Effect of Pt precursor salt on the performance of $Pt/CeO_2/MgAl_2O_4$ in low temperature steam reforming of ethanol

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Resumo / Abstract

RESUMO - A produção de H_2 a partir da reforma a vapor do etanol a baixa temperatura foi estudada utilizando catalisadores de platina suportados em $CeO_2/MgAl_2O_4$ preparados a partir de diferentes sais precursores de Pt: H_2PtCl_6, $(NH_4)_4Pt(NO_3)_2$, $(NH_4)_4Pt(OH)_2$. Diferentes técnicas de caracterização foram empregadas para fornecer informações sobre o efeito do sal precursor de Pt na estrutura da fase ativa dos catalisadores na LTSRE. Os catalisadores não clorados foram mais ativos e apresentaram maior estabilidade, principalmente o catalisador preparado com o precursor $(NH_4)_4Pt(OH)_2$. Por outro lado, a conversão de etanol diminuiu fortemente durante a reação para o catalisador clorado. A perda da capacidade redox do catalisador $Pt/CeO_2/MgAl_2O_4$ (Cl) devido à presença de residuos de cloro contribui para o seu pior desempenho.

Palavras-chave: Hidrogênio renovável, Reforma a vapor do etanol a baixa temperatura, desativação, Precursores de Pt.

ABSTRACT - The production of H_2 from the steam reforming of ethanol at low temperature was studied using different platinum catalysts supported on $CeO_2/MgAl_2O_4$ were prepared using different precursor of Pt: H_2PtCl_6, $(NH_4)_4Pt(NO_3)_2$, $(NH_4)_4Pt(OH)_2$. Different characterization techniques were employed to provide information about the effect of the Pt precursor salt on the structure of the active phase of the catalysts in LTSRE. The non-chlorinated catalysts were more active and showed greater stability, especially the catalyst prepared with the precursor $(NH_4)_4Pt(OH)_2$. On the other hand, the ethanol conversion strongly decreased during the reaction for the chlorinated catalyst. The loss of redox capabilities of the $Pt/CeO_2/MgAl_2O_4$ (Cl) catalyst due to the presence of chlorine residues contributes to its worse performance.

Keywords: Renewable hydrogen, Low temperature steam reforming of ethanol, deactivation, Pt precursors.

Introduction

The transition to a sustainable, low-carbon energy production will require a combination of established technologies with new technologies and processes in the short term. Renewable hydrogen-powered fuel cells stand out for sustainable energy conversion.

Hydrogen can be produced from ethanol by steam reforming (SRE).[1] Ethanol obtained via biomass fermentation has been proposed as a promising renewable source of hydrogen for fuel cells.[2] One of the main challenges of this technology is the catalyst deactivation due to carbon formation and/or metal sintering caused by the elevated temperatures used.[1] One approach to suppress metal sintering and carbon formation is to carry out the reaction at low temperature (LTSR). In addition to requiring less energy, the water-gas-shift reaction (WGS) is favoured under these operating conditions, contributing to a reduction in CO concentration and an increase in H_2 yield.[3,4] Among the various metals that have been investigated for the LTSR of ethanol (LTSRE), supported Pt catalysts generally seem to present the highest activity and selectivity and therefore they are more widely studied.[3-5]

According to Ciambelli *et al.*,[4] the formation of Ce-PtO_x species during the calcination step, in Pt/CeO_2 catalysts, promotes a strong metal-support interaction, which minimizes the sintering of Pt particles and, consequently, improves the catalytic activity, selectivity and stability of catalysts during LTSRE. In a previous work,[5] the effect of support morphology of a Pt/CeO_2 catalyst for LTSRE was studied. It was verified that the morphology of the support affected the stability of the catalysts due to the different degrees of Pt and Ce reduction revealed by *in situ* XPS measurements.[5] DRIFTS experiments under reaction conditions showed that the accumulation of acetates species was responsible for catalyst deactivation, which was attributed to the presence of a higher fraction of unreduced Pt and Ce species.

