

Effect of Metal Substitution on the Layered perovskite Catalysts $\text{La}_2\text{Ti}_{2-x}\text{Ru}_x\text{O}_{7-\delta}$ for Oxidative Steam Reforming of Ethanol

Ho-Chen Hsieh (謝和謹)^{a, c}, Rou-Cian Chen (陳柔蒨)^a, Yu-Chun Chuang (莊裕鈞)^d, Jyh-Fu Lee (李志甫)^d, Hwo-Shuenn Sheu (許火順)^{c, d} and Chi-Shen Lee (李積琛)^{a, b*}

^aDepartment of Applied Chemistry, National Chiao-Tung University, 1001 University Rd., Hsinchu 30010, Taiwan

^bCenter for Emergent Functional Matter Science, National Chiao-Tung University, Hsinchu 30010, Taiwan.

^cGraduate Degree Program of Science and Technology of Accelerator Light Source, National Chiao-Tung University, Hsinchu 30010, Taiwan

^dNational Synchrotron Radiation Research Center, Hsinchu, 30010, Taiwan
E-mail address: chishen@mail.nctu.edu.tw

Abstract

The structure and catalytic properties of layered perovskite $\text{La}_2\text{Ti}_{2-x}\text{Ru}_x\text{O}_7$ ($x=0.1-0.4$) were synthesized by sol-gel method and studied for oxidative steam reforming of ethanol (OSRE). Within the series of $\text{La}_2\text{Ti}_{2-x}\text{Ru}_x\text{O}_7$ ($x=0.1-0.4$), the catalyst, $\text{La}_2\text{Ti}_{1.7}\text{Ru}_{0.3}\text{O}_7$ exhibits optimized activity ($X_{\text{EtOH}} = 99.2(6)\%$; $S_{\text{H}_2} = 98.0(6)\%$) at $\text{C/O}=0.6$ and furnace temperature = 400°C . The time-on-stream OSRE experiment of the catalyst $\text{La}_2\text{Ti}_{1.7}\text{Ru}_{0.3}\text{O}_7$ supported by $\text{La}_2\text{Zr}_2\text{O}_7$ remains stable and no detectable coke deposition over the used catalyst by Raman spectroscopy. With the powder X-ray diffraction and Rietveld refinements, the substituted ruthenium ions were mixed occupied in titanium positions with site preference in the center of the slab. The in-situ experiments showed that oxygen vacancies were created in two steps during the reduction process and in consistent with the temperature reduction measurements. The X-ray photoelectron spectra (XPS) and temperature-programmed reduction (TPR) analysis indicate that the oxidation state of Ru ions is higher than +4 and Ru3d binding energy is gradually shifted to higher energy as the doping amount increases, which affect the catalytic performance. Different distribution of ruthenium ions in the center and edge positions of slab not only affect ethanol conversion during OSRE reaction but also create oxygen vacancies on the surfaces of the catalyst that promoted the oxidation of ethanol and reduce carbon deposition. The results show that the solid solution of $\text{La}_2\text{Ti}_{2-x}\text{Ru}_x\text{O}_7$ ($x=0.1-0.4$) supported by $\text{La}_2\text{Zr}_2\text{O}_7$ is a stable and active catalyst for hydrogen production with OSRE.

Keywords: Oxidative steam reforming of ethanol; Perovskite structure; Solid solution structure; Metal oxide catalyst; Hydrogen production

