



## Investigation of the Behaviour of Mn doped CeO<sub>2</sub> Catalyst for Ethanol Steam Reforming Reaction

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### Abstract

The effect of Mn on performance of CeO<sub>2</sub> in ethanol steam reforming was studied. Mn doped CeO<sub>2</sub> was prepared by co-precipitation method and analyzed by BET, XRD and TPR. CeMnO<sub>2</sub> showed the acceptable conversion (31%) and hydrogen yield (57%). The result of the analysis revealed higher specific surface area of the introduced catalyst than CeO<sub>2</sub> and MnO<sub>x</sub>. It was also indicated that although Ce without Mn had the higher conversion but it happened because of more CH<sub>4</sub> selectivity (34% @ 500 °C). Mn conducted the reaction to more CO<sub>2</sub> generation and also it was an effective metal for WGS and ESR reactions by adsorbing steam and ability of oxygen mobility.

**Keywords:** Hydrogen production; Ethanol; Steam reforming; CeMnO<sub>2</sub>.

### Introduction

Interest in renewable energy sources and high specific energy content of hydrogen led to widespread research about dehydrogenation and steam reforming of hydrocarbons. Because hydrogen is not existed in elemental form, it shall be obtained from sources that ethanol has been attractive among them because of relative low cost, hydrogen rich and production capability from biomass [1]. According to eq. (1), steam reforming (SR) of ethanol possesses the highest theoretical yield of hydrogen among other methods such as oxidative steam reforming, dry reforming and partial oxidation [2].



Catalysts aid to enhance hydrogen selectivity and minimize the coke formation by choosing the best reaction route [3]. The activity of CeO<sub>2</sub> and ZrO<sub>2</sub> as a support in micro and nano particle size has been examined and was found that although both nano catalysts showed excellent hydrogen selectivity (>80%) but the best was obtained by CeO<sub>2</sub> due to the highest surface area (72.9 m<sup>2</sup> gr<sup>-1</sup>) and active metal dispersion [4]. Very favorable effect of Ni, Co and Mn on CuZn at low temperature in ethanol steam reforming has been proved [5]. Results endorsed positive function of Ce on activity and stability of catalyst which was relevant to self-oxidizing ability of Ce and prevention of carbon precipitation [6]. Catalytic performance



of  $\text{Co}_x\text{O}_y/\text{SBA-15}$  with and without  $\text{MnO}_x$  was investigated [2]. Results revealed an improvement in term of stability on the case with  $\text{MnO}_x$ .

The aim of this paper was to study the effect of Mn on  $\text{CeO}_2$  as a catalyst in ethanol steam reforming. Ethanol conversion, hydrogen yield,  $\text{CO}_2$ , CO and  $\text{CH}_4$  selectivity were evaluated at temperature range of 300-500 °C.

## Experimental

### Catalyst Preparation

CeMn oxide was prepared by co-precipitation method. Measured values of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  were solved in deionized water on a stirrer (400 rpm) at room temperature. A solution of sodium carbonate in deionized water was added slowly to acid solution to reach desired PH (nearly 8). Then resulting suspension was kept at room temperature for 6 hr on the stirrer (400 rpm). After filtration and washing with ethanol and water, the precipitation was dried at 80 °C for 18 hr and calcined for 4 hr at 500 °C in air.

### Catalyst Characterization

X-Ray Diffraction (XRD) patterns were recorded on an X-ray diffractometer (PANalytical X'Pert-Pro) using a  $\text{Cu-K}\alpha$  radiation source in the range of  $2\theta=0-80^\circ$ . The crystallite sizes of the samples were estimated by Scherrer's equation. The specific surface areas were determined by Brunauer-Emmett-Teller method (BET) and using Belsorp mini II device at the boiling temperature of liquid nitrogen (-196°C).

Temperature programmed reduction (TPR) analysis was used for evaluating the reducibility of prepared catalysts by means of an automatic apparatus (Chemisorb 2750, Micromeritics). In the TPR measurement, the fresh catalyst (~100 mg) was exposed to a heat treatment (10°C/min up to 900°C) in a gas flow (30 ml/min) containing a mixture of 10 vol%  $\text{H}_2$  in Argon. Before the TPR experiment, the samples were degassed under an inert atmosphere at 200°C for 1 h.

### Catalyst Evaluation

Performance of the prepared catalyst was evaluated in a tubular quartz fixed bed reactor, in atmospheric pressure and different temperatures of 300-500 °C (by intervals of 50 degrees) and total feed flow rate of 70 ml min<sup>-1</sup>. Molar ratio of ethanol/steam was 1:6.

