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論 文 要 旨

THESIS SUMMARY

専攻： Department of	機械宇宙システム　　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	（工学）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Experimental investigation on the reduction of NOx emissions by HC-SCR process over the Cu-impregnated zeolite-based catalysts has been presented and discussed in this research thesis for the practical application of passive type HC-SCR system. The Cu/zeolite catalysts were prepared by an incipient wetness impregnation method by varying the Cu loading in a range of 1–10 wt%. The zeolite supports have different their frameworks, including SSZ-13 (CHA framework), ZSM-5 (MFI framework), and BETA (BEA framework). A series of Cu/zeolite catalysts were explored in detail for the main purpose of reducing NOx emissions by the 'C_3H_6-SCR' and 'C_4H_{10}-SCR' process. Several techniques, including HC/NOx ratio, hydrocarbon reductant, Cu content, zeolite framework, coexistent gas, and reaction environment (catalytic reactor system), were systematically explored and their effects on the NOx removal efficiency of Cu/zeolite catalysts were assessed. The key conclusions drawn from the experimental results of this thesis are summarized.

In chapter 1, recent de-NOx techniques and relevant reaction mechanisms using automotive catalysts were reviewed including HC-SCR. To investigate the effectiveness of HC-SCR, major preceding research was reviewed for various catalytic components and reducing agents.

In chapter 2, the parent zeolites and Cu/zeolites were characterized by various technique. The loading levels of Cu metal species were close to the theoretical loading amount, suggesting successfully introduction of Cu species. The Cu loading led to a drop of BET specific surface area because Cu species covered both the internal and external surface of zeolite, resulting in blocking the accessible zeolite pores. The XRD patterns demonstrated that the impregnation of Cu did not affect any modification of the respective zeolite structures. When increasing the Cu loading, chemical shift of ^{27}Al shifted to lower region, indicating the variation of average Al–O–Si angles in the zeolite framework. The valence states of Cu species were mainly presented as isolated Cu^{2+}, d-d transition of Cu^{2+}, and CuO clusters. The Cu/zeolites were more in favorable for the formation of CuO clusters with an increase in the Cu loading. The intra-crystalline diffuse diameter of respective zeolites affected the particle diameter of Cu, which was severely agglomerated over the SSZ-13 zeolite.

In chapter 3, Cu/zeolite catalysts were evaluated for the main purpose of reducing NOx emissions by the C_3H_6-SCR process in the presence of O_2, CO, CO_2, and H_2O. To reach a high NOx conversion, a high HC/NOx ratio was needed. Increasing the HC/NOx ratio was favorable for the catalytic activity because more reducing agent could be available during the C_3H_6-SCR process. Among the prepared Cu/zeolite catalysts, 2Cu/ZSM-5 demonstrated the highest NOx conversion to N_2 (68.5% at T = 360℃) at the highest HC/NOx ratio, followed by 1Cu/SSZ-13 (58.2% at T = 420℃) and 10Cu/BETA (56.1% at T = 375℃). Thus, the ZSM-5 zeolite, with a medium pore framework, was better suited for the C_3H_6-SCR process than SSZ-13, with a small pore framework, and BETA, with a large pore framework. The presence of isolated Cu^{2+} ions provided active sites for NOx reduction.

In chapter 4, the effects of the zeolite framework and Cu loading on the catalytic activity for the C_4H_{10}-SCR were evaluated. The Cu loading improved the NOx conversion and shifted the temperature window of the maximum NOx conversion to lower regions compared to those for the parent zeolites. 2Cu/ZSM-5 exhibited the best de-NOx performance with nearly 74% at 465℃, followed by 10Cu/BETA (58% at T = 465℃) and 1Cu/SSZ-13 (38% at T = 585℃). These results were related to the effect of geometry-limited diffusion of C_4H_{10} in the respective zeolite channel system, in which the reductant had easy access to the active sites in the channels of ZSM-5 and BETA zeolite, but C_4H_{10} was highly restricted in the SSZ-13 channels.

In chapter 5, the effects of coexistent gases and hydrothermal aging on the catalytic activity were investigated in both C_3H_6- and C_4H_{10}-SCR. Increasing the O_2 concentration in the feed gas had a positive effect on the de-NOx performance because the partial oxidation of hydrocarbons was enhanced at relatively low temperature with an increase in O_2 concentration, indicating that O_2 is essential gas in HC-SCR process. However, a negative effect was observed when CO_2 was introduced in the feed gas because NOx adsorption and partial oxidation of hydrocarbons were highly inhibited by coexistent CO_2. When O_2 was not introduced in the feed gas, the NOx conversion increased at a relatively higher reaction temperature, reaching 98% NOx conversion, but this condition induced an undesired side-reaction, producing a large amount of NH_3. The drop in NOx conversion after hydrothermal aging was attributed to the inhibitory effect of the partial oxidation of hydrocarbons. The hydrothermal aging also induced the collapse of micropores, Cu sintering, and a drop in the zeolite crystallinity, thereby deactivating the catalytic activities.

In Chapter 6, from the experimental results of all the present research, key findings of respective chapter are summarized. And, research recommendations and relevant developments of HC-SCR system are also suggested.