

Steam Reforming of Bio-ethanol on Alkali Doped Ni/MgO Catalysts: Hydrogen Production for MC Fuel Cell

F. Frusteri^{1*}, S. Freni¹, V. Chiodo¹, G. Bonura¹, N. Mondello and S. Cavallaro²

¹ Istituto CNR-TAE, Via Salita S. Lucia Sopra Contesse 39, I-98126, Messina - Italy

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

francesco.frusteri@itae.cnr.it

The need to improve air quality has contribute to move towards a hydrogen economy. The consolidated technologies for H₂ production are mainly based on use of fossil fuels as raw material. However, the use of biomass has recently received particular attention as it is considered CO₂ neutral energy source. In particular bio-ethanol obtained by biomass fermentation could be an useful fuel for H₂ production if an appropriate technology allowing its use without a previous distillation may be individualized. In such contest, molten carbonate fuel cell (MCFC) operating at 650°C could represent a valid example for bio-ethanol use since FC is a co-generative system and heat produced at electrodes could be exploited to sustain an endothermic process like ethanol steam reforming to produce H₂.

Recently different catalytic systems were proposed to perform steam reforming of ethanol [1-5]. In this work alkali doped Ni/MgO catalysts in the steam reforming of simulated bio-ethanol to produce hydrogen for MC fuel cell were investigated. The study was finalized to evaluate the effects of alkali on Ni/MgO catalytic performance mainly in terms of catalyst activity, H₂ selectivity and stability.

21%Ni/MgO catalyst (A sample) was prepared by impregnation (incipient wetness method) of MgO Martin Marietta (120 m² g⁻¹) with a absolute ethanol solution of Ni nitrate used as precursor. Alkali were added by incipient wetness impregnation using a isopropyl solution of acetate salts. After impregnation alkali-doped catalysts (1%K1-A , 1%Na1-A and 1%L1-A samples) were dried at 80 °C and then calcined at 400 °C for 12 h.

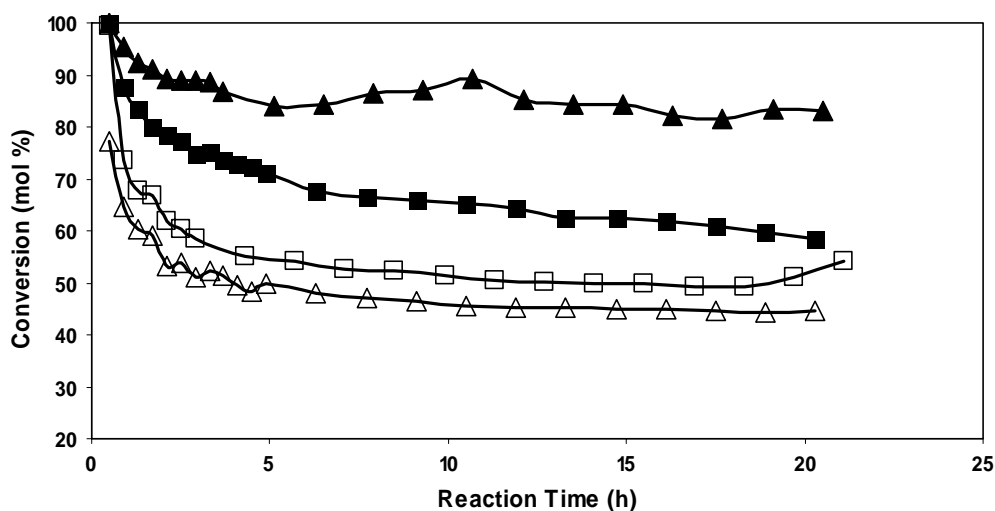


Fig.1. Steam reforming of Bio-ethanol at 650°C and GHSV= 40,000h⁻¹: Comparison between bare and alkali doped Ni/MgO catalysts. ▲) 1%Li1-A; ■) 1%K1-A; □) 1%Na1-A ; △) A

Experiments were performed at atmospheric pressure in a fixed-bed linear quartz microreactor (i.d. = 4 mm; H_{bed} = 1.0-2.0 cm). 0.010 – 0.060g of catalyst (grain size: 40-70 mesh) diluted with 150 -

