Adjusted interactions of nickel nanoparticles with cobalt-modified $MgAl_2O_4$-SiC for an enhanced catalytic stability during steam reforming of propane

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Abstract: Steam reforming of propane (SRP) for a stable production of hydrogen-rich reformates was investigated using Ni-supported on cobalt-modified SiC-embedded $MgAl_2O_4$ support (denoted as NCMAS). The adjusted interactions of the Ni nanoparticles with the support and its narrow crystallite size distributions largely altered the catalytic activity and stability of the NCMAS. The positive roles of the cobalt promoter on the $MgAl_2O_4$-SiC matrices were mainly responsible for the suppressed aggregations of nickel nanoparticles by their stronger and intimate interactions with the cobalt-modified $MgAl_2O_4$.

Keywords: Metal-support interaction, Cobalt-modified on SiC-embedded $MgAl_2O_4$, Steam Reforming of Propane (SRP).

1. Introduction

For a hydrogen-rich syngas production, the steam reforming of propane (SRP) was investigated due to its easy-liquefying nature with a higher capacity for hydrogen production per unit volume of propane than that of methane[1]. The supported Ni-based reforming catalysts are preferred industrially due to their low cost, however the thermal deactivation and severe coke deposition have been induced the large deactivation of Ni-based catalysts. To overcome those problems, the metal-support interaction between Ni nanoparticles and the cobalt-modified SiC-embedded $MgAl_2O_4$ support was mediated, where the cobalt promoter largely enhanced the catalytic activity and stability due to its intrinsic oxophilic natures.

2. Experimental

Cobalt-modified SiC-embedded $MgAl_2O_4$ supporting materials (CMAS) were prepared by a sol-gel method using a gelation agent of propylene oxide based on the previously reported work[2] at a fixed weight ratio of $MgAl_2O_4$/SiC = 7/3 with addition of cobalt promoter of 1, 5 and 8 wt% based on the weight of $MgAl_2O_4$. For the further preparation of nickel supported catalysts, the active nickel metal was introduced on the CMAS support by wet impregnation method at a fixed amount of 10 wt% Ni using $Ni(NO_3)_2 \cdot 6H_2O$ precursor. The as-prepared final catalysts, which were calcined at 700 ^oC for 3 h were denoted as NCMAS(x) with the different cobalt x wt%. The catalytic activity of NCMAS catalysts were tested in a 3/8 inch fixed-bed reactor at the following reaction conditions; T = 650 ^oC, P = 0.1 MPa, SV = 33,600 $L/kg_{cat} \cdot h$ and the feed molar ratio of $C_3H_8/N_2/H_2O=1/4/9$. The effluent products were analyzed using online gas chromatography equipped with TCD and FID. The different metal-support interactions and surface properties of the NCMAS catalysts were confirmed by TPR, XPS, STEM-EDS and so on.

3. Results and discussion

As summarized in **Figure 1**, the small amount of SiC embedment in the $MgAl_2O_4$ support at ~30 wt% enhanced the catalytic activity and stability of NMAS-7 than the NMA, where SiC was not included. However, more amount of SiC revealed the decreased activity of the NMAS-5 and significant deactivation of the NMAS-3. The cobalt promoter showed a highly active and stable conversion of propane in all the NCMAS catalysts. Among them, NCMAS(5) was optimal catalyst by showing the best activity of 100 % conversion even at a longer activity test of 100 h (**Figure 1**).

