} \qquad \text{(Eq. 1)}$$

Pseudo-first-order rate constants were calculated using the formula in Eq. 2,

$$k = -\frac{\ln(1-x)\,F}{m_{cat}\,P} \qquad \text{(Eq. 2)}$$

where x is the N_2O conversion, F was referred to total gases flow through the reactor and P always refer to the total pressure. Meanwhile m_{cat} is the amount of the catalyst and T is the reaction temperature in Kelvin unit. The ln (k) versus $1/T$ was plotted accordingly to the data collected under steady-state reaction. The apparent activation energy presented in slope of this plot, and the intercept represents associated pre-exponential factor.

2.3. Stability Testing

Stability test on samples of supported catalyst was conducted under the following experimental conditions: weight over flow (W/F) = 0.18 gs/mL, ambient pressure, reaction temperature 600°C for 10 hours. gas composition of 1.0% N_2O with balance of He, in total flow rate of 100 mL/min used up for N_2O decomposition,. Meanwhile, for N_2O reduction with CH_4, reaction, gas mixture was composed of 1.0 % N_2O and 1.0 % CH_4 in He at a total flow rate of 100 mL/min.

3. RESULTS AND DISCUSSION

3.1. Catalytic Activity of N_2O reduction

The comparison among catalytic activity of N_2O decomposition and N_2O reduction by CH_4 on copper on SBA-15 catalysts under different preparation condition (physical mixture, impregnation and pH adjustment method) was shows as in Figure 1. All samples show the N_2O conversion in N_2O reduction by CH_4 reactions was much higher compare to N_2O decomposition reactions. The N_2O decomposition with addition of CH_4 was significant improvement in catalytic condition for N_2O conversion on all Cu on SBA-15 catalysts under different preparation.

3.2. Kinetic studies

The Arrhenius plots of N_2O decomposition and N_2O reduction by CH_4 on various copper conditions on SBA-15 are shown in Figure 2. For Cu/SBA-15 pH adjustment sample, decreased of activation energy from 92 kJ/mol to 63 kJ/mol for N_2O decomposition and N_2O reduction by CH_4 was obtain. In general, the activation energies become lower for N_2O decomposition with present of CH_4. Meanwhile for Cu-SBA-15 impregnated and CuO-SBA-15 physical mixtures samples show the similar activation energies indicated that the same active copper species operates during N_2O catalytic decomposition and reduction by CH_4.

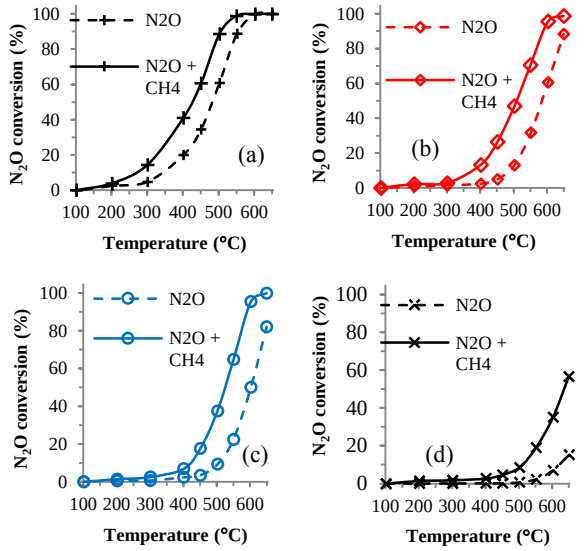

Figure 1. The catalytic activity of N_2O decomposition (- - -) and N_2O reduction by CH_4 (——) on various copper on SBA-15 at N_2O:CH_4 (1:1) ratio for (a) Cu/SBA-15 pH adjustment, (b) Cu-SBA-15 impregnated, (c) CuO-SBA-15 physical mixture and (d) SBA-15.

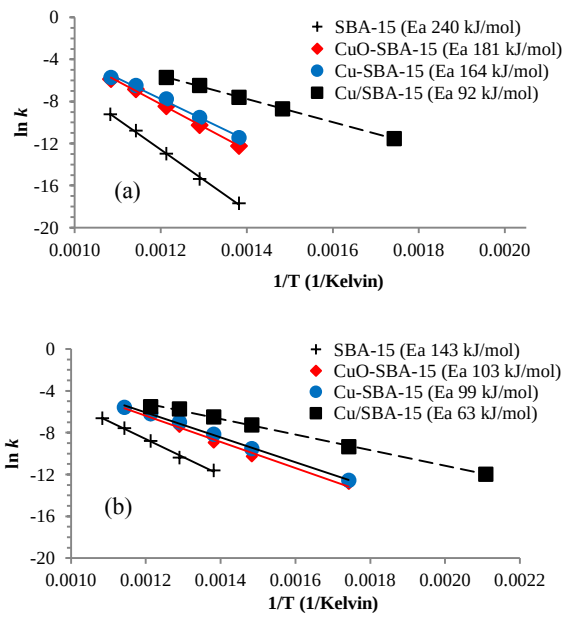

Figure 2. Arrhenius plot of ln K verses 1/T of (a) N_2O decomposition and (b) N_2O reduction by CH_4 for various copper on SBA-15.

3.3. Stability activity

The excellent performance of the types of catalyst under realistic conditions not only refers to activity but also involves stability. All Cu on SBA-15 catalysts under different preparation catalyst samples were exposed to reaction conditions for 600 min on stream at 600 °C for the N_2O decomposition and N_2O reduction by CH_4 as shown in Figure 3. The Cu on SBA-15 pH adjustment, shows with better stability compare to other samples, was decreased 5-10% N_2O conversion after 10 hours.

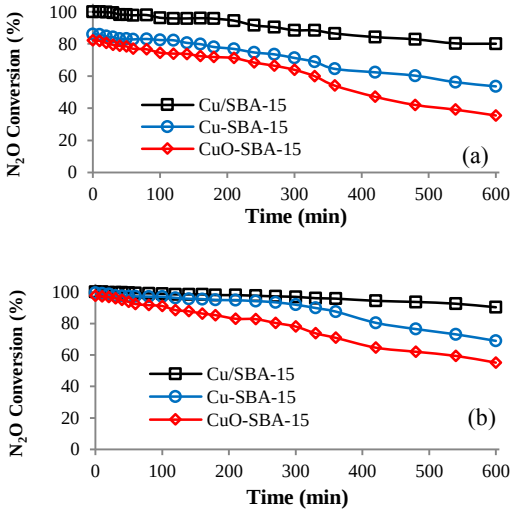

Figure 3. Stability test of (a) N_2O decomposition and (b) N_2O reduction by CH_4 various copper on SBA-15.

4. CONCLUSIONS

This paper has successfully demonstrated that the Cu/SBA-15 prepared by pH adjustment method has highest activity and good stability. Furthermore, the sample also shows lower activation energy compared to physical mixture and impregnation samples method preparation. The activation energy of Cu/SBA-15 pH adjustment sample for N_2O decomposition compare to N_2O reduction by CH_4 was decreased from 92 to 63 kJ/mol at at 550 ºC reaction temperature, indicated that the activation energies become lower for N_2O decomposition with present of CH_4.

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