Before each test, catalyst was reduced in situ at 550 °C for 3 hr under  $\text{H}_2:\text{Ar}$  mixture flow (10:20 ml min<sup>-1</sup>). The effluent gas was passed through a cold trap to separate liquid from gas before subjected to gas chromatograph (GC). Ethanol conversion ( $X_{\text{Et}}$ ), hydrogen yield ( $Y_{\text{H}}$ ) and CO,  $\text{CO}_2$  and  $\text{CH}_4$  selectivities ( $S_i$ ) based on molar flow rate of species (F) were calculated by:

$$X_{\text{Et}}(\%) = ((F_{\text{Et,in}} - F_{\text{Et,out}}) / F_{\text{Et,in}}) * 100 \quad (2)$$

$$Y_{\text{H}}(\%) = (F_{\text{H,out}} / (6 * F_{\text{Et,in}})) * 100 \quad (3)$$

$$S_i(\%) = (F_{i,\text{out}} / (2 * (F_{\text{Et,in}} - F_{\text{Et,out}}))) * 100 \quad (4)$$

## Results and discussion

### Catalyst Characterization

The results of BET analysis are summarized in table 1. Although specific surface area of  $\text{MnO}_x$  was really low but it increased in case of co-precipitation of Ce and Mn. Existing of more pores in CeMn oxide towards  $\text{CeO}_2$  led to High specific surface area even despite of more pore diameter and volume.



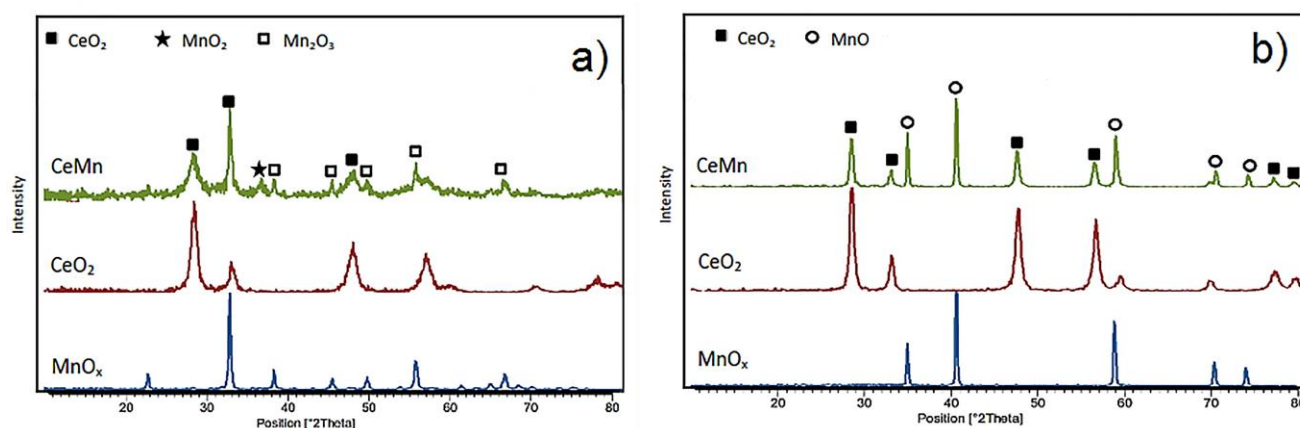
**Table 1. Prepared samples characterization results**

	BET analysis			XRD analysis
	$S_{\text{BET}}$ ( $\text{m}^2 \text{gr}^{-1}$ )	Total Pore Volume ( $\text{cm}^3 \text{gr}^{-1}$ )	Mean Pore Diameter (nm)	Crystallite Size (nm)
CeO <sub>2</sub>	76	0.14	7.2	10.87
MnO <sub>x</sub>	19	0.26	54.54	27.98
CeMnO <sub>2</sub>	80.41	0.25	12.24	18.06

Fig. 1 shows XRD patterns of prepared samples before (a), and after reaction (b). Mn doped CeO<sub>2</sub> samples have peaks in position corresponding to (111), (200), (220), (311), (222) and (400) planes according to XRD patterns that is in agreement with JCPDS cards [7-9]. Differences in intensity or a little position shift compared to CeO<sub>2</sub> indicates formation of Mn doped CeO<sub>2</sub> and peaks related to Mn<sub>x</sub>O<sub>y</sub> can be justified by more dopant from CeO<sub>2</sub> lattice, so remaining on the surface is detected. Generally, peaks related to CeO<sub>2</sub> became weaker in case of doped with Mn. The crystallite size of Ce and Mn estimated from Debye-Scherrer equation was about 10.87 and 27.98 nm, respectively. So the crystallite size of Ce became larger by addition of Mn (18.06 nm).

XRD patterns of samples after SR (fig. 2b) show that no and/or the small amount of carbon formed which could not be detected by XRD analysis.

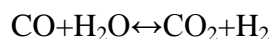
The peaks after test are thinner comparing to before, that indicated increase of crystallite size and agglomeration of catalysts during test. Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> reduced to MnO in one and two step, respectively.



