

XPS Identification of Deposited Carbon on Ni/Ce-Zr-O Catalyst

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Introduction

Ni-based catalysts have been used for several decades for methane steam reforming [1]. Deactivation of Ni/Ce-ZrO catalysts due to carbon formation during autothermal reforming of gasoline, however, is still a problem [2]. A good strategy for developing coking-resistance catalyst would be to identify formulations with higher carbon gasification ability than carbon formation. Many efforts have been made using imaging (including SEM and TEM) to understand the nature of carbon formation and to elucidate the morphology of carbon deposited during methane reforming. It is known that carbon grows in different forms (whiskers, encapsulated and pyrolytic carbon, and even carbide) [1], and other morphologies (filamentous, nanofibers, and nanotube) [3] have been observed during methane decomposition. Carbon formation could be minimized by controlling surface properties of catalysts through the addition of promoters. The physical and/or chemical characteristics of deposited carbon, however, are still poorly understood, especially for gasoline reforming catalysts. In this work, XPS combined with SEM, TGA, and XRD were used to identify the status of deposited carbon after autothermal reforming (ATR) of iso-octane on Ni/Ce-Zr-O (Ni/CZO) catalysts having different Ni loadings.

Materials and Methods

CZO ($\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$) and Ni/CZO were synthesized by co-precipitation and wet impregnation followed by drying and calcination [2]. Prior to reaction, the samples were reduced in a 5% H_2/N_2 flow at 600 °C. ATR reaction was carried out in a quartz reactor by a mechanical mixture of Ni/CZO with silica (1:3 ratio). Starting at a temperature of 350 °C with iso-octane, steam, air ($\text{O}/\text{C}=0.5$, $\text{H}_2\text{O}/\text{C}=2$), and an additional flow of Ar, the furnace was ramped to 650 °C and held for two hours at 650 °C. Then Ar flow was stopped and the $\text{H}_2\text{O}/\text{C}$ ratio was decreased to 1.0, and the catalysts were kept on stream under ATR conditions for an additional 4 hours for carbon deposition. XPS experiments (Krato Axis Ultra) were performed to identify the status of various carbon species by changing XPS operation conditions to analyze the fresh and post-reaction catalysts with as prepared and ground post-reaction particles, and the mechanical mixtures of ground catalyst with $\alpha\text{-Al}_2\text{O}_3$. SEM (FEI Nova Nanolab), TGA-IR (Perkin-Elmer), and XRD (Rigaku) were used to characterize the morphologies, the composition and amounts, and crystallographic phase of deposited carbon.

Results and Discussion

The amount of deposited carbon following iso-octane ATR was measured by TGA (Table 1). Two peaks attributed to deposited carbon were observed in XPS C1s spectra located at 284.4 and 281.6 eV, respectively, depending on sample preparation (ground or unground) prior to XPS measurement for 1% and 2% Ni/CZO (Table 1). It was also found that the C1s peak at 281.6 eV disappeared if XPS was run with charge neutralizer off. Only one C1s peak of deposited carbon at 284.4 eV was observed for 5% Ni/CZO and CZO, regardless of the XPS

conditions used. Further experiments with the ground mixture of $\alpha\text{-Al}_2\text{O}_3$ and carbon-deposited 5% Ni/CZO showed an additional C1s peak at 281.9 eV ($\alpha\text{-Al}_2\text{O}_3$ to carbon-deposited 5% Ni/CZO = 3:1), which also disappeared with the charge neutralizer off. Comparing the C1s and Zr3d spectra suggests that the two deposited carbon species are identical in chemical structure. The change of C1s binding energy is attributed to the electrical conductivity derived from whether the deposited carbon is "isolated" or "continuous" (linked to each other on the surface of Ni/CZO catalysts). Huge filamentous and nanotube carbon structures were observed in SEM images of 2% and 5% Ni loading catalysts. There was no evidence from SEM and X-ray EDAX for carbon deposition on the surface of silica. XRD showed no graphite peaks for any catalysts following carbon deposition under ATR conditions.

Significance

Structural identification of deposited carbon provides physical and chemical insight to understanding the carbon formation and optimizing formulation design of reforming catalyst.

Table 1. XPS C1s peaks (eV) attributed to deposited carbon with charge neutralizer on

Catalyst	%Ni/CZO	%C	Post ATR particle	Ground particle
A	1	1.6	281.5 284.3	281.5
B	2	3.1	284.3	281.8 284.4
C	5	27.4	284.3	284.5

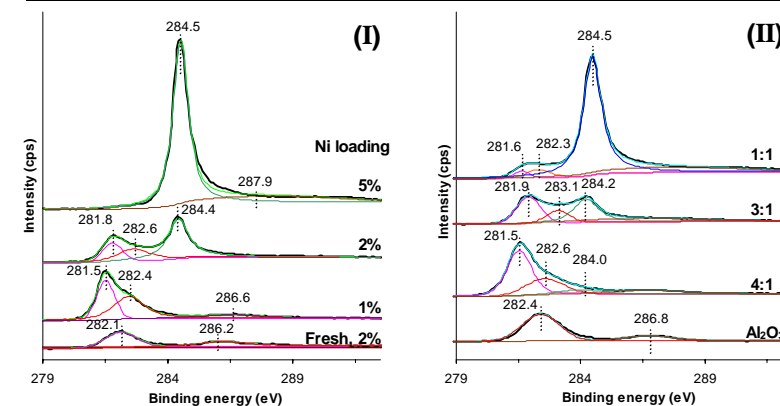


Figure 1. C1s spectra for (I) fresh 2% Ni/CZO and carbon-deposited Ni/CZO catalysts having different Ni loadings; (II) $\alpha\text{-Al}_2\text{O}_3$ and the mechanical mixtures of $\alpha\text{-Al}_2\text{O}_3$ and carbon-deposited 5% Ni/CZO having different ratios.

References

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