TOMSK
POLYTECHNIC
UNIVERSITY

Available online at www.sciencedirect.com

ScienceDirect

Resource-Efficient Technologies ■■ (2017) ■■–■■

www.elsevier.com/locate/reffit

Research paper

Ethanol steam reforming with Co^0 (111) for hydrogen and carbon nanofilament generation

Ashutosh Kumar [a], Ram Prasad [b], Yogesh Chandra Sharma [a,*]

[a] *Department of Chemistry, Indian Institute of Technology (BHU), Varanasi 221005, India*
[b] *Department of Chemical Engineering and Technology, Indian Institute of Technology (BHU), Varanasi 221005, India*

Received 6 February 2017; received in revised form 4 March 2017; accepted 8 March 2017

Abstract

The cobalt metal catalysts are highly active at low temperature ESR. In this study, ESR was studied over barren Co metal (Co^0) from oxalate precursor without any pre-reduction to find out its role in hydrogen and carbon nano-filament generation. The ethanol conversion was found to be 100% with 96.5% hydrogen selectivity at 723K. The time on stream (TOS) study has shown stability up to 19h for Co catalyst. The diameter of Co-carbon nanofilament was calculated and found to be typically in the range of 70–80 nm by the TEM image analysis of spent catalyst. The SEM with EDS analysis revealed that Co^0 state was found in between the carbon nanofilament as well as at the tip of carbon nanofilament. The obtained Co-C nanofilament displayed an adsorption capacity of 552 mg/g at optimum parameter of pH = 2, contact time = 60 minute, concentration = 30 ppm, dose = 0.05g for Orange G dye removal without any chemical or physical treatment. This approach has shown significant results in terms of hydrogen generation and method of Co carbon nanofilament for further utilization in different prospects.

Keywords: Catalyst deactivation; Characterization; ESR; Hydrogen production

1. Introduction

Energy demands and water pollution are always universal issues in front of the world. The resource's requirement in the world is increasing day by day to meet the energy and water demands of the population. The resources are inadequate for enormously increasing population and so it needs proper planning for water resources [1]. The water quality with land use prospective studies suggests that urbanization leads to increment of pollution load over fresh water holy river Ganga rather than agriculture [2]. Urbanization cannot be stopped but sustained. Hence, the recycling of waste or use of resources in a cyclic manner has a greater consequence in upcoming days. Near future assessment of prerequisite energy suggests opting hydrogen as a best one among renewable energy carriers. One of the potential methods for hydrogen generation is steam reforming process [3–5]. Among which utilization of renewable sources ethanol is the best feedstock because it is nontoxic and renewable. The work of George et al. suggests and enlightens the possibilities of using integrated steam reformer with Polymer Electrolyte Membrane Fuel Cell (PEMFC). However, the cost-effective catalyst must be needed during ethanol steam reforming because it has significance in overall cost of hydrogen. Therefore, non-noble metal based catalyst can be a sustainable option [6]. Literature survey suggests that among non-noble metal, Co and Ni based catalysts have shown better C-C bond scission ability as compared to other metal catalysts. Furthermore, between Co and Ni, Co has better efficiency at lower temperature (673K-773K) than Ni. Except, few noble metal catalyst most of the catalysts suffered from deactivation due to carbonaceous deposition during ESR.

The different phase stability and activity suggest that Co is not only highly active for ethanol steam reforming (ESR) in its metallic form but also a major contributor for carbon deposition [7,8]. Co^{2+} and Co^0 states are also active in acetaldehyde as well as ethanol steam reforming [9,10]. Yue et al. suggested that addition of Co in the Ni metal catalyst alloy is able to reduce the carbon deposition during ESR [11]. Among non-noble metal catalysts, cobalt based catalyst with various supports was used

---

* Corresponding author. Department of Chemistry, Indian Institute of Technology (BHU), Varanasi 221005, India. Tel.: +91 542 6702865; fax: +91 542 670 2876.

E-mail address: ysharma.apc@iitbhu.ac.in (Y.C. Sharma).

http://dx.doi.org/10.1016/j.reffit.2017.03.006

Please cite this article in press as: Ashutosh Kumar, Ram Prasad, Yogesh Chandra Sharma, Ethanol steam reforming with Co^0 (111) for hydrogen and carbon nanofilament generation, Resource-Efficient Technologies (2017), doi: 10.1016/j.reffit.2017.03.006

by several authors for ethanol steam reforming (ESR) process [12–21]. This reveals that cobalt is highly active for ESR especially at 753K. However, carbonaceous deposition is a great issue regarding catalyst stability. Different cobalt precursors have also significant contribution in carbon deposition at catalyst surface. The effect of different precursors over carbon deposition was reported by Song et al. with nitrate, chloride, sulphate, acetate, octacarbonyl, carbonate, acetyl acetonate and oxalate, but ESR performances were not reported with cobalt oxalate precursor [22]. One objectionable point was the use of ethanol as an impregnation medium for each precursor to impregnate over CeO_2. Because the cobalt oxalate precursor is insoluble in ethanol, it is not a good impregnation medium for the aforementioned precursor. Cobalt oxalate is soluble in ammonia solution, and so it can be used as an impregnated medium for better distribution of active metals.

