Effect of metal oxide additives on the properties of $Cu/ZnO/Al_2O_3$ catalysts in methanol synthesis from syngas

F.Meshkini,[a] M.Taghizadeh Mazandarani,[a] M.Bahmani[b]

[a]*Chemical Engineering Department, Faculty of Engineering, Mazandaran University, P.O.Box:484, Babol, Iran, E-mail: taghizadehfr@yahoo.com , Tel: +98111-3234204, Fax: +98111-3234201*
[b]*Catalyst Research Group, Petrochemical Research and Technology Co., National Petrochemical Co., P.O.Box: 14458, Tehran, Iran*

Abstract

The $Cu/ZnO/Al_2O_3$ catalysts, prepared by co-precipitation method, has been modified by adding small amount of Mn, Mg, Zr, Cr, Ba, W and Ce oxide using design of experiments ($^1/_{16}$ full factorial design). Performance of the prepared catalysts for CO/CO_2 hydrogenation to methanol was evaluated by using a stainless steel fixed-bed reactor at 5MPa and 513 K. The oxide additives were found to influence the catalytic activity, dispersion of Cu, Cu crystallite size, surface composition of catalyst and stability of catalysts during their operations. The results showed that the Mn, Zr and Ba promoted catalysts have high performance for methanol synthesis from syngas.

Keywords: Methanol synthesis, $Cu/ZnO/Al_2O_3$ catalysts, metal oxide additives

1. Introduction

Methanol (MeOH) is an important feedstock for the production of many chemicals and potentially a cleaner alternative fuel for the future [1].
Furthermore, as methanol is expected to be used for fuel cell systems and power plants, it could be more important in energy field and hence considered a safe medium for the storage and transportation of hydrogen [2, 3]. Commercially, methanol is produced from syngas prepared from natural gas or coal, which mainly contains CO and H_2 along with a small amount of CO_2.
Recently, methanol synthesis from CO_2 hydrogenation has received much attention because it has been considered to be one of the promising ways for CO_2 migration. Many researchers have studied methanol synthesis from CO_2 rich feed hydrogenation [4].
Methanol is currently produced from syngas using using copper–zinc-based oxide catalysts at 5.0–10.0 MPa and 473–523 K. $Cu/ZnO/Al_2O_3$ catalysts have long been used in industrial methanol synthesis because of their high catalytic activity, long life time, high poison durability and relatively low reaction temperature and pressure [5,

6]. Nevertheless, finding a better catalyst for methanol synthesis is still a subject of intense investigations. In order to increase $Cu/ZnO/Al_2O_3$ activity and stability, this basic catalyst was often modified by different oxide additives such as boron [2], silica [4, 7], Chromium [8], palladium [9], tungsten [10], manganese [5, 11] and Zirconium [12]. In this work, a small amount of different oxide (Mn, Mg, Zr, Ce, Ba, Cr and W) were added to $Cu/ZnO/Al_2O_3$ catalyst to evaluate the catalytic activity and stability by using design of experiments ($^1/_{16}$ full factorial design) in a stainless steel fixed-bed reactor at 5MPa and 513 K.

2. Experimental

2.1. Design of experiments

By means of experimental designing method, optimizing the different process variables is possible and number of required runs would be reduced. A full factorial experiment considers potential interactions between the factors, and the conclusions are highly reproducible. Therefore it is economical for characterizing a complicated process [13, 14]. In this study, this method is chosen to investigate the effect of each promoter on the properties of catalyst and interaction between them. The design includes $^1/_{16}$ of total runs. Because of considering two levels for each variable (presence or absence of each promoter), 8 ($^1/_{16}\times 2^7$) runs would be required. A design of experiments which is chosen to determine the experimental plan by MINITAB release 14 is shown in Table 1. The catalysts are named in the form of A-M which A indicates the catalyst with no promoter ($Cu/ZnO/Al_2O_3$) and M indicates the promoter which is added.

