Catalyst development for hydrogen production through steam reforming of ethanol: from laboratory scale to pilot plant

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Abstract: This work studied the performance of metal (Ni, Co, Ru, Rh) supported on $SiCeO_2$ catalysts for the steam reforming of ethanol. All catalysts deactivated during SR of ethanol at 773 K, except for Rh/$SiCeO_2$ catalyst, which remained quite stable. TG analyses of used catalysts revealed the presence of carbon deposits over Ni, Co and Ru-based catalysts, whereas no carbon formation was detected for Rh supported catalyst. The high stability of Rh/$SiCeO_2$ catalyst is attributed to the ability of Rh to turnover the adsorbed molecules and the high mobility of oxygen from the support that assist in removing carbonaceous species.

Keywords: Steam reforming of ethanol, hydrogen production, catalyst deactivation.

1. Introduction

The technology for hydrogen production is well-known for large units and it is mainly based on catalytic steam reforming of natural gas in the refineries[1]. However, hydrogen must be produced on site (called distributed hydrogen) for energy generation through fuel cells. The decentralized hydrogen production faces new challenges such as the development of small-scale reformers and the fuel to be used[1]. Large scale hydrogen plants cannot simply be reduced in size to meet the economic, safety, and frequent duty cycle requirements for fuel cell applications and hydrogen fueling stations. Lower pressure and temperature are needed to make small-scale reforming competitive. Furthermore, the natural gas infrastructure does not extend to all areas in countries like Brazil. In this particular case, bioethanol has the advantage of a well-established distribution infrastructure, because it is currently distributed and blended with gasoline in large cities as well as in remote areas. However, the development of new processes for the production of hydrogen requires new reactors designs and catalysts. This work describes the development of a steam reforming (SR) of ethanol catalyst from the laboratory tests to the fuel processor for the production of hydrogen for a PEM fuel cell.

2. Experimental

The support $CeO_2.SiO_2$ ($SiCeO_2$) was prepared by precipitation. Initially an alkaline solution containing dissolved SiO_2 (Aerosil 380) was added to an ammonium hydroxide solution. This was added to a solution of $(NH_4)_2Ce(NO_3)_6.6H_2O$ (Aldrich 98%). The precipitate formed was dried at 383 K for 12 h and then calcined at 773 K for 5 h under air flow. The catalyst was obtained by impregnation of the support with an aqueous solution of precursor salts of different metals ($RhCl_3.xH_2O$, $Ru(NO)(NO_3)_3$, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$) in order to obtain 1% wt Rh, 5% wt Ru, 10% wt Ni, 10% wt Co. The samples were dried at 383 K and calcined at 673 K for 5 h under air flow. The catalysts were characterized by N_2 physisorption, X-ray diffraction (XRD), temperature programmed reduction (TPR), thermogravimetric (TG) analysis, scanning electron microscopy (SEM), and *in situ* X-ray absorption spectroscopy (XAS). SR of ethanol was performed using a fixed-bed reactor at 773 and 1023 K and atmospheric pressure. Prior to reaction, samples were reduced under pure hydrogen at 773 K for 1 h. The reactant mixture (2.5% ethanol; 7.5% water, 90.0% nitrogen) was obtained by flowing two N_2 streams through each saturator containing ethanol and water separately.

