

The effect of the metal nature on deactivation during steam reforming of ethanol for hydrogen production over Pt/CeO₂ and Co/CeO₂ catalysts.

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Introduction

Catalyst stability is probably the most important issue in catalyst design for hydrogen production from ethanol. Catalyst deactivation is generally attributed to the deposition of carbonaceous species or sintering of the metal particles. The carbon deposits following ethanol steam reforming (SR) are comprised of both carbon filaments and amorphous carbon covering the metallic particle and the support [1]. Recently, we studied the deactivation mechanism of Pt/CeZrO₂ catalyst for the steam reforming of ethanol reaction [2]. Diffuse reflectance infrared spectroscopy (DRIFTS) showed that the loss of the Pt-support synergy is, at least in part, due to a buildup of carbonaceous residue, which is a likely reason for the deactivation of Pt/CeZrO₂. The deposition of carbon blocked sites between the oxide and the Pt, obstructing the Pt from demethanating the acetate species located on the CeZrO₂ support.

However, the nature of carbon deposits formed depends on both the metal and the support used. The literature reports the formation of carbon filaments over supported Co or Ni catalysts during SR [3]. The aim of this work is to provide further insight into the deactivation mechanism of SR and the effect of the metal nature using a combination of reaction testing, temperature programmed oxidation (TPO) and temperature programmed desorption (TPD), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements and transmission electron microscopy (HR-TEM).

Materials and Methods

CeO₂ support was calcined at 1073 K for 1 h. Pt (1.0 wt.%) and Co (10.0 wt.%) were added to the support by incipient wetness impregnation with an aqueous solution containing H₂PtCl₆·6H₂O and Co(NO₃)₃·H₂O, respectively. The catalysts were characterized by BET surface area, X-ray diffraction, transmission electron microscopy (HR-TEM), scanning electron microscopy (SEM), thermogravimetry, temperature programmed oxidation and desorption analyses. The DRIFTS analysis was carried out by using an ethanol + water mixture containing a H₂O/ethanol ratio of 2.0. The reactions were performed in a fixed bed reactor at atmospheric pressure. Prior to reaction, the catalysts were reduced at 773 K for 1 h. The reactions were carried out at 773 K and W/Q = 0.02 g.s/cm³. It was used H₂O/ethanol molar ratio = 3.0 or 10.0 (for SR), H₂O/ethanol molar ratio = 3.0 and O₂/ethanol molar ratio = 0.5 (for POX and OSR).

Results and Discussion

Catalytic performance parameters of Pt/CeO₂ and Co/CeO₂ catalysts were evaluated for ethanol steam reforming, partial oxidation and oxidative steam reforming. At low temperature (773K), the Pt/CeO₂ catalyst underwent significant deactivation during ethanol steam reforming reaction. HR-TEM revealed some carbonaceous deposits after SR. Co-feeding oxygen attenuated the deactivation rate of the catalyst but significantly decreased the selectivity to hydrogen. Increasing the reaction temperature to 1073K greatly improved the stability of the catalyst. Co/CeO₂ catalyst exhibited higher stability than Pt/CeO₂ for all the reactions at 773K and deactivation was not observed during OSR. However, SEM analysis revealed the presence of carbon filaments at different extents, depending on the reaction conditions. At 1073K, Co/CeO₂ catalyst was also quite stable while carbon filaments were no longer detected. DRIFTS experiments at different reaction temperatures showed basically the same intermediate species on both catalysts, except for the CO band, which was not detected on Co-based catalyst. A reaction mechanism was proposed based on DRIFTS results. DRIFTS spectra revealed the increase of the intensity of the bands attributed to acetate species during the SR at 773K (Figure 1). For Pt/CeO₂ catalyst, the loss of the Pt-support interface leads to a buildup of carbonaceous residue, which is the likely reason of the deactivation of Pt/CeO₂.

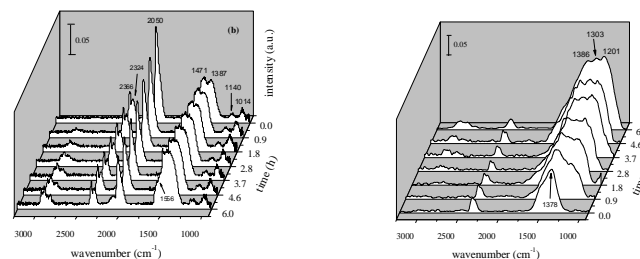


Figure 1. DRIFTS spectra obtained over (a) Pt/CeO₂ and (b) Co/CeO₂ at 773 K and under the reaction mixture containing ethanol and water (water/ethanol ratio = 2.0) during 6 hours TOS.

Significance

This paper provides further insight on the reaction mechanism and sheds light on the nature of catalyst deactivation during ethanol conversion reactions, which are fundamental to the design of appropriated catalysts for these reactions.

References

1. Galetti, A.E., Gomez, M.F., Arrua, L.A., Marchi, A.J., Abello, M.C., *Catal. Commun.* 9, 1201 (2008).
2. de Lima, S.M., Silva, A.M., Graham, M.U., G., Jacobs, G., Davis, B.H., Mattos, L.V., Noronha, F.B. *Appl. Catal. A: General* in press, doi:10.1016/j.apcata.2008.09.040 (2008).
3. Guil, J.M., Homs, N., Llorca, J., de la Piscina, P.R., *J. Phys. Chem. B* 109, 10813 (2005).