Passive NO adsorption ability of hydrothermally activated Pd/SSZ-13 for cold start application

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Abstract: Effective Pd ion exchange in SSZ-13 is difficult due to hydrolysis of Pd and small pore of SSZ-13. Therefore, the major Pd state in fresh Pd/SSZ-13 is PdO regardless of preparation method such as impregnation, ion exchange, and solid-state ion exchange. Since PdO could not adsorb NO, NO adsorption ability of fresh Pd/SSZ-13 catalyst is insignificant. However, hydrothermal aging(HTA) on fresh Pd/SSZ-13 induces the mobility of Pd, leading to the formation of Pd ion irrespective of preparation method. As a result, HTA Pd/SSZ-13 shows an improved NO adsorption ability at low temperature, which is potentially used for cold start application.

Keywords: Pd/SSZ-13, Hydrothermal aging treatment, low temperature NO adsorption

1. Introduction

As the stringent regulation on NOx emission in exhaust gas has been issued and enforced internationally, the control of NOx from diesel engine is considered as a great challenge. Although selective catalytic reduction (SCR) catalyst efficiently reduces NOx, this system cannot operate appropriately below 200 ℃ (i.e. during cold start period, initial ca. 100 – 200 sec of engine operation). Therefore, during the warm-up of NOx reduction catalyst, the significant amount of NOx is released into atmosphere without any catalytic treatment[1]. Hence, to fulfil the current and future regulation, NOx emission during cold start period must be controlled.

Recently, passive NOx adsorption catalysts draw significant attention with a function of adsorbing NOx at low temperature (i.e. during cold start) and desorbing them at raised temperature, where SCR operates properly. It is known that Ce-based material can store NOx at low temperature (below 200 ℃). However, since sulfur poisoning of ceria strongly inhibits the adsorption of NOx, it is hard to apply to the practical conditions[2]. Therefore, Pd/zeolite catalysts having high tolerance against sulfur are considered as a promising material of a cold start NOx trap catalyst. In this work, we tried to examine various Pd/SSZ-13 catalysts with different preparation method and investigate the effects of hydrothermal aging(HTA) treatment on the NO adsorption ability and the physicochemical change of Pd/SSZ-13, which is of practical importance to develop novel NOx adsorption catalyst for cold start application.

2. Experimental

NH_4-SSZ-13 was used as a support. 2 wt% of Pd was loaded on the SSZ-13 with various Pd loading methods such as incipient wetness impregnation (IWI), wet impregnation (WET), ion exchange (ION), and solid-state ion exchange (S-S). After loading Pd, all samples were dried at 100 ℃ and calcined at 500 ℃ under 15 % O_2 in N_2 balance for 2 hr, which were designated as “fresh”. Calcined catalysts were hydrothermally treated at 750 ℃ with H_2O. Those samples were designated as “HTA (hydrothermal aging)”.

NO adsorption/desorption were conducted in a fixed-bed quartz reactor. During NO adsorption process, 100 ppm of NO was introduced for 100 sec with H_2O, CO_2, O_2 and N_2 at 120 ℃. After NO adsorption, the temperature of catalyst was elevated under lean gas condition from 120 ℃ to 500 ℃ at a rate of 10 ℃/min. NOx concentration was recorded with NOx analyzer (Thermo electron Corp., 42i-HL). DRIFT spectra were recorded in the range of 2000 – 1700 cm^{-1} (128 scans and resolution 4 cm^{-1}) on a Nicolet 6700 (Thermo Fisher Scientific) with a MCT detector using DRIFT cell.

3. Results and discussion

Figure 1a exhibits the NO_x desorption curves of fresh and HTA Pd(2)/SSZ-13 IWI catalysts. It must be pointed out that the NO adsorption ability of fresh Pd(2)/SSZ-13 catalyst is insignificant, as verified by the NOx desorption curve in the Figure 1a that exhibits only small NOx signal at 360 ℃. On the other hand, HTA Pd(2)/SSZ-13 IWI clearly displays two desorption peaks having a maximum intensity at around 250 ℃ and 400 ℃, indicating that HTA treatment improves NO adsorption ability of Pd/SSZ-13. Regardless of Pd loading method, WET, ION, and S-S catalysts exhibit the similar NO adsorption/desorption behavior with IWI sample. Combined H_2-TPR and Pd EXAFS results clearly indicate that the primary state of Pd in fresh catalysts is PdO on which NO hardly adsorb[3], explaining the reason why fresh Pd/SSZ-13 has the negligible NO adsorption ability, whereas HTA treatment on Pd/SSZ-13 induces the redispersion of PdO to form Pd ion species in SSZ-13 zeolite.

