Regeneration of hydrothermally aged Cu-SSZ-13 catalyst treated with citric acid solution

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Zeolite catalysts, especially Cu-SSZ-13, are commercially used for NH_3-SCR (Selective Catalytic Reduction) reaction because of its high thermal stability and excellent NOx removal ability. However, deactivation by hydrothermal aging (HTA) is a main problem because zeolite framework Al site is vulnerable to H_2O at high temperature so that Al-O-Si bonds are dissociated by the hydrolysis reaction and located outside the framework, which is called dealumination [1]. The dealumination process makes zeolite lose its acidic properties and SCR activity because Cu ions which is active site of SCR reaction form $CuAlO_x$ species by combining with the dealuminated Al. Such $CuAlO_x$ species can deactivate catalysts and increase unwanted N_2O formation. In this study, we investigated the regeneration of dealuminated Cu-SSZ-13 by treating the hydrothermally aged sample with citric acid solution.

We used citric acid solution for acid treatment to regenerate Cu-SSZ-13(Si/Al_2=40, Cu/Al=0.4) initially aged at 850℃ for 16h with 10% H_2O in N_2 balance. It is known that acidic protons of citric acid can catalyze condensation reaction between Si-OH and Al-OH which causes dealuminated Al to be realuminated in framework [2]. Figure 1 showed that the NH_3 desorption peaks at 350 °C and 500 °C, which are assigned to and Cu related acid site and brønsted acid, respectively, decrease after hydrothermal aging [3]. It means that zeolite acid sites from zeolite Al site and Cu ion decrease together because of dealumination. After treating with citric acid solution, however, the intensity of acid peak at 500 °C increases slightly, which demonstrates that brønsted acid is restored. Figure 2 showed that the hydrothermal aging induced the removal of reduction of Cu ion (200-300°C) and the appearance of the reduction of $CuAlO_x$ species (500-700°C) [4]. However, the treatment with citric acid made the sample having the similar reduction behavior to that of fresh Cu-SSZ-13 as shown in Figure 2, implying the remarkable regeneration of hydrothermally aged Cu-SSZ-13. Such a physicochemical change resulting from acid treatment was correlated with activity result.

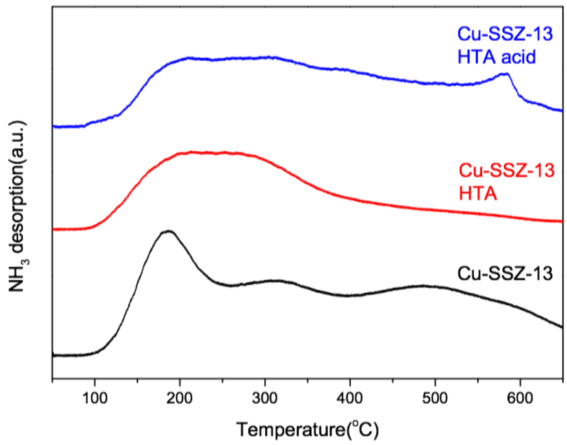

Figure 1. NH_3-TPD profile of Cu-SSZ-13 catalysts (fresh, HTA and acid treated).

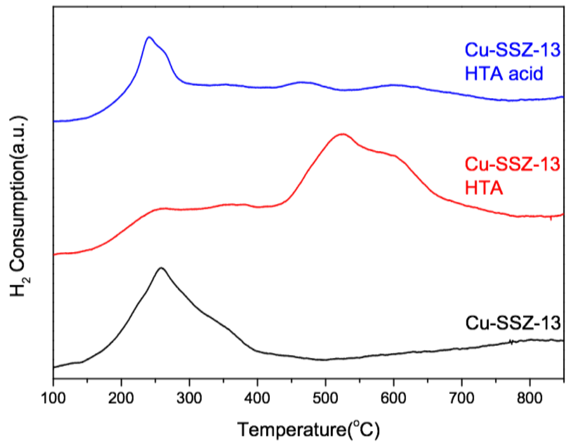

Figure 2. H_2-TPR profile of Cu-SSZ-13 catalysts (fresh, HTA and acid treated).

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