catalysts

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Supplementary Materials

Lanthanum–Cerium-Modified Nickel Catalysts for Dry Reforming of Methane

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Abstract: The catalyst $MNi_{0.9}Zr_{0.1}O_3$ (M = La, Ce, and Cs) was prepared using the sol–gel preparation technique investigated for the dry reforming of methane reaction to examine activity, stability, and H_2/CO ratio. The lanthanum in the catalyst $LaNi_{0.9}Zr_{0.1}O_3$ was partially substituted for cerium and zirconium for yttrium to give $La_{0.6}Ce_{0.4}Ni_{0.9}Zr_{0.1-x}Y_xO_3$ (x = 0.05, 0.07, and 0.09). The $La_{0.6}Ce_{0.4}Ni_{0.9}Zr_{0.1-x}Y_xO_3$ catalyst's activity increases with an increase in yttrium loading. The activities of the yttrium-modified catalysts $La_{0.6}Ce_{0.4}Ni_{0.9}Zr_{0.03}Y_{0.07}O_3$ and $La_{0.6}Ce_{0.4}Ni_{0.9}Zr_{0.01}Y_{0.09}O_3$ are higher than the unmodified $La_{0.6}Ce_{0.4}Ni_{0.9}Zr_{0.1}O_3$ catalyst, the latter having methane and carbon dioxide conversion values of 84% and 87%, respectively, and the former with methane and carbon dioxide conversion values of 86% and 90% for $La_{0.6}Ce_{0.4}Ni_{0.9}Zr_{0.03}Y_{0.07}O_3$ and 89% and 91% for $La_{0.6}Ce_{0.4}Ni_{0.9}Zr_{0.01}Y_{0.09}O_3$, respectively. The BET analysis depicted a low surface area of samples ranging from 2 to 9 m^2/g. The XRD peaks confirmed the formation of a monoclinic phase of zirconium. The TPR showed that apparent reduction peaks occurred in moderate temperature regions. The TGA curve showed weight loss steps in the range 773 K–973 K, with $CsNi_{0.9}Zr_{0.1}O_3$ carbon deposition being the most severe. The coke deposit on $La_{0.6}Ce_{0.4}Ni_{0.9}Zr_{0.1}O_3$ after 7h time on stream (TOS) was the lowest, with 20% weight loss. The amount of weight loss increases with a decrease in zirconium loading.

Keywords: dry reforming of methane; catalyst activity; oxygen vacancies; carbon deposit

Supplementary Characterization

Figure S1 illustrates the Energy Dispersive X-ray results of the catalyst samples. It denotes the qualitative elemental compositions of the freshly prepared samples. the percentage composition of elements corresponds to the computed composition during the synthesis.