300mg of same sized carborundum (SiC) were used for the catalytic tests. Prior to each run, catalysts were reduced "in-situ" at $T = 725^{\circ}\text{C}$ for 1h under flowing hydrogen and then cooled down to reaction temperature. Water/ethanol mixture was fed by an isocratic HP 1100 pump and vaporized at 120°C in a current of N_2 . Experiments were performed at $T = 650^{\circ}\text{C}$, gas hourly space velocities (GHSV) ranging from 5,000 to 300,000 $\text{ml}_{\text{EtOH}} \text{h}^{-1} \text{ml}_{\text{cat}}^{-1}$ and steam to carbon ratio (mol/mol) 4.2. The total flow corresponding at GHSV of 40,000 h^{-1} was 124 ml/min (24 vol% N_2 – 68 vol% H_2O – 8 vol% EtOH).

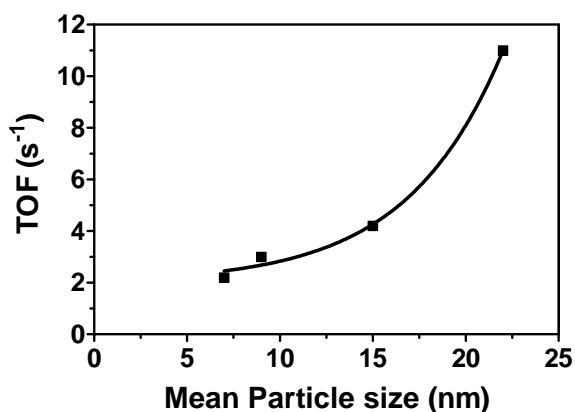


Fig.2. TOF values v.s. mean particle size .

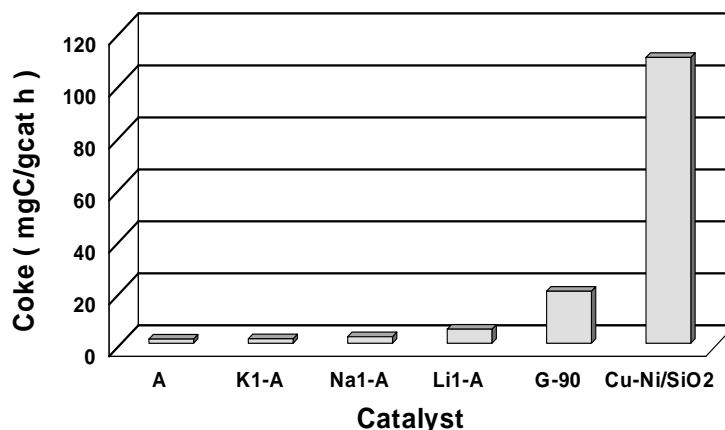


Fig. 3. A comparison in terms of coke formation on different Ni based catalysts.

Results obtained clearly demonstrated that alkali modify Ni/MgO catalytic properties either enhancing stability or improving the specific activity of Ni. Results shown in Fig.1 clearly reveal that mainly Li promotes catalyst stability drastically reducing the initial deactivation observed on bare Ni/MgO system. Unexpectedly, as it can be seen from Fig. 2, catalysts characterized by larger Ni particles resulted to be more active, then reaction appear to be "structure sensitive". The interpretation of such result is postponed to the discussion of reaction mechanism that for brevity reasons cannot be reported in the present abstract.

As regard the coke formation (see Fig.3) which is one of the main problem in steam reforming of ethanol, results demonstrated that it occurs with very low rate on all Ni/MgO catalysts. In addition, endurance tests performed for 700h revealed that coke formation is not progressive and an equilibrium between formation and gasification established during reaction.

H_2 productivity close to the stoichiometric value (5.8 mol of H_2 per mol of ethanol) were obtained while methane selectivity values lower than 3% where observed by operating at equilibrium.

References

1. S. Freni, S. Cavallaro, N. Mondello, L. Spadaio, F. Frusteri, J. Of Power Sources 108(2002) 53
2. S. Cavallaro, V. Chiodo, S. Freni, N. Mondello, F. Frusteri, Appl. Catal A: general 249(2003) 119
3. D.K. Liguras, D. I. Kondarides, X. E. Verykios, Appl. Catal. B: Environmental 43(2003)345
4. F. Auprêtre, C. Descorme, D. Duprez, Catal. Communication 3(2002)263
5. V. Klouz, V. Fierro, P. Denton, H. Katz, J.P. Lisse, S. Bouvot-Mauduit, C. Mirodatos, J. of Power Sources 105(2002)26