Preparation of catalysts to produce hydrogen by ethanol steam reforming (an overview)

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Introduction

The literature of noble metals supported or non-supported is very large and in some times very special because there are many factors which are involved, for example: metal dispersion, metal-support interaction, acidity, the total amount of noble metal and the preparation method. There is an extensive literature on the preparation of catalysts of no noble metals mainly Ni, Co, Cu[1,2] and other metals or coimpregnated supported with a large number of supports. In the case of noble metals Rh, Pt, Ru,Pd,Ir, Au and Ag, were the most studied [3]. The alumina support is still the most widely used for these catalytic systems, then followed in order: CeO_2, ZrO_2, MgO, ZnO, TiO_2, hydrotalcites, Y_2O_3, La_2O_3,zeolites, V_2O_5[3]. The most widely used methods of preparation are impregnation, coprecipitation, sol-gel synthesis and incipient wetness. This work aims to provide an overview of the main catalytic studies for H_2 production by steam reforming of ethanol (ESR)[4].

Preparation of Noble Metal Catalysts

The noble metal catalysts supported on Al_2O_3 were active at high temperatures and ethanol was converted into H_2, CO, CO_2 and CH_4. The activity order of metals was: Rh > Pd> Ni = Pt. Several supports have been tested (Table 1) for example with CeO_2/ZrO_2 ethylene formation was not observed and the order of activity was: Pt > Rh > Pd [5]. Rh metal has been more active and selective towards H_2 formation than Ru, Pt and Pd. Rh/MgO showed the best performance in the ESR at 650°C in terms of activity and stability [6].

Table 1. Number of publications related to the preparation of noble metal catalysts and their supports. Number of publications of all preparation methods to produce H_2 by ESR reaction.

Metal	NP	Support	NP	Support	NP	Preparation Method	NP
Rh	29	Al_2O_3	49	Zeolytes	12	Impregnation	28
Pt	29	CeO_2	44	TiO_2	10	Coprecipitation	28
Pd	16	ZrO_2	25	Y_2O_3	5	Incipient Wetness	8
Ru	12	ZnO	17	La_2O_3	5	Sol- Gel	13
Ir	7	MgO	14	V_2O_5	3	Flame Pyrolysis	7
Au	2	SiO_2	14			Hydrothermal	4
Ag	2	Hydrotalcite	14			Ion exchange	2

NP= Number of publications

Kinetic measurements revealed large difference in metal specific activities: Rh sites were 2.3, 3.7 and 5.8 times more active than Pd, Co and Ni sites respectively [7]. Several distributions of products were affected by the type of support, preparation method basic promoters such as Na and K and reaction conditions (temperature, H_2O/ethanol ratio, presence of inert gas and the gas hour space velocity (GHSV).

Preparation of No-Noble Metal Catalysts

The Ni-based catalysts have proved to be the most studied and where more combinations with other metals have been observed, for example NiLaZr, NiCuLaZr, Ni-Fe based hydrotalcites , Ni-Cu/ZrO_2, $LaNiO_3$ perovskite, Ni/CeO_2-ZrO_2, Ni/$MgAl_2O_4$, Ni/TiO_2, Ni/ZnO, Ni/ZnO-TiO_2, Ni-Cu/ZnO-TiO_2, Ni-Cu/ZnO-TiO_2 and others. Cobalt was the second metal most studied.

Active Metal	NP	Support or Active metal	NP	Support or Active metal	NP	Support or Active metal	NP
Ni	112	CeO_2-ZrO_2	10	ZnO/Al_2O_3	4	CeO_2-TiO_2	1
Co	49	$MgAl_2O_4$	4	$La(OH)_3$	1	$CeTiO_2$	1
Cu	18	$La_2O_2CO_3$	5	La- Al_2O_3	1	CeGd	1
Fe	6	Sm_2O_3	2	$LaCeNiO_3$	1	ZnO/ZrO_2	1
Zn	2	$CePrO_2$	2	CeO_2-ΥAl_2O_3	1	ZnO/TiO_2	1
Sn	2	$CeZrO_2$	7	CeO_2/Al_2O_3	1	$Y_2O_3ZrO_2$	1
		CeO_2/YSZ	2	$SrCeO_3$	1	Y_2O_3-Al_2O_3	1

NP = Number of publications

Significance

This review shows that the preparation of catalysts for the ESR reaction is divided into catalysts prepared with noble metals and non-noble metals. The Pt and Rh preparations were the most frequent while Ni and Co were the metals most used in catalysts with non-noble metals. In this review was cited the investigations from 2000 to 2013 and we found some important details related with the preparation and evaluation of catalysts such as the addition of basic metals (Na and K) and the H_2O/ethanol ratio.

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