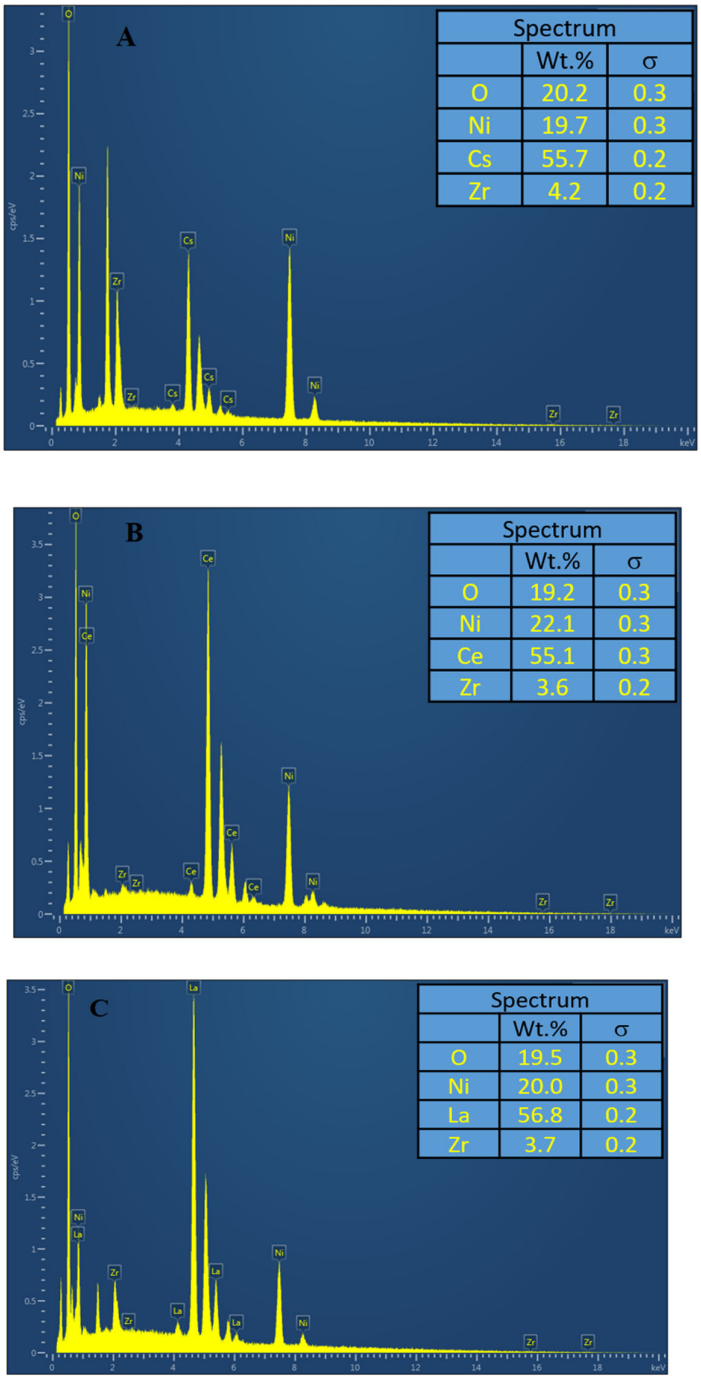

Figure S1. The EDX analysis of fresh catalysts (A) $CsNi_{0.9}Zr_{0.1}O_3$ (B) $CeNi_{0.9}Zr_{0.1}O_3$ (C) $LaNi_{0.9}Zr_{0.1}O_3$.

Figure S2 displays the CO_2-TPD results which highlight the basicity of different calcined samples. Apparently, there are two peaks in the profiles of the catalysts. The peaks around 100 °C and 250 °C can be ascribed to the weak basic sites of catalysts. Obviously, the addition of yttria has somewhat increased the content of weak basic sites. The peak at about 410 °C was attributed to the medium-strength basic sites.

