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Activity, propene poisoning resistance and hydrothermal stability of copper exchanged chabazite-like zeolite catalysts for SCR of NO with ammonia in comparison to Cu/ZSM-5

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ABSTRACT

Copper, iron, and mixed copper/iron exchanged zeolites containing ZSM-5 and chabazite-like zeolites (SSZ-13, SAPO-18 and SAPO-34) were studied for selective catalytic reduction (SCR) of NO with NH_3 with or without propene. Cu/ZSM-5, Cu/SSZ-13, Cu/SAPO-18 and Cu/SAPO-34 exhibited high NO conversions without propene. However, as compared to Cu/ZSM-5, NO conversions over Cu/SSZ-13, Cu/SAPO-18 and Cu/SAPO-34 were more stable with propene, due to coke formation over Cu/ZSM-5. The results of N_2-adsorption/desorption and XPS showed that the surface area, Cu^+/Cu^{2+} ratio and the surface amount of Cu content of Cu/ZSM-5 catalysts changed from 324 m^2/g, 0.03 and 11.5 wt% for the fresh Cu/ZSM-5 catalyst to 68 m^2/g, 0.34 and 5.3 wt% for the used sample. However, there were little changes between fresh and used Cu/SSZ-13, Cu/SAPO-18 and Cu/SAPO-34 catalysts. Moreover, Cu/ZSM-5 catalyst showed a larger decline in NO conversion with time on stream and a higher adsorption amount of propene compared to Cu/SSZ-13, Cu/SAPO-18 and Cu/SAPO-34 catalysts. The resistance to hydrocarbon poisoning depended on the pore geometry of the zeolites. During NH_3-SCR, the presence of medium-pore sizes in Cu/ZSM-5 led to hydrocarbon deposition, which blocked the active sites and also decreased the active intermediates needed for NO conversion. Cu/SSZ-13, Cu/SAPO-18 and Cu/SAPO-34 catalysts, on the other hand, with small pores and cage diameters and with one-dimensional channel structures, showed higher hydrocarbon poison resistance. Moreover, these copper exchanged small-pore zeolites showed much higher hydrothermal stability than the medium-pore Cu/ZSM-5.

1. Introduction

Nitrogen oxides (NO_x) from combustion of fossil fuel are a major source for air pollution and can cause photochemical smog, production of acid rain and respiratory problems to mankind [1]. It is known that over 50% of NO_x emissions are from automotive sources, such as gasoline cars and diesel engine trucks, and over 40% of NO_x are from stationary sources, such as power plants using fossil fuels. A most challenging research objective is to remove NO_x from oxygen rich exhaust gas of diesel engines and design a practical diesel SCR catalyst system [2]. Several approaches have been proposed for lean-NO_x abatement, each of them with its own specific sets of problems. The two technologies that seem to have clear advantages among the processes proposed are the selective catalytic reduction either with hydrocarbons (HC-SCR) or with ammonia (NH_3-SCR), and lean-NO_x traps (LNT). The selective catalytic reduction (SCR) of nitrogen oxides with NH_3 as reducing agent, where NH_3 is generated by thermal decomposition of urea, is presently considered as one of the most promising techniques for the removal of NO_x from lean exhaust gases from diesel trucks.

There are several groups of catalysts reported in the literature, which are suitable for this reaction at different temperatures [3]. Noble metals, such as Pt, Pd, and Rh, were active in the selective reduction of NO_x at low temperatures, but the N_2 product selectivity is poor at higher temperatures. These catalysts are less suitable for SCR because they catalyze not only the SCR reaction but also the oxidation of NH_3 to NO, N_2O, and N_2 [4,5]. Metal oxides were also widely studied for this reaction. Among the various mixed metal oxides, V_2O_5–WO_3/TiO_2 has been widely used since 1980s for reducing NO_x emission from stationary power plants; however, concerns remain such as oxidation of SO_2, stability of the catalyst and toxicity of vanadia [6,7]. Zeolite-based catalysts promoted (via ion exchange) by transition metals, such as Fe and Cu, are being considered for practical applications in diesel emission control due to their high activities and better stability at high temperatures [8–12]. These catalysts have high activities for NO decomposition [13] and selective catalytic reduction by hydrocarbons [14]. However, Cu/ZSM-5 and Fe/ZSM-5 are limited by their relatively low

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