Influence of CO_2 feed on steam reforming of toluene over supported Ni catalyst of Ni/Mg/Al catalyst.

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Abstract: Development of Exhaust Gas Recirculation (EGR) with fuel reforming technology can greatly improve the fuel economy of automobiles, but the conventional supported Rh catalyst is very costly. Therefore, we focused on supported Ni catalyst to reduce the cost. In this study we applied Ni/Mg/Al catalyst, which is known to exhibit high activity in steam reforming, to steam + CO_2 reforming of toluene which is a model compound of gasoline. Addition of CO_2 greatly decreased the activity and coke deposition resistance of Ni/Mg/Al catalyst.

Keywords: Supported Ni catalyst, Steam reforming reaction, Coke deposition resistance.

1. Introduction

Currently, depletion of petroleum fuel is a problem. Therefore, techniques for improving fuel economy of automobile engines have been extensively studied. Exhaust Gas Recirculation (EGR) is one of them. Especially, EGR with reforming techniques is promising where a small amount of gasoline is mixed with the circulating exhaust gas and is reformed over catalyst to highly flammable synthesis gas. The addition of synthesis gas to the feed stabilizes the combustion in the engine under EGR conditions. The catalysts should have high activity at low temperature and high coke deposition resistance in the presence of both water and CO_2. Supported Rh catalysts have been tested; however they are very expensive. Therefore, we focused on supported Ni catalyst prepared from hydrotalcite-like compounds (Ni/Mg/Al), which is known to have high activity and coke deposition resistance in steam reforming reactions. We investigate the influence of CO_2 in the feed on the performance of steam reforming of toluene, which is a model compound of gasoline, over Ni/Mg/Al catalyst.

2. Experimental

All the catalysts were prepared by co-precipitation method1). The amount of supported Ni was 12 wt%, and the ratio of divalent metal ions (Ni^{2+}+Mg^{2+}) to trivalent ions (Al^{3+}) was typically 3. After co-precipitation, they were dried overnight at 383 K and calcined at 1073 K for 5 h in air atmosphere. After that, the catalysts were sieved to 30-60 mesh. For reforming reaction of toluene, an atmospheric pressure fixed bed flow reactor was used. Reduction was carried out under a flow of H_2/N_2 (30/30 ml/min) at 1073 K as a catalyst pretreatment. The reaction temperature was set at 673-873 K. Toluene and H_2O were supplied using micro feeders. The reaction conditions were W_{cat} = 100 mg, W/F = 0.18 g h/mol, toluene/H_2O/N_2 = 1/23.6/71.2 or toluene/$H_2O/N_2/CO_2$ = 1/11.8/71.2/11.8. Coke deposition amount was measured by TG-DTA using catalyst after reaction for about 270 min.

3. Results and discussion

Figure 1 shows the results of steam reforming of toluene over Ni/Mg/Al catalyst in the absence (A) and presence (B) of CO_2. The toluene conversion in the absence of CO_2 was 31.7 % and 99.9 % at 673 K and 773 K, respectively. In contrast, the toluene conversion in the presence of CO_2 was 12.6 % and 43.3 % at 673 K and 773 K, respectively, showing that toluene conversion was greatly decreased by the CO_2 addition. In addition, the amount of coke deposition was increased from 0.02 g_{coke}/g_{cat} to 0.11 g_{coke}/g_{cat} by the CO_2 addition.