3. Results and discussion

The diffractograms of all samples exhibited the lines corresponding to CeO_2 with cubic structure. The addition of silica significantly decreased the CeO_2 crystallite size, which agrees very well with the strong increase in the specific area. These results are likely due to the formation of Ce^{3+} and oxygen vacancies in the structure of ceria due to the addition of silica. As the ionic radius of Ce^{3+} is larger than Ce^{4+} ion, the expansion of the lattice parameter can be attributed to the variation in the ionic radius. These results were confirmed by the in situ XANES spectra at the Ce L_{III} edge. The performance of ceria supported metal catalysts for SR of ethanol was investigated. All catalysts deactivated during SR of ethanol at 500^{o}C, except for Rh/SiCeO_2 catalyst, which remained quite stable without any carbon deposition as revealed by TG analysis. DRIFTS spectra recorded during 6 h under a steady flow of the ethanol + water mixture at 773K for the Rh/SiCeO_2 catalyst is shown in Fig. 1a. The bands in the ν(OCO) stretching region of carbonates and acetate remained quite constant during TOS for Rh/SiCeO_2.This result was likely due to the ability of Rh to turnover the adsorbed molecules and the high mobility of oxygen from the support that assist in removing carbonaceous species[2]. This catalyst was deposited on a plate reactor and its performance was evaluated on a fuel processor for hydrogen production for a PEM fuel cell (Fig. 1b). The catalyst remained stable for long-term tests with the production of 1 Nm^3/h of hydrogen required by the fuel cell.

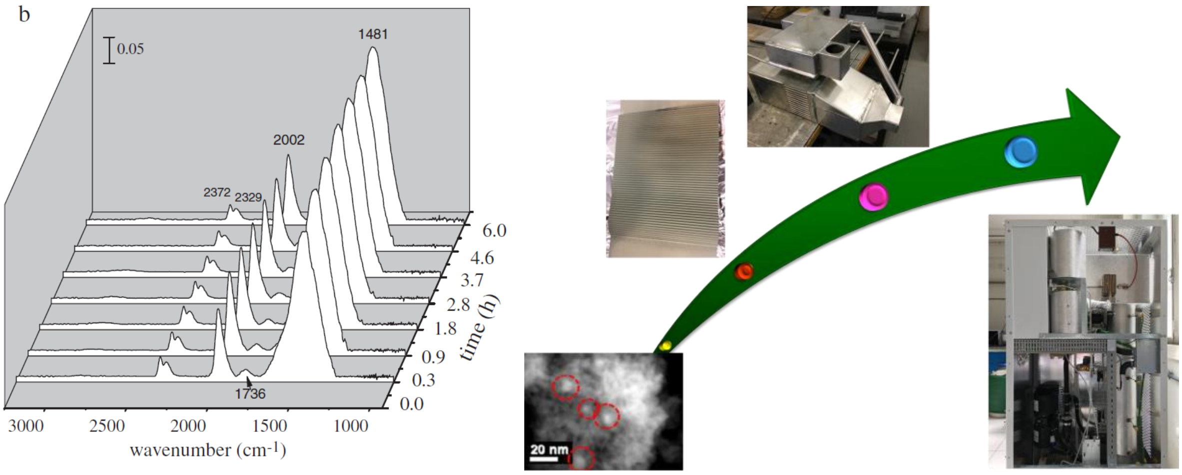

Figure 1. (a) DRIFTS spectra obtained on Rh/SiCeO_2 catalyst during 6 h under a steady flow of the ethanol + water mixture (H_2O/ethanol molar ratio of 2.0) at 773 K. (b) Different steps in the catalyst development for a fuel processor.

4. Conclusions

The stability of the SiCeO_2 supported metal catalysts depended on the type of the metal (Ni, Co, Ru and Rh). The deactivation degree followed the order: Ni >> Co > Ru > Rh. No carbon deposits were found over Rh-based catalysts. The best performance of Rh/SiCeO_2 catalyst was attributed to the ability of Rh to turn over the adsorbed molecules and the high mobility of oxygen from the support that assist in removing carbonaceous species. The scale up of the Rh-based catalyst revealed that it remained quite stable under operating conditions of the fuel processor, producing 1 Nm^3/h of hydrogen required by a PEM fuel cell.

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References

1. T. Rostrup-Nielsen, Catalysis Today 106 (2005) 293.
2. A.M. da Silva, K.R. de Souza, G.Jacobs, U.M. Graham, B.H. Davis, L.V. Mattos, F.B. Noronha, Appl. Catal. B 102 (2011) 94.