Iron based monolithic catalysts supported on Al_2O_3, SiO_2, and TiO_2: A comparison for NO reduction with propane

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Abstract: The support effects on iron based monolithic catalysts for NO reduction with propane have been investigated. The C_3H_8-SCR performance over different supports (alumina, silica, and titania) decreased in the order as $Fe/Al_2O_3/CM > Fe/SiO_2/CM > Fe/TiO_2/CM$ at temperatures from 200 to 600 °C. The high activity of $Fe/Al_2O_3/CM$ is mainly attributed to the good redox properties and the abundant Lewis acid sites. Based on in situ DRIFT studies, the increase of Lewis acid sites will enhance the formation of NO_2/NO^{3-} species and acetate/formate species, then promote the catalytic activity.

Keywords: SCR of NO, C_3H_8, Support.

1. Introduction

The selective catalytic reduction of NO_x with hydrocarbons (SCR-HC) is a promising method for the removal of NOx from various exhausts [1]. Metal oxide-based catalysts have attracted considerable attention as potential candidates for the SCR-HC because of their high stability under hydrothermal conditions [2]. Recently, we formulated a series of monolithic cordierite-based Fe/Al_2O_3 catalysts by sol-gel and impregnation method for NO reduction with C_2H_6 [3] and C_3H_8 [4]. The catalysts exhibited more than 90% NO reduction and the good resistance to SO_2 and H_2O. For real industrial applications, the catalysts have to prepare as a shaped substrate (e.g., honeycomb cordierite). The common practice is to firstly coat a porous support on the surface of the honeycomb cordierite before loading the active metals. However, the support effects on monolithic catalysts for NO_x adsorption and reduction with hydrocarbons were not well studied. In this study, the support effects on iron based monolithic catalysts for NO reduction with propane will be investigated.

2. Experimental

Ceramic block matrices with a honeycomb cordierite were used as catalyst shaped structure. In order to distribute the iron species evenly on the surface of substrate, the raw monolithic cordierite samples were coated with sol solution (alumina, silica, and titania) by immersing and then drying and calcining in series respectively. The iron species were introduced via wet impregnation by using $Fe(NO_3)_3$ solution, with details reported previously [5]. The resulting catalysts are named Fe/SU/CM, where “SU” denotes the different support (e.g., $Fe/TiO_2/CM$ denotes a cordierite matrix sample coated 20% titania support with iron loading of about 5%). Their characterization and application in C_3H_8-SCR have been investigated. These samples were characterized by means of N_2-physisorption, XRD, XPS, SEM, H_2-TPR, Py-FTIR and in situ DRIFTS technologies to reveal the support effects on their catalytic properties.

3. Results and discussion

As shown in Fig. 1, the C_3H_8-SCR performance decreased in the order as $Fe/Al_2O_3/CM > Fe/SiO_2/CM > Fe/TiO_2/CM$ at temperatures from 200 to 600 °C. $Fe/Al_2O_3/CM$ showed the highest activity with a NO conversion of 100% in the presence of oxygen at 500 ℃. The results of catalytic activity tests indicate that support over iron based catalyst have a significant effect on the performance of NO reduction with C_3H_8. Combined with the characterization results, the different supports had a great influence on specific surface area, surface morphology, lattice oxygen, redox properties and the acid sites, which resulted in differences in the catalytic activity of C_3H_8-SCR. The redox ability of catalyst samples, which is an important factor to affect HC-SCR reaction, followed the order of $Fe/Al_2O_3/CM$ > $Fe/SiO_2/CM$ > $Fe/TiO_2/CM$. Therefore, it is reasonable that $Fe/Al_2O_3/CM$ sample exhibited higher C_3H_8-SCR activity than other samples.

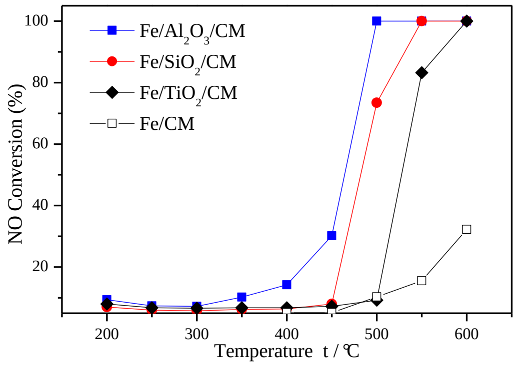

Figure 1. NO conversion over iron based monolithic catalysts on different supports. (Reaction conditions: 0.05% NO, 0.3% C_3H_8, 1% O_2, GHSV=15,000 $mLg^{-1}h^{-1}$)

As can be concluded form the catalytic activity (Fig. 1) and Py-FTIR spectra (Fig. 2), Lewis acid sites are beneficial to catalytic performance for C_3H_8-SCR over iron based monolithic catalysts, while Brønsted acid sites may be not correlated with the catalytic activity. Based on In situ DRIFTS analysis, the intensity of NO_2/NO^{3-} and acetate/formate species was enhanced with elevating the quantity of Lewis acid sites. However, it was not correlated with the Brønsted acid sites. According to our previous work [3-4], the NO_2/NO^{3-} species are reactive toward acetate and formate species, and they act as the key intermediates in the HC-SCR reaction. Therefore, Lewis acid sites seem to play a vital role in the formation of adsorption intermediates for C_3H_8-SCR over iron based monolithic catalysts, the abundant Lewis acid sites will enhance the formation of NO_2/NO^{3-} and acetate/formate species, then promote the catalytic activity.

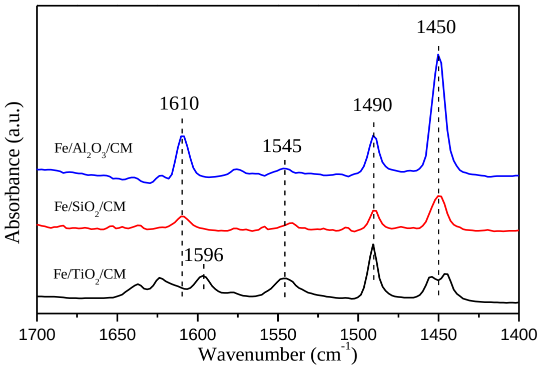

Figure 2. FTIR spectra of pyridine adsorbed at 150 ℃ of iron based monolithic catalysts on different supports.

4. Conclusions

The selective catalytic reduction of NO with propane has been investigated with iron based monolithic catalysts supported on alumina, silica, and titania. Combined with the characterization results, the different supports had a great influence on specific surface area, surface morphology, lattice oxygen, redox properties and the acid sites, which resulted in differences in the catalytic activity of C_3H_8-SCR. $Fe/Al_2O_3/CM$ showed the highest activity with a nitrogen oxide conversion of 100% in the presence of oxygen at 500 ℃. The high activity of $Fe/Al_2O_3/CM$ is mainly attributed to the good redox properties and the abundant Lewis acid sites. Based on in situ DRIFT studies, the increase of Lewis acid sites will enhance the formation of NO_2/NO^{3-} species and acetate/formate species, then promote the catalytic activity.

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