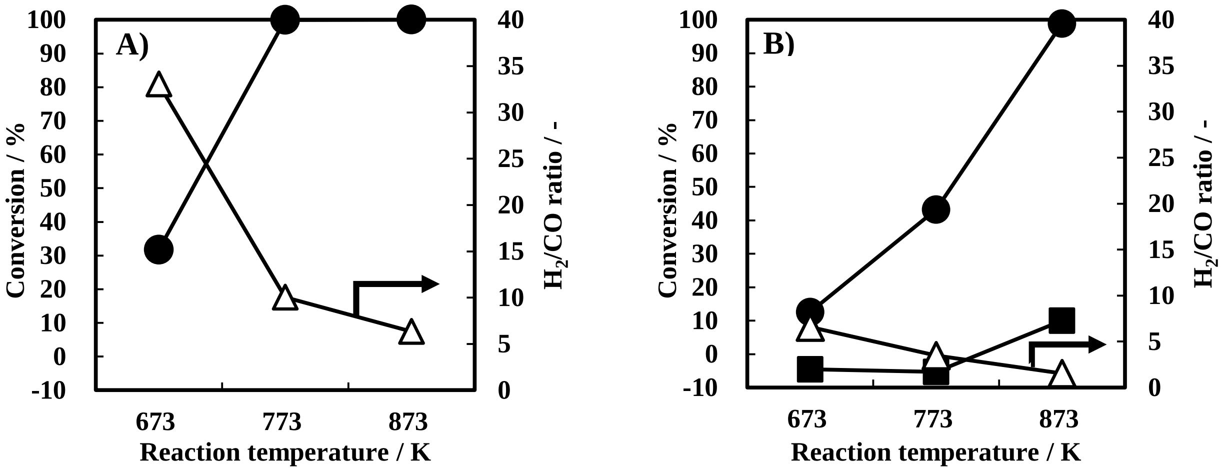

Figure 1. Effect of CO_2 feeding in steam reforming of toluene over Ni/Mg/Al catalyst A) toluene/H_2O/N_2 = 1/23.6/71.2, B) toluene/$H_2O/N_2/CO_2$ = 1/11.8/71.2/11.8. (●) Toluene conversion, (■) CO_2 conversion, (△) H_2/CO ratio.

Figure 2 shows the XRD patterns for fresh and spent Ni/Mg/Al catalysts after A) 270 min and B) 260 min of steam reforming of toluene. The peak area of Ni metal decreased in the case with CO_2 (Figure 2C), indicating that the catalyst was oxidized during the reaction. By contrast, in the case without CO_2, the peak area of Ni metal was comparative to that of fresh Ni/Mg/Al catalyst[2]. Therefore, addition of CO_2 promoted the oxidation of Ni metal species of the catalyst. In addition, in the case with CO_2, the peak due to coke was observed, agreeing with the fact that the amount of coke deposition was increased by CO_2 addition.

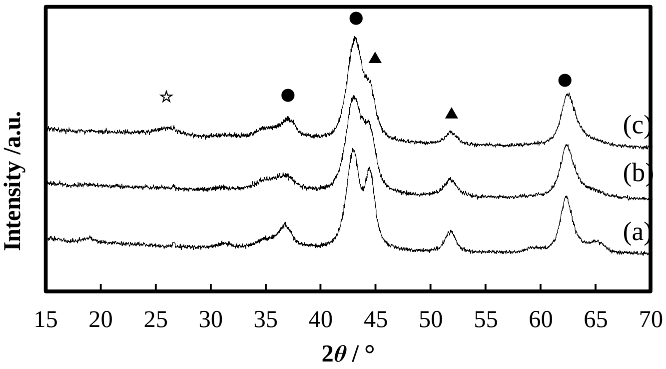

Figure 2. XRD patterns of Ni/Mg/Al catalyst (a) after the reduction at 1073 K, (b, c) after the steam reforming of toluene in the absence (b) and presence (c) of CO_2 at 673 − 873 K for about 270 min. Crystalline phases: (☆) coke, (●) Mg(Ni, Al)O, (▲) Ni metal.

4. Conclusions

The toluene conversion in the steam reforming of toluene over Ni/Mg/Al catalyst was much decreased by addition CO_2 to the feed. The amount of reduced Ni species and the resistance to coke deposition were decreased by CO_2 addition.

References

1. D. Li, L. Wang, M. Koike, Y. Nakagawa, K. Tomishige, Appl. Catal. B: Environ. 102 (2011) 528.
2. M. Koike, D. Li, Y. Nakagawa, K. Tomishige, ChemSusChem 5 (2012) 2312.