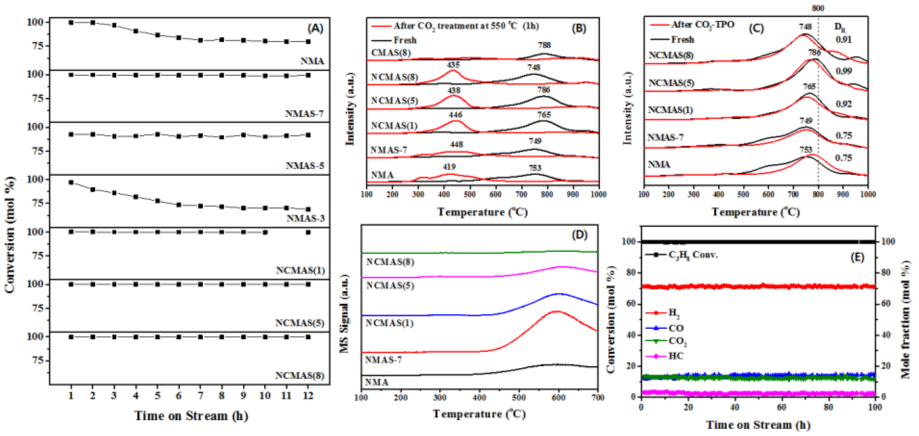

Figure 1. (A) Catalytic activities of NCMAS with time on stream, (B) TPR profiles at different pretreatment conditions fresh NMAS, (C) after CO_2 treatment at 550 ^{o}C for 1 h on the reduced NCMAS, (C) after CO_2-TPO treatment up to 800 ^{o}C on the temperature-programmed reduced NCMAS (D) TPSR patterns on the used NCMAS catalysts, and (E) long-run test on the NCMAS(5) at the reaction conditions of T = 650 ^{o}C, P = 0.1 MPa and SV = 33600 mL/(g_{cat}·h) of mixed gas ($C_3H_8/N_2/H_2O$ =1:4:9)

Furthermore, the amounts of coke depositions were clearly decreased with increasing the amounts of cobalt promoter on the MAS support due to its oxophilic characters[3] as shown in **Figure 1**. Interestingly, the significant resistance to re-oxidation of nickel nanoparticles by mild oxidant CO_2 formed was verified by successive temperature programmed analyses, in which showing the best resistance to the oxidation to the inactive spinel formation by preserving metallic Ni nanoparticles on the NCMAS(5) as shown in **Figure 1**. The resistance for the re-oxidation of NCMAS(5) was well related with binding energy shifts from XPS and the schematic diagrams of the superior stability of NCMAS(5) were also proposed in **Figure 2**. Based on the kinetics experiments on the NCMAS(5), the kinetic parameters of SRP reaction was well derived using the LHHW mechanisms and optimal operating conditions were further estimated as shown in **Figure 2**.

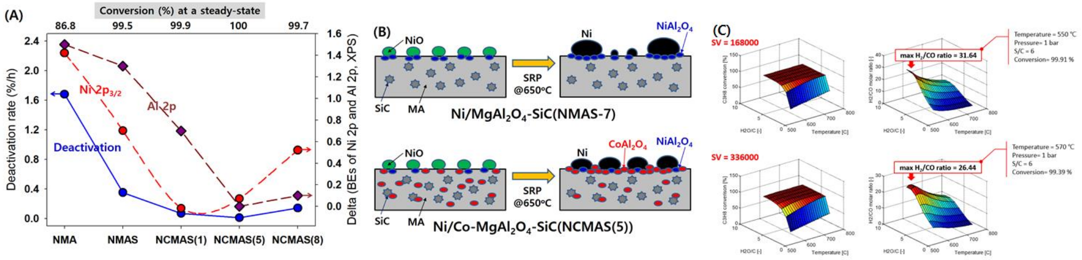

Figure 2. (A) Correlations of deactivation rates with the summarized results of XPS, (B) Proposed schematic diagrams of the possible aggregations of Ni nanoparticles on two representative NMAS-7 and NCMAS(5), (C) Estimated optimal reaction conditions and contour plots to maximize the C_3H_8 conversion and H_2/CO molar ratio

4. Conclusions

The effects of cobalt promoter on the Ni nanoparticles supported on the SiC-embedded $MgAl_2O_4$ were investigated for the steam reforming of propane (SRP) reaction in terms of the adjusted interactions between intimate Co-Ni nanoparticles and $MgAl_2O_4$-SiC supports. At an optimal 5wt%Co promoter modified on the $MgAl_2O_4$-SiC (NCMAS(5)), the facile re-reducibility of the Ni nanoparticles with a less formation of metal aluminates can increase the catalytic activity and stability by lessening heavy coke depositions due to its intrinsic oxophilic natures.

References

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