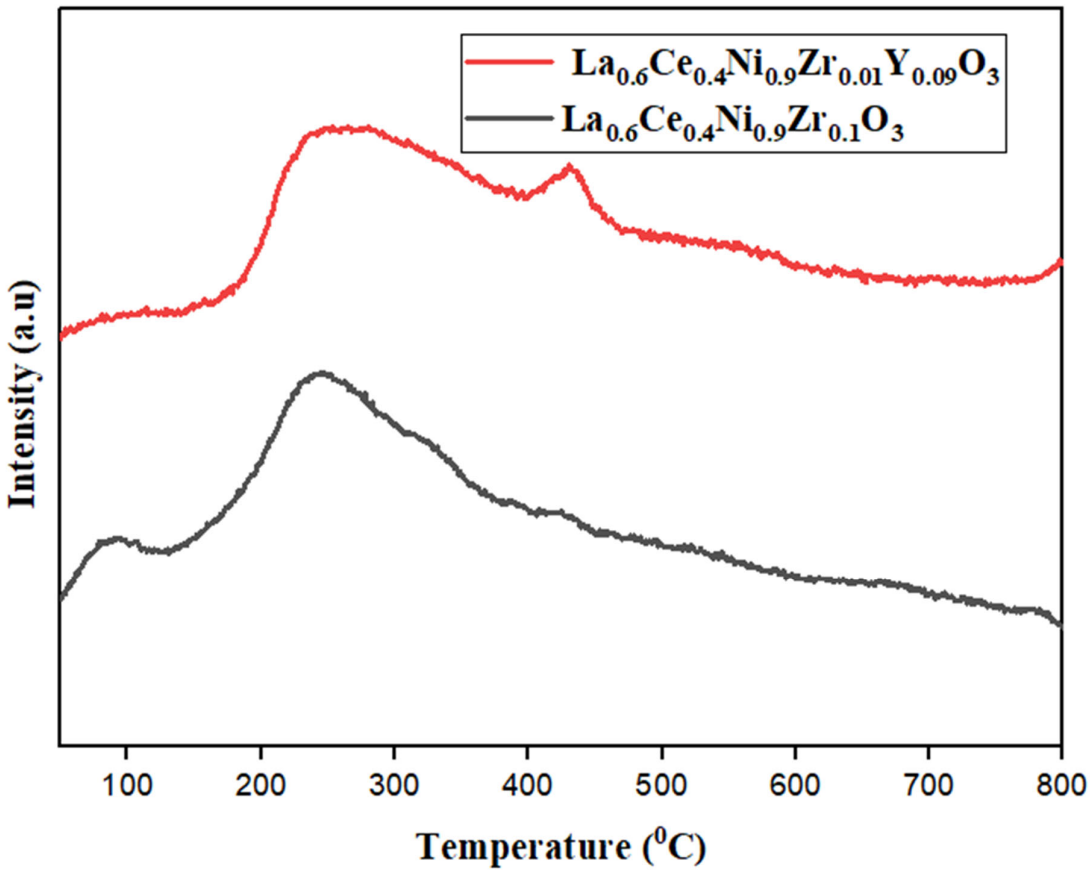

Figure S2. CO_2-TPD profiles of fresh catalysts: $La_{0.6}Ce_{0.4}Ni_{0.9}Zr_{0.01}Y_{0.09}O_3$ and $La_{0.6}Ce_{0.4}Ni_{0.9}Zr_{0.1}O_3$.

The TPO analysis of $La_{0.6}Ce_{0.4}Ni_{0.9}Zr_{0.01}Y_{0.09}O_3$ is shown in figure S3. The TPO profile exhibits only one distinct peak at around 600 °C indicating the formation of graphitic carbon type.

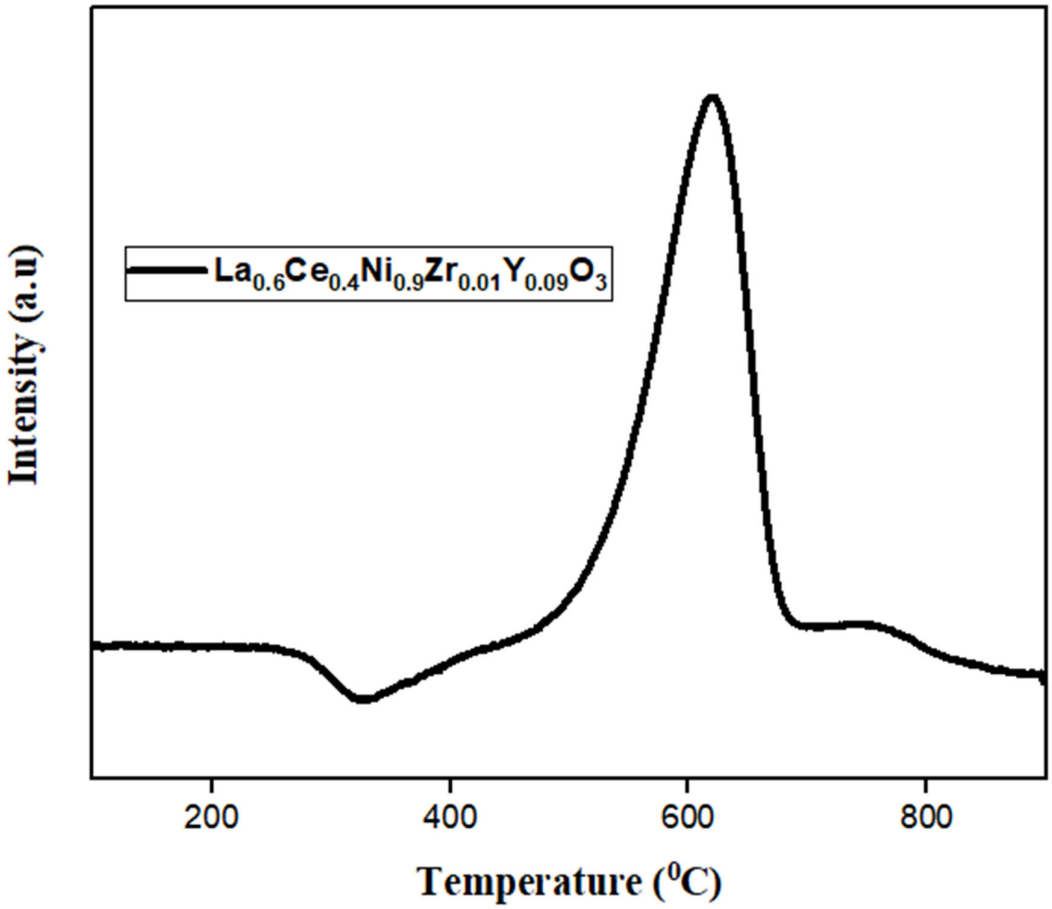

Figure S3. TPO profile of used catalysts: $La_{0.6}Ce_{0.4}Ni_{0.9}Zr_{0.01}Y_{0.09}O_3$.