Studies show that the nature of the precursor salts of noble metals, used in the preparation of supported ceria catalysts, significantly affect the metal-support interaction (Pt-CeO_x) and the redox properties of the catalysts, influencing the activity, selectivity, and stability.[6,7] The objective of this work was to investigate the effect of Pt precursor salt on the performance of $Pt/CeO_2/MgAl_2O_4$ catalysts in the LTSRE.

Experimental

Support was obtained by calcination of commercial $MgAl_2O_4$ (SASOL) at 1073 K for 6 h, followed by wet impregnation with an aqueous solution containing $(NH_4)_2Ce(NO_3)_6$ (Aldrich) in order to achieve 20 wt.% of CeO_2. The samples were dried overnight at 373 K followed by calcination at 673 K for 5 h. The catalysts (1 wt.% Pt) were prepared by incipient wetness impregnation of the support with an aqueous solution containing different precursor salts: $(NH_3)_4Pt(OH)_2$, $(NH_3)_4Pt(NO_3)_2$ and H_2PtCl_6. The samples were dried at 373 K for 24 h and calcined at 673 K for 3 h. The catalysts were named as $Pt/Ce/MgAl_2O_4$ (OH), $Pt/Ce/MgAl_2O_4$ (NO_3), and $Pt/Ce/MgAl_2O_4$ (Cl).

All catalysts were characterized by N_2 physisorption, XRD, TPR, TPO and Pt dispersion was estimated through the dehydrogenation of cyclohexane. The steam reforming of ethanol was carried out in a fixed-bed reactor at 623 K with a water/ethanol molar ratio of 3 without and with reduction of the catalyst at 423 K.

Results and Discussion

The textural and structural properties of the catalysts were not affected by the type of Pt precursor. Due to the low content and high dispersion of platinum, it was not possible to observe the characteristic lines of the Pt species in the diffractograms.

Figure 1 shows the ethanol conversion as a function of time on stream (TOS) for LTSRE at 623 K over all unreduced catalysts. All catalysts exhibited high initial ethanol conversion (above 50 %). Considering that metallic Pt is the active phase for steam reforming, it should be expected an activation period at the beginning of reaction. These results suggest that Pt oxide was rapidly reduced regardless of the precursor according to the eqs. 1 and 2[1].

$$CH_3CH_2OH + 2CeO_2 \leftrightarrows CH_3CHO + H_2O + Ce_2O_3 \qquad (1)$$

$$PtO_2 + 2H_2 \leftrightarrows Pt^0 + 2H_2O \qquad (2)$$

Nonetheless, ethanol conversion strongly decreased with TOS for $Pt/Ce/MgAl_2O_4$ (Cl) while the deactivation of $Pt/Ce/MgAl_2O_4$ (NO_3) was less severe. On the other hand, $Pt/Ce/MgAl_2O_4$ (OH) catalyst remained quite stable during TOS.

The main products observed were H_2, CO, CH_4, CO_2 and low amounts of acetaldehyde. These results indicate that ethanol decomposition, or ethanol dehydrogenation with subsequent acetaldehyde decomposition to CH_4 and CO, and WGS are the main reactions taking place. It should be noted that no ethylene was detected, suggesting that ethanol dehydration does not take place on the surface of $CeO_2/MgAl_2O_4$. For $Pt/Ce/MgAl_2O_4$ (Cl), the deactivation was accompanied by the increase in the production of acetaldehyde and the reduction of the formation of CO and CH_4, which shows that the acetaldehyde decomposition reaction is inhibited with deactivation.

The reduced catalysts exhibited the same trend for ethanol conversion than the non-reduced ones regardless of the precursor salts: $Pt/Ce/MgAl_2O_4$ (Cl) and $Pt/Ce/MgAl_2O_4$ (NO_3) deactivated while $Pt/Ce/MgAl_2O_4$ (OH) was stable. According to the literature, the presence of chlorine ion residues can affect the redox properties of ceria due to the formation of cerium oxychloride species,[7] which inhibits its ability to donate oxygen and contributes to the accumulation of acetate species adsorbed on its surface.

