Low temperature production of hydrogen through ethanol catalytic decomposition over commercial copper chromite

A. Vinci[2], A. Brouzgou[1], K. Papagerides[1], F. Tzorbaztoglou[1], S. Cavallaro[2] and P. Tsiakaras[1]*
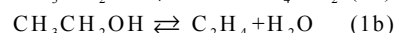
[1]*Department of Mechanical Engineering, School of Engineering, University of Thessaly, Pedion Areos, 383 34 Volos, Greece*

[2] *Dipartimento di Chimica Industriale e Ingegneria dei Materiali, Università di Messina, P.O. Box 29, I-98166S. Agata di Messina, Italy*

*e-mail: tsiak@uth.gr

Introduction

Hydrogen is anticipated to become a major source of energy in the future. This can be produced from many resources: fossil fuels, such as coal, natural gas and biomass or by using nuclear energy and renewable energy sources, such as wind, solar, geothermal and hydroelectric power. Ethanol is an energy carrier that can be produced from renewable energy sources and a good resource of hydrogen production. Hydrogen can be produced via ethanol steam [1], liquid [2], dry [3] and auto-thermal reforming [4] of ethanol. An alternative approach of hydrogen production is also ethanol decomposition through the following three reactions [5]:

$$CH_3CH_2OH \rightleftarrows CO + CH_4 + H_2 \quad (1a)$$
$$CH_3CH_2OH \rightleftarrows C_2H_4 + H_2O \quad (1b)$$
$$CH_3CH_2OH \rightleftarrows CH_3CHO + H_2 \quad (1c)$$

Another possible reaction of the ethanol decomposition is the direct conversion of ethanol to ethyl acetate, according to the following reaction [6]:

$$2C_2H_5OH \rightarrow CH_3COOC_2H_5 + 2H_2 \quad (1d)$$
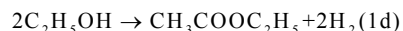
In the present work, it is investigated hydrogen production from ethanol catalytic decomposition over commercial copper chromite catalyst ($Cu_2Cr_2O_5$) at low temperature values (120-280∘C) and at atmospheric pressure in a fixed-bed tubular reactor.

Experimental

A. Catalyst preparation and characterization

The commercial copper chromite catalyst ($Cu_2Cr_2O_5$) was used untreated, as received. The as-received catalyst was characterized by the analytical methods: BET, X-ray fluorescence (XRF) and temperature-programmed reduction (TPR). The amount of the catalyst that was loaded to the reactor was 200 mg.

B. Ethanol catalytic decomposition experiments

The ethanol catalytic decomposition experiments in presence and in absence of steam were conducted in a continuous- flow fixed-bed tubular reactor (Fig.1).
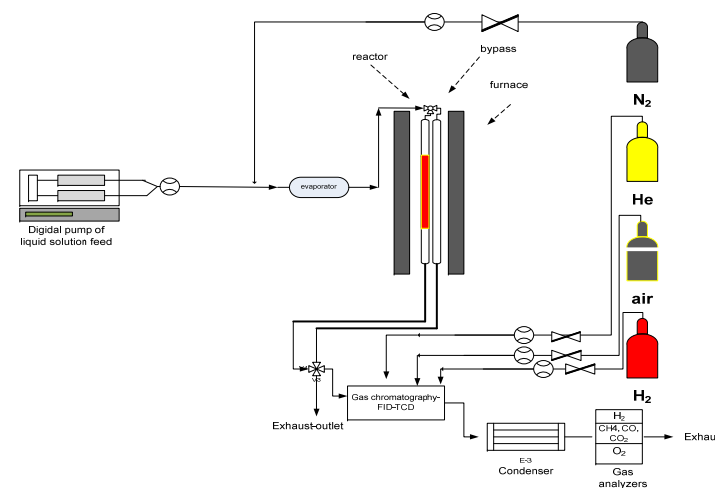

Figure 1. Flow chart of the analysis system.

The ethanol solution (or pure ethanol) is fed in the reactor with the help of a digital pump. Also, nitrogen is fed before the evaporator in order to control the partial pressure of the reactants inside the reactor. The flow of the nitrogen is controlled by flow-meters. In the following, the reactants with the nitrogen are inserted into the evaporator. Before the entrance of the evaporator the line has been covered with thermo-tapes, in order to insure the formation of the gas phase of the reactants. Also the line from the outlet of the evaporator to the entrance of the reactor and from the outlet form the reactor to the entrance of the gas chromatographer has been covered with thermo-tapes for being sure that the reactants and the possible products remain at the gas phase. Next, the gas sample inserts the gas chromatographer where the analysis takes place. In order to be sure that only gas will be fed in the gas analyzers, a condenser has been placed between the gas chromatographer and the gas analyzers.

The experiments were conducted from 120 to 280 ∘C and at atmospheric pressure. The total flux of the feed (calculated in gas phase) was kept at 30 cc/min and the Gas Hourly Space Velocity (GHSPV) was 12000 h^{-1}. The measurements were conducted for steam to carbon ratios (S/C): 0, 0.18, 0.5 and 1.15.

Results/Discussion

A. Characterization of the catalyst

In the Table 1 are given the characteristics from the examined catalyst. As it can be seen the catalyst is consisted of 42% wt of CuO and 38.37 %wt of Cr_2O_3. The area of the catalyst is 37.74 m^2/g.

Table 1. The characterization results

	CuO	Cr_2O_3	A_{BET}	BJH Area Pores	BJH Volume Pores	BJH Aver. Pore Diam.
Catalyst	%wt	%wt	m^2/g	m^2/g	cm^3/g	Å
$Cu_2Cr_2O_5$	42,41	38,37	37,74	42,93	0,23	217,32

B. Effect of the steam to carbon (S/C) ratio on the H_2-yield

In Fig. 2 is reported indicative for the temperature of 230 °C the effect of the examined steam to carbon ratios to the hydrogen yield.
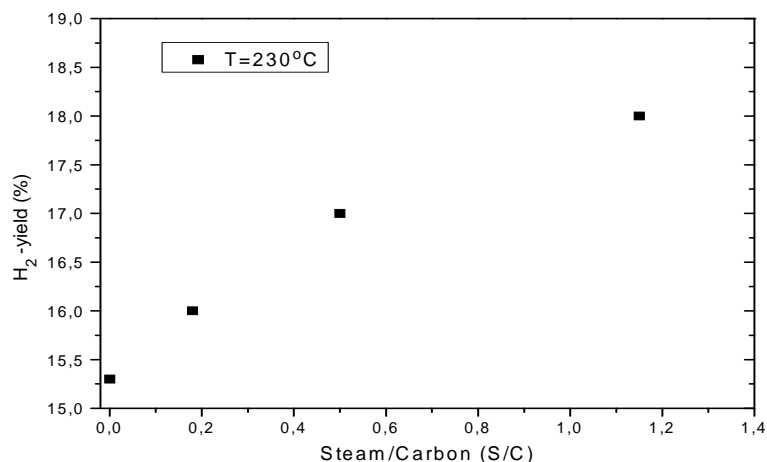

Figure 2. Effect of the steam to carbon (S/C) ratio on the H_2-yield (%).

As it can be deduced, the presence of steam enhances the hydrogen yield. When there is no steam, the hydrogen yield reaches the value of 10%. For ratio S/C = 0.18 the percentage of the hydrogen yield is 16%, for S/C = 0.5 it goes 17%, while with S/C = 1.15 the hydrogen yield is 18%. The same behaviour was observed also for other temperature values.

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