

**Evaluating the optimum molar ratio of  $Mn^{2+}/Co^{2+}$  and mass percent of  $Al_2O_3$  for preparing a catalyst for secondary alcohol oxidation**

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### ABSTRACT

Alcohol oxidation is an important reaction in organic syntheses. Some of these reactions must be under difficult conditions in respect of high temperature and pressure. In many cases, reactions are conducted by environmentally in appropriate solutions. In this study, preparing an effective nanocatalyst and estimating the optimum provisions of its production processes are assessed. Two major and crucial factors of  $(Mn^{2+}/Co^{2+})-Al_2O_3$  catalyst are molar ratio of  $Mn^{2+}/Co^{2+}$  and mass percent of  $Al_2O_3$ . Our experimental results showed that 1:1 molar ratio and 15% of  $Al_2O_3$  by mass are fairly suitable. Prepared catalyst was used in the oxidation reaction.

**Keywords:** Nanocatalyst; Optimum ratio; Mass percent

## INTRODUCTION

Catalysts may be physically solid, liquid, gas or as solute, examples of solid catalysts are: Platinum, Iron powder ..., gas catalysts such as:  $NO_2$ ,  $NO$ , ... and in solution :  $H^+$  in solution or some kind of ions in solutions . In this work we focused on the solid catalysts.

Gas adsorption is a process in which a gas accumulates on surface and not penetrates, but absorption process in general is where the absorbent penetrates into the absorptive medium. In general a solid catalyst adsorbs a gas on its surface and the result is an adsorption process. Two types of adsorption processes are:

1. Physical adsorption or physisorption
2. Chemical adsorption or chemisorption.

Nanoparticles mostly are used as adsorbents and catalysts in several areas, such as: oil industries [1-5].

The porosity of catalysts has an important role in catalysts efficiency, hence it should pay attention to the extend of catalyst porosity[3-5]. Moreover, the particles' size also have an influential role in catalyzed reactions[6-14].

In this work, a new nanocatalyst based on nano-  $Al_2O_3$  and the optimum ratio of  $Mn^{2+}/Co^{2+}$  was prepared and used in the considered oxidation reaction.

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## EXPERIMENTAL

Developing  $Mn^{2+}/Co^{2+}$  nanocatalyst based on nano-  $Al_2O_3$  and assessment of the optimum  $Mn^{2+}/Co^{2+}$  ratio we mixed 50 mL manganese(II) nitrate 0.5 molar with 50 mL cobalt(II) nitrate 0.5 molar in a suitable balloon, then added to the resultant solution 2.20 gr of  $Al_2O_3$  nano powder. The mixture was heated up to  $80^\circ C$  and then 0.5 gr of sodium carbonate was solved in 10 ml of water and was added to the mixture. The balloon content was stirred continuously and finally kept in this situation for 5 hours, while, the balloon was connected to a cooling apparatus. Finally, the sediments were separated and washed with distilled water many times. The washed sediments were dried at  $150^\circ C$  for 16 Hours and then exposed to air at  $500^\circ C$  for 24 hours to become calcified. The resulted product was fairly nano-composite which was used as a catalyst for oxidizing the benzyl alcohol.

The procedure was repeated with the following ratio of  $Mn^{2+}/Co^{2+}$  at the same conditions:

1:2,1:3,1:4,1:5,1:6,2:1,3:1,4:1,5:1,6:1

### Assessing the impact of produced catalyst on the benzyl alcohol oxidation rate

1mmol of benzyl alcohol (0.16 g) was poured in a thoroughly clean cup and 0.05 gr. of produced catalyst was added to it and temperature was set at  $80^\circ C$  and the solution was stirred by a micro-magnet. From the beginning of the reaction, every 10 minutes a small quantity of mixture was picked out by a little spatula