Impact of Al distribution in the Cu-exchanged CHA-type zeolite on the catalytic performance in CH_4 conversion

Toshiyuki Yokoi[a, b, *], **Yusuke Kunitake**[a], **Ryota Osuga**[a], **Takaya Kimura**[a], **Junko N. Kondo**[a]
[a] *Institute of Innovative Research, Tokyo Institute of Technology, Yokohama 226-8503, Japan*
[b] *JST PRESTO, Yokohama 226-8503, Japan*
**Corresponding author: +81-45-924-5282, yokoi@cat.res.titech.ac.jp*

Abstract: The impact of Al distribution in the Cu-exchanged CHA-type zeolite on the catalytic performance in CH4 conversion was investigated. the Al distribution affected the catalytic performance in CH_4 conversion; Q^4(1Al)-rich catalysts are advantageous in terms of the production of target products from CH_4.

Keywords: CH_4 conversion, Zeolite, Al distribution, Cu ion-exchange

1. Introduction

Methane is a highly abundant and inexpensive source of fuel and chemicals. The development of novel technologies that can convert methane easily into chemicals has strongly been desired. However, its kinetic inertness and low reactivity limit the industrial utilization of methane. Recently, it was reported that Cu-exchanged zeolites are a promising catalyst for the catalytic conversion of methane. We are also tackling the development of novel zeolite-based catalysts for direct conversion of methane into methanol followed by lower olefins.

Meanwhile, recently, we have developed a facile method for preparing the CHA-type zeolite with controlling the Al distribution, *i.e.*, proportion of Q^4(2Al)/Q^4(1Al) ratio, where Q^4(*n*Al) is $Si(OSi)_{4-n}(OAl)_n$. In this work, the impact of Al distribution in the Cu-exchanged CHA-type zeolite on the catalytic performance in CH_4 conversion was investigated.

2. Experimental

The CHA-type aluminosilicate zeolites with different proportions of Q^4(2Al)/Q^4(1Al) ratios were synthesized in the presence of *N*,*N*,*N*-trimethyl-1-adamantammonium cation ($TMAda^+$) from the different starting materials including fumed silica, aluminum hydroxide, and the FAU-type zeolite (JRC-Z-Y5.5, Si/Al = 2.8), with their proportions varied. Cu-ion exchange was carried out using $Cu(NO_3)_2 \cdot 3H_2O$.

The catalytic reaction was performed in a fixed bed reactor. The flow rates of the reactants were $CH_4/O_2/Ar$ = 16/4/5 (SCCM). The catalyst amount was 100 mg. The reaction temperature was varied ranging from 400 to 600 °C, and the reaction time at each temperature was 1 min. The products including CO and CO_2 were analyzed by GC-TCD, and other hydrocarbon products were analyzed by GC-FID.

3. Results and discussion

The ^{29}Si MAS NMR spectra clearly showed that thus obtained CHA-type zeolites had different Al distributions depending on the proportion of the **FAU**-type zeolite as the starting material. The use of the FAU-type zeolite with a high proportion led to the high proportion of Q^4(2Al). Here, representative catalysts were designated as "Q^4(1Al)-rich" and "Q^4(2Al)-rich", respectively. The Si/Al ratios of Q^4(1Al)-rich and Q^4(2Al)-rich were 9 and 13, respectively, and the Cu content for both catalysts were almost similar, ca. 1.4 wt%. The Cu state was evaluated by UV.-vis technique; both catalysts gave only one peak at 220 nm, indicating Cu species were highly isolated.

The results of the catalytic reactions were shown in Figure 1. Both catalysts showed similar CH_4 conversion, and it was increased along with the temperature. However, there was a significant difference in the products selectivities between Q^4(1Al)-rich and Q^4(2Al)-rich catalysts. The yield of CO_2 on Q^4(2Al)-rich catalyst was higher than that on Q4(1Al)-rich. The yields of target products, CH_3OH, DME, C_2H_6 and C_2H_4 on Q4(1Al)-rich were higher than those on Q4(2Al)-rich. These results clearly suggest that the Al distribution affected the catalytic performance in CH_4 conversion; Q4(1Al)-rich catalysts are advantageous in terms of the production of target products from CH_4.