Table1. Experimental layout using $^1/_{16}$ full factorial

Run	Catalyst name	Mg	Mn	Zr	Ce	Ba	Cr	W
1	A-Ce-Ba-Cr	-1	-1	-1	+1	+1	+1	-1
2	A-Mn-Cr-W	+1	-1	-1	-1	-1	+1	+1
3	A-Mg-Ba-W	-1	+1	-1	-1	+1	-1	+1
4	A-Mn-Mg-Ce	+1	+1	-1	+1	-1	-1	-1
5	A-Zr-Ce-W	-1	-1	+1	+1	-1	-1	+1
6	A-Zr-Ba-Mn	+1	-1	+1	-1	+1	-1	-1
7	A-Mg-Zr-Cr	-1	+1	+1	-1	-1	+1	-1
8	A-Mn-Mg-Zr-Ba-Ce-W-Cr	+1	+1	+1	+1	+1	+1	+1
"+" means presence of each promoter and "-" means absence of each promoter								

2.2. Preparation of catalysts

The oxide precursors of $Cu/ZnO/Al_2O_3/MO$ (M_2O_3 or MO_2), where M is Mn, Mg, Zr, Ce, Ba, Cr and W, with a nominal composition of 65 mol% Cu, 25 mol% ZnO and 10 mol% Al_2O_3 and 2 mol% of each promoter were prepared by the conventional co-precipitation method. An aqueous solution of metal nitrate (only tungsten was introduced as Ammonium tungstate) and an aqueous solution of Na_2CO_3 were added

simultaneously to a vessel containing deionized water under vigorous stirring. The precipitation was carried out at 343 K and a constant pH 7. The precipitates were aged in mother liquid at 343 K for 5 hr under stirring.

2.3. Catalytic activity

CO/CO_2 hydrogenation tests were carried out using a stainless steel tubular, down flow, high pressure, fixed bed reactor (interior ID: 10 mm), which contained 1.1 gr (1 Cm^3) catalysts placed between two layers of SiC. All catalysts were reduced in diluted H_2 (3% in N_2) flow at 513 K and atmospheric pressure for 15 h before syngas exposure.
The catalytic activity in the methanol synthesis was determined at 5 MPa pressure and 513 K with a mixture of $CO/CO_2/H_2$ = 1/1/14.5 and GHSV=12400 hr^{-1}. The outlet gases (products and unconverted feed) were cooled up to 255K and the water and methanol in liquids were analyzed by Varian Star GC (CP-3800). H_2, CO, CO_2 and small amount of CH_4 were determined by RGA (Agilent 6890N) chromatographs.

3. Results and discussion

The results of catalytic activity tests on catalysts with different promoters are given in Table 2. In this table, initial activity and the activity after 64 hrs, average carbon conversion (mol %) and methanol selectivity are shown.

Table 2: The activity and selectivity of the catalysts for methanol synthesis

Catalyst name	MeOH Space time yield ($gr_{CH3OH}/Kg_{Cat}.hr$)		Carbon conversion (mol%)	MeOH selectivity
	Initial activity	Activity after 64 hr		
A-Zr-Ba-Mn	684.06	642.04	28.77	99.49
A-Mn-Cr-W	608.33	505.43	24.78	99.62
A-Mg-Zr-Cr	599.38	567.29	24.85	99.49
A-Mg-Ba-W	574.69	481.89	23.18	99.08
A-Mn-Mg-Ce	488.14	507.00	21.68	98.32
A-Ce-Ba-Cr	440.63	400.24	18.41	99.17
A-Zr-Ce-W	423.06	440.63	18.77	98.54
A-Mn-Mg-Zr-Ba-Ce-W-Cr	376.68	395.44	16.69	98.97

According to the results obtained from the design of experiments with regarding each response individually, four catalysts (catalyst without any promoter, with Mn, with Zr and with Mn-Zr) were prepared and tested again at the same conditions. MeOH space time yield of these catalysts are illustrated in Figures 1-4. A small amount of Mn added to the $CuO/ZnO/Al_2O_3$ increased the catalyst activity but had no effect on the catalyst stability. The activity of the catalyst with Zr as a promoter became higher after 50 hrs than that of the catalyst without promoter.
By using Mn and Zr as promoters together, the catalyst became stable and its activity after nearly 30 hrs was more than that of the catalyst without any promoter (Figure 4).

