Hydrogen Production from raw bioethanol over a Rh/MgAl$_2$O$_4$ catalyst. Impact of impurities

Anthony Le Valant, Nicolas Bion*, Florence Epron and Daniel Duprez
Laboratoire de Catalyse en Chimie organique, UMR6503 CNRS, Université de Poitiers
40 avenue du recteur Pineau
86022 Poitiers Cedex (France)
*nicolas.bion@univ-poitiers.fr

Introduction

With the aim of reducing the global emissions of greenhouse gases, hydrogen should be produced from renewable resources such as bioethanol, which can be obtained by fermentation of several biomass sources. The catalytic steam reforming of bioethanol constitutes thus a promising route to hydrogen production [1-5] since the CO$_2$ produced during this process is consumed by the plant during its growth. Except the paper of Vargas et al. [6], studies reported in the literature on bioethanol steam reforming generally deal with the use of a mixture of water and pure ethanol. However, the use of a raw bioethanol feed, limiting the purification steps, is of a major importance for a cost effective industrial application. But the presence of impurities in the feed could induce the deactivation of the catalyst. Then, the aim of this presentation is to show the effect of impurities present in raw bioethanol, such as esters, aldehydes, propanol or acetic acid, on the stability of a Rh/MgAl$_2$O$_4$ catalyst during bioethanol steam reforming for hydrogen production.

Experimental procedure

The support was prepared by impregnation of magnesium acetate onto γAl$_2$O$_3$ (Rhodia). The amount of salt was adjusted to obtain 5 wt% Mg in the support. The spinel structure was obtained by calcination under air at 1000°C for 15h.[5]. The 1wt.%Rh/MgAl$_2$O$_4$ catalyst was prepared by impregnation of a rhodium chloride precursor salt on the support, followed by a calcination under air at 700°C for 4h.

The steam reforming of ethanol was carried out with a fixed bed reactor. A sample (0.25 g) mixed with carborundum (2.75 g) was pretreated under flowing H$_2$ for 15 h at 500°C. Then the temperature was increased up to 700°C under flowing N$_2$. After suppressing the gas flowing, ethanol and water were introduced in the reactor with a HPLC pump. The reaction was performed at temperatures between 600 and 700°C and pressures between 1 and 3 bar. The experimental conditions (especially the WHW) were chosen in order to obtain less than 100% of ethanol conversion at the beginning of the reaction to evidence the deactivation of the catalyst as a function of time. The ethanol chosen for the reaction is either pure ethanol modified by one selected impurity (ethyl acetate, isobutanol, acetic acid …) or raw bioethanol. The stability of the catalyst was examined taking into account the evolution of the ethanol conversion, hydrogen yield, gas phase composition and gas flowrate.

Results and Discussion

Different parameters were studied such as the nature and the concentration of the impurity, the reaction pressure and temperature, the water to (ethanol + impurity) ratio. As expected, the presence of impurities in the ethanol feed causes a deactivation of the catalyst. An example of the catalytic performances obtained with pure ethanol and with ethanol containing 1% of an ester is presented in Table 1.

Table 1 : Effect of the presence of ethyl acetate in the feed on the catalytic performances (T=700°C, P=3 Bar, R=4, flowrate (eau/ethanol)=0.23mL/min)

Test	X$_{EtOH}$ (%)	Yield H$_2$ (g$_{H2}$/h/g$_{cat}$)	Flowrate (mL/min)
Water + ethanol	99	2.8	230
Eau +(ethanol + 1 wt.% ethyl acetate)	97	2.2	195

The presence of impurities in the water + ethanol feed leads to a deactivation of the catalyst as a function of time more pronounced than that observed with a pure feed. This is mainly due the formation of more important quantities of carbonaceous products. However, depending on the nature of the impurity, it appears that the performances could be affected from the beginning of the reaction. For example, in the presence of an ester, the yield in hydrogen is always lower than that obtained with a pure feed. This is explained by the poisoning effect of the ester on the support, limiting the water activation. Then, in the presentation, the deactivation of the catalysts will be discussed for each impurity in terms of (i) formation of coke as well as (ii) modification or poisoning of the metal function and/or the support.

Significance

The knowledge of the impact of impurities present in a raw bioethanol feed on the catalytic performances is of a major importance for the industrial hydrogen production.

References

[1] E. Y. Garcia, M. A. Laborde, Int. J. Hydrogen Energy, 16 (1991) 307.
[2] F. Aupretre, C. Descorme, D. Duprez, Catal. Comm. 3 (2002) 263.
[3] D.K. Liguras, D.I. Kondarides, X.E. Verykios, Appl. Catal.B, 43 (2003) 345.
[4] A.N. Fatsikostas, X.E. Verykios, J. Catal., 225 (2004) 439.
[5] F. Aupretre, C. Descorme, D. Duprez, D. Casanave, D. Uzio, J. Catal., 233 (2005) 464.
[6] J.C. Vargas, S. Libs, A.-C. Roger and A. Kienneman, Catal. Today, 107-108 (2005) 417.