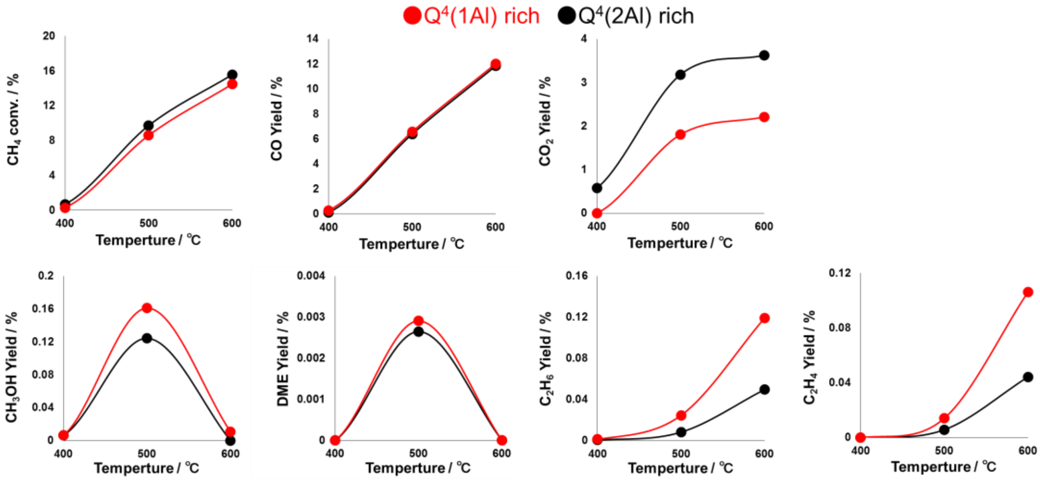

Figure 1. The results of the catalytic conversion of CH_4 over Q4(1Al)-rich and Q4(2Al)-rich catalysts.

The Cu state was also investigated by NO-adsorbed FT-IR technique as follow [4]. First, the catalysts were evacuation at 723 K, and then NO molecules was adsorbed onto the catalysts at 293 K. Figures 2 (a) and (b) show the NO-adsorbed FT-IR spectra with different NO loadings of Q4(1Al)-rich and Q4(2Al)-rich. The peaks around 1900-1950 cm^{-1} are derived from to NO adsorbed on Cu^{2+} species, and ones around 1810 cm^{-1} are derived from NO adsorbed on Cu^{+} species. There was a marked change in the peaks derived from NO adsorbed on Cu^{+} species; Q4(1Al)-rich first gave a peak at 1809 cm^{-1}, but another peak at 1816 cm^{-1} was observed when NO loading was increased. However, Q4(2Al)-rich did not exhibit such change. Thus, we have considered that the Al distribution would affect the state of Cu species, resulting in different catalytic performance.

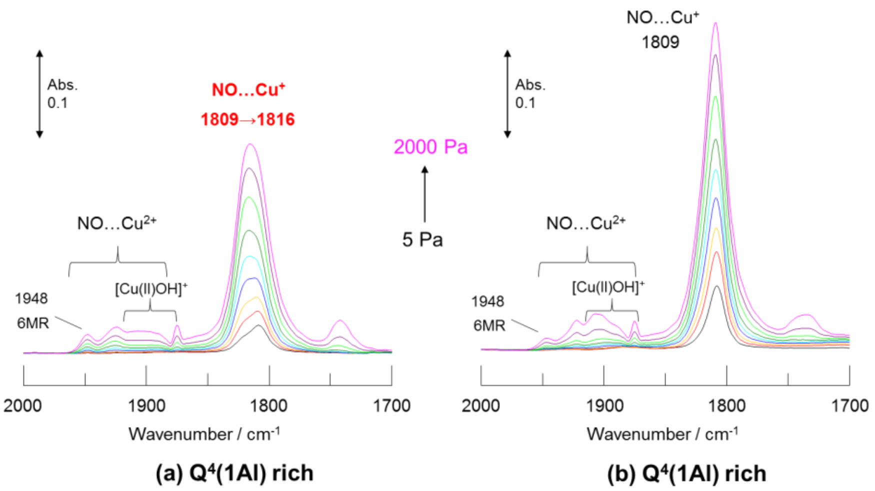

Figure 2. CHA-type aluminosilicate zeolites with different proportions of Q4(2Al)/Q4(1Al) ratios.

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