**Fig. 1. XRD patterns of a) prepared samples, b) Samples after reaction**

### Catalyst Evaluation

Ethanol conversion and product distribution as a function of temperature for SR of ethanol over CeMn oxide are shown in fig. 2. Although it is clear that high temperature is favored for eq. 2 due to be an endothermic reaction, but water-gas shift reaction (WGS), eq. 5, conducted to CO generation in this condition, so H<sub>2</sub> and CO, unlike CO<sub>2</sub>, improved by increasing the temperature.



(5)



Since CH<sub>4</sub> selectivity increased by temperature, so it can be resulted that methane steam reforming (eq. 6) has not happened, on the other hand total hydrogen generation was related to ethanol. In addition, more CH<sub>4</sub> selectivity by increasing the temperature can be obtained from ethanol decomposition (eq. 7) or methanation (eq. 8) which may be occurred with higher rate than ethanol reforming.

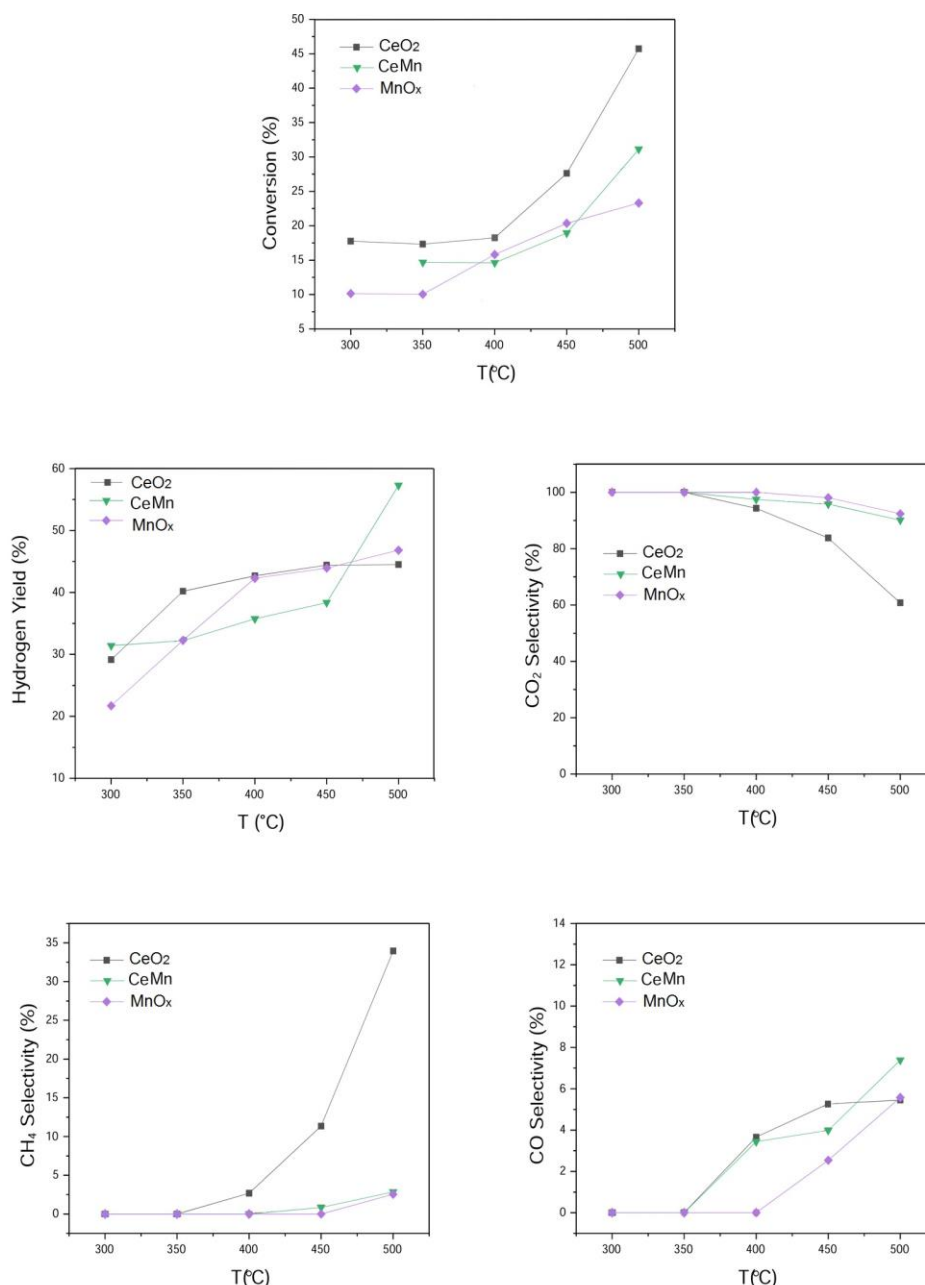
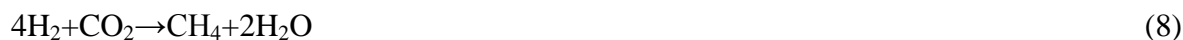