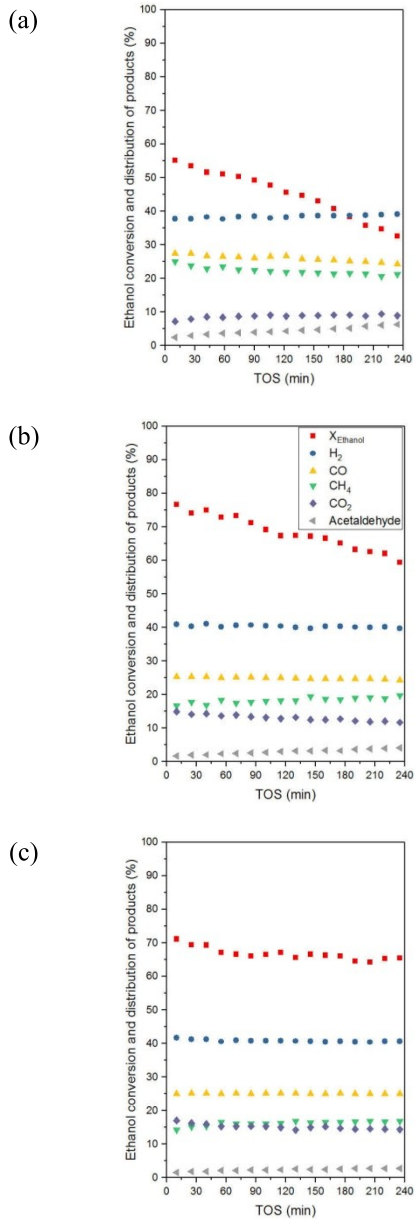

Figure 1 - Ethanol conversion and distribution of products as a function of time on stream for LTSRE at 423 K. (a) $Pt/Ce/MgAl_2O_4$ (Cl), (b) $Pt/Ce/MgAl_2O_4$ (NO_3), and (c) $Pt/Ce/MgAl_2O_4$ (OH).

TPO analyses did not reveal the formation of carbon deposits during the reaction for all catalysts. The metallic dispersion of the catalysts reduced to 423 K was around 80 %, indicating that the initial particle size was not a preponderant factor for the stability of the catalysts. These results revealed that the stability of Pt-based catalysts was significantly affected by the presence of chlorine residues.

Conclusions

The results of the non-reduced catalysts indicate that the Pt oxide particles are rapidly reduced when in contact with the hydrogen produced by dehydrogenation of ethanol on the support. Ethanol conversion strongly decreased with TOS for the chlorinated catalyst, while deactivation was less severe on the other non-chlorine catalysts. The deactivation observed in the $Pt/CeO_2/MgAl_2O_4$ (Cl) catalyst was associated with the chlorine in the ceria support, which reduce its redox capacity and, consequently, lead to the accumulation of acetate species.

Acknowledgements

The authors would like to thank FUNDEP, Programa Rota 2030, Acordo de Parceria 27192.01.01/2020.07-00, Projeto 201798*08, for the financial support.

References

1. L.V. Mattos, G. Jacobs, B.H. Davis, F.B. Noronha, Chem. Rev., 112 (2012) 4094−4123.
2. T.S. Moraes, H. C. da Silva, L.P. Zotes, L.V. Mattos, L.E.P. Borges, R. F., F. B. Noronha, *International Journal of Hydrogen Energy*, 2019, 44, 21205 – 21219.
3. A.C. Basagiannis, P. Panagiotopoulou, X.E. Verykios, Top. Catal., **2008**, 51, 2–12.
4. P. Ciambelli, V. Palma, A. Ruggiero, Appl. Catal. B Environ. **2010**, 96, 18-27.
5. M. Kourtelesis, T.S. Moraes, L.V. Mattos, D.K. Niakolas, F.B. Noronha, X. Verykios, Appl. Catal. B: Environ., 2021, 284, 119757.
6. Z. Abdelouahab-Reddam, R. El Mail, F. Coloma, A. Sepúlveda-Escribano, Catal. Today, 2015, 249, 109-116.
7. A.C. Piedras, R.M.R. Zamora, B.C.A. Vázquez, A.G. Martínez, G.M. Galicia, F.M. Anzures, R.P. Hernández, Catal. Today, **2021**, 360, 55-62.
8. D. Zanchet, J.B.O. Santos, S. Damyanova, J.M.R Gallo, J.M.C. Bueno, ACS Catal. **2015**, 5, 3841–3863.