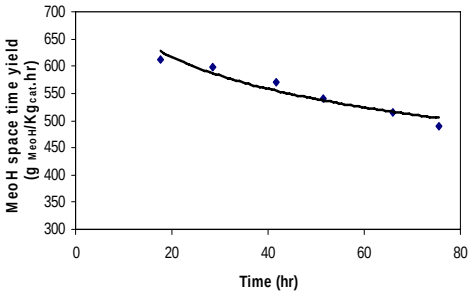

Figure 1: MeOH space time yield for catalyst A (without any promoter).

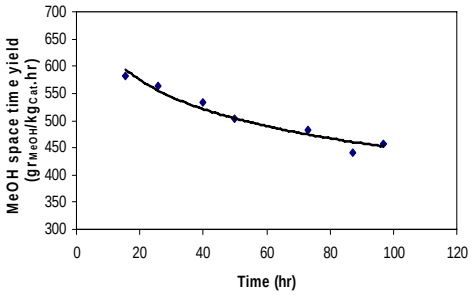

Figure 2: MeOH space time yield for catalyst A-Mn (containing Mn as a promoter).

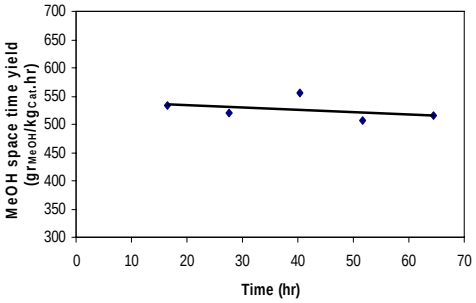

Figure 3: MeOH space time yield for catalyst A-Zr (containing Zr as a promoter).

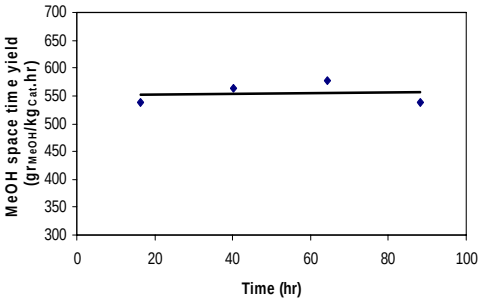

Figure 4: MeOH space time yield for catalyst A-Zr-Mn (containing Zr and Mn as promoters).

Figure 5 shows the variations of the methanol yield with time on stream for the catalyst without any promoter (A) and the catalyst having the high activity and stability (A-Mn-Zr).

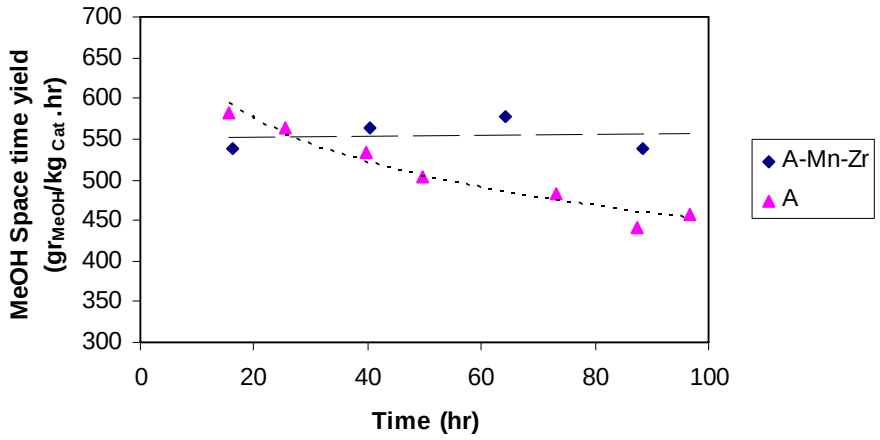

Figure 1: MeOH space time yield for catalyst A and catalyst A-Mn-Zr.

4. Conclusions

Design of experiments, a good way for reducing the number of runs, applied in the field of catalyst preparation. The full factorial design using individual response evaluation was a useful tool to explore the influence of the additives on the catalyst activity and stability.

If Zr and Mn were used as promoters together, $Cu/ZnO/Al_2O_3$ catalyst became more stable and its activity after nearly 30 hrs was more than that of the catalyst without any promoter.

It seems that Zr could be a good support for Cu/ZnO catalyst because it makes the catalyst more stable and also increase its activity.

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