Fig. 2. Effect of reaction temperature on the conversion and product distribution for SR of ethanol on CeMn oxide at condition of ethanol/water ratio: 1/6 and GHSV: 14000 hr<sup>-1</sup>



As expected from catalysts characteristics, CeMn oxide showed the acceptable conversion (31% @500 °C). Mn is known as an effective metal in improving the catalyst performance [10] by adsorbing the steam rather than other metals and transferring the oxygen to active sites after steam decomposition that lead to more hydrogen generation [11]. Conversion improved with increasing temperature. Hydrogen yield of CeMn oxide reached 57% at 500 °C. Only weakness of CeMn oxide appeared in CO selectivity especially at high temperature (about 7.4% @500 °C). CeMn oxide exhibited the acceptable hydrogen yield at 300 °C with a little amount of CO, CO<sub>2</sub> and CH<sub>4</sub> which have not been detected by GC so that no conversion has been registered for CeMn oxide at 300 °C.

CeO<sub>2</sub> showed the highest conversion at all temperatures but with a clear look at results of CH<sub>4</sub> and CO<sub>2</sub> selectivity, it was specified that Ce unlike Mn, conducted the reaction to CH<sub>4</sub> generation which tended to lead the reaction to CO<sub>2</sub> production. On the other hand, the results revealed that Mn is more effective than Ce for WGS reaction and maybe methane reforming too. It is clear that CeMn composition has better performance than Ce and Mn separately, so we can say there is a synergism between them.

According to high surface area, crystallite size and acceptable results of CeMn oxide, TPR analysis performed to know its reducibility behavior (Fig. 3). Reduction is necessary to provide a favorable surface for the reaction with introduction of oxygen vacancies. Therefore, selection of the appropriate reduction temperature plays an important role in catalyst activity. Oxygen vacancies have been introduced as active sites for steam decomposition [11]. Researchers [12] believe that oxygen storage capacity and oxygen mobility of metal oxides effects on catalyst performance in reforming reaction.

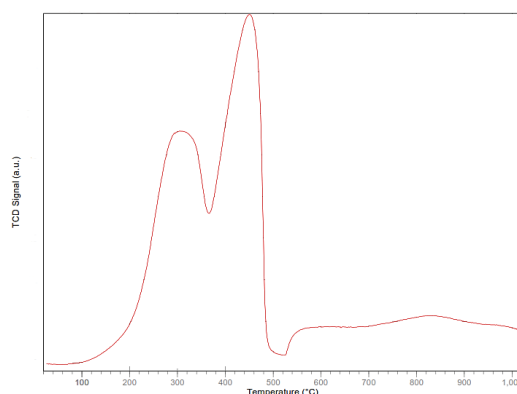


Fig. 3. TPR analysis of CeMn oxide

The small peak at high temperature (820 °C) in both samples related to reduction of bulk CeO<sub>2</sub> so turn of CeO<sub>2</sub> to Ce<sub>2</sub>O<sub>3</sub> was happened [12]. The peak at low temperature is appeared due to reduction of dopant, MnO<sub>2</sub> to Mn<sub>2</sub>O<sub>3</sub> at 310 °C. The peak at middle temperature (>500 °C) dedicated to reduction of surface CeO<sub>2</sub> and also Mn<sub>3</sub>O<sub>4</sub> to MnO. It has been found that the peak related to surface reduction of CeO<sub>2</sub> changed to lower temperature by addition of Mn, so Mn could improve the reducibility of CeO<sub>2</sub> [13]. On the other hand positive effect of CeO<sub>2</sub> on increasing the rate of Mn<sup>4+</sup>/Mn<sup>x+</sup> has been proven [14].

### Conclusions

The effect of Mn on CeO<sub>2</sub> was studied for hydrogen generation in ethanol steam reforming at temperature range of 300-500 °C and pressure of 1 atm in fixed bed reactor. Mn-doped Ce



exhibited acceptable conversion (31%) and hydrogen yield (57%) which was affected by high specific surface area ( $80.41 \text{ m}^2 \text{ gr}^{-1}$ ) accompanied with synergistic interaction. Ce with high conversion resulted from methane production was modified by addition of appropriate amount of Mn which conducted the reaction to higher  $\text{CO}_2$  generation. Eventually CeMn oxide can be introduced as a suitable catalyst for hydrogen generation from SR of ethanol. It also can be as a support for active metals like Ni and its specification and performance can be improved by addition of promoters.

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