Figure 1b shows DRIFT spectra of HTA Pd(2)/SSZ-13 IWI catalysts recorded during NOx desorption after NO adsorption at 120 ℃ for 1 hr. After NO adsorption, HTA Pd/SSZ-13 exhibits two ionic Pd-NO complex peaks at 1810 and 1860 cm^{-1}, demonstrating the presence of Pd ion species in HTA treated sample. In Figure 1b, during the temperature ramping from 120 to 300 ℃, the peak at 1810 cm^{-1} considerable decreases, indicating that the low temperature NOx desorption peak (at 250 ℃) is derived from the ionic Pd-NO species at 1810 cm^{-1}. Above 300 ℃, since ionic Pd-NO complex at 1860 cm^{-1} begin to decrease, the desorption of NO between 300 and 500 ℃ is primarily related to the band at 1860 cm^{-1}. Combined NO adsorption/desorption and DRIFT results clearly demonstrate that Pd ion species are the active site for NOx storage.

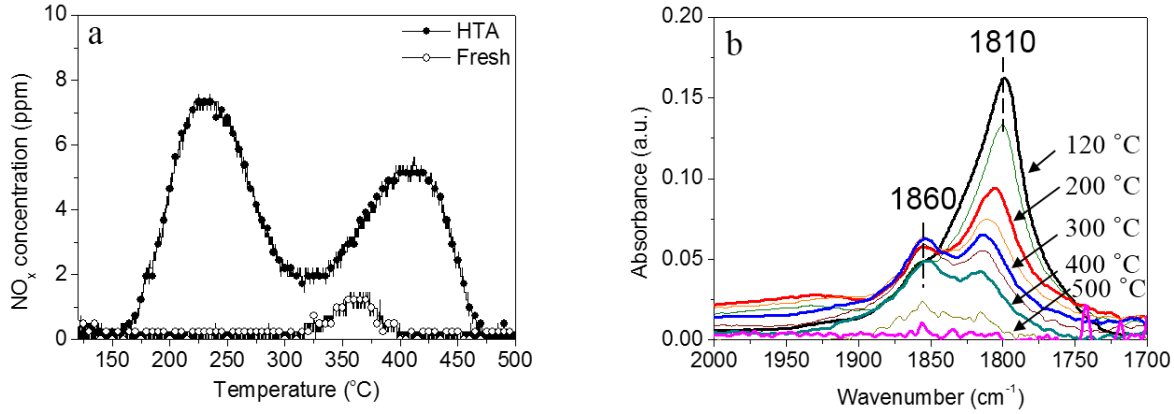

Figure 1. (a) NOx-TPD curves of fresh and HTA Pd(2)/SSZ-13 IWI (prepared by IWI) after NO adsorption for 100 sec and (b) DRIFT spectra of HTA Pd(2)/SSZ-13 IWI catalyst during NOx-TPD after NO adsorption for 1 hr.

4. Conclusions

The effect of HTA treatment on the adsorption of NO at low temperature over Pd/SSZ-13 has been extensively investigated. It is found that the primary Pd state in fresh Pd/SSZ-13 with any Pd loading method is PdO, which cannot adsorb NO, resulting in the negligible NO adsorption ability. However, HTA treatment on fresh Pd/SSZ-13 enhances the NO adsorption ability. The analysis for the physicochemical change in Pd state by using H_2-TPR, EXAFS, and STEM-EDS obviously demonstrates that the redistribution of Pd species takes places in Pd/SSZ-13 during HTA. Consequently, DRIFT spectra demonstrate the presence of two ionic Pd-NO complex which are the origins of the NOx desorption peak at 250 and 400 ℃. In conclusion, HTA treatment transforms bulk PdO species into Pd ion species, which could adsorb NO at low temperature to reduce the amount of NOx emitted during the cold start period.

References

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