Orange G is an azo dye used by several dye industries. It contains a colour producing azo (-N = N-) group and others having higher affinity towards fibres and water auxochromes ($-SO_3$,-OH etc) group. Azo dye is largely used (70%) group among all dyes globally [23]. The dye is carcinogenic, affects water vegetation and is reported to be non-biodegradable [24]. Several approaches of dye removal from waste water through adsorption with carbon are comparatively cheaper. Adsorption of Orange G over carbon shows transfer of the dye from liquid to a solid medium. However, it needs further disposal but oxidation of this dye with carbon at higher temperature or photo degradation in non-harmful form is a sustainable alternative.

The literature survey suggests that metallic cobalt phase is active for C-C bond scission but it also contributes for carbon filament formation [25–27]. The significant property of cobalt oxalate is that in situ thermal treatment in inert atmosphere at 673K typically forms cobalt metallic phase [28]. There is no need to pre-reduce the catalyst to be in active phase and with little support Co needs promoter to be reduced in metallic phase completely [29]. However, Tuti and Pepe worked over barren Co metallic catalyst by pre-reducing Co_3O_4 catalyst. The time on stream study and carbon formation study were also not testified [30]. Therefore, cobalt oxalate precursor was used first time in ESR as a catalyst for in situ formation of cobalt metal through thermal decomposition without any prereduction or chemical treatment. This method reduces the cost for reduction of Co_3O_4 into Co in metallic state. The study about filamentous carbon formation during ESR is still under study. Few authors had suggested the tip growth phenomenon occurs during ESR, whereas, few contradicted this mechanism [31–33]. Therefore, the study over barren active cobalt metal gives new insight of this probable mechanism. Moreover, first time the waste generated after ESR as a mixture of carbon and catalyst was used for the dye (Orange G) abatement.

2. Experimental

The experiment was performed in two stages. First of all ethanol steam reforming was performed for 31h continuously. At the next stage, catalyst with carbonaceous deposition (Co + Carbon) was used for waste water treatment.

2.1. Catalyst preparation

Analytical reagent grade cobalt (II) oxalate dihydrate ($CoC_2O_4.2H_2O$) precursor was used for active Co catalyst preparation. The cobalt metal catalyst was thermally prepared from $CoC_2O_4.2H_2O$ precursor in inert atmosphere at 773K. The $CoC_2O_4.2H_2O$ (5g) was kept in a tubular reactor and N_2 gas was continuously fed (10 ml/min) from room temperature. The temperature was increased at the rate of 20K/min up to 773K and subsequently thermal treatment was continued for 1h. After 1h the catalyst bed was cooled in N_2 atmosphere up to room temperature and the formed Co metal was collected for further characterization and experimentation.

2.2. ESR performance

ESR was performed at atmospheric pressure with cobalt catalyst (500 mg) in a fixed bed flowed quartz tubular vertical reactor having length 40 cm and inner diameter of 3.2 cm. Ahead of reactor, the preheater was assembled to evaporate the ethanol and water mixture (molar ratio = 3:1) fed with the help of syringe pump at the rate of 4 ml/hr. The ESR was performed in 573K–923K range with 50K temperature interval. The time on stream performance was done at 723K reaction temperature, since it was found as a best optimum temperature. The concentration of gaseous mixture was analysed with an online Thermo scientific Trace 1110 gas chromatogram equipped with thermal conductivity detector and flame ionization detector with methanizer. The Porapack Q column (80–100 mesh size) was used for the analysis of liquid mixture residue and hydrocarbon gaseous mixture (CO, CO_2, CH_4, CH_3CHO, H_2O, C_2H_5OH, C_2H_2 and C_4H_{10}). Hydrogen gas was analysed in Molecular sieve column. The selectivity of gases, yield of hydrogen and conversion were calculated by following expressions [34]:

$$H_2\ yield\ (\%) = \frac{moles\ of\ H_2\ produced\ by\ ESR}{moles\ of\ ethanol\ fed \times 6} \times 100$$

$$X_{reactant}\ (\%) = \frac{F_{reactant\ in} - F_{reactant\ out}}{F_{reactant\ in}} \times 100$$

$$Selectivity\ of\ product\ Y\ (\%) = \frac{N \times moles\ of\ Y\ produced}{2 \times moles\ of\ ethanol\ converted} \times 100$$

$$Selectivity\ of\ H_2\ (\%) = \frac{N \times moles\ of\ H_2\ produced}{\left[3 \times (F_{ethanol\ in} - F_{ethanol\ out}) + (F_{water\ in} - F_{water\ out})\right)} \times 100$$

After ESR performance N_2 was flushed for 30 minutes to remove the (ethanol–water mixture) vaporized feed mixture.

2.3. Orange G dye removal performance

The chemicals used, NaOH, HCl and Orange G ($C_{16}H_{10}N_2Na_2O_7S_2$) dye were purchased from Merck, India, with analytical grade purity. The coloured dye was stable within the pH range of study. The stock solution (100 mg/l) of Orange G dye was prepared and further lower concentration of solution

Please cite this article in press as: Ashutosh Kumar, Ram Prasad, Yogesh Chandra Sharma, Ethanol steam reforming with Co^0 (111) for hydrogen and carbon nanofilament generation, Resource-Efficient Technologies (2017), doi: 10.1016/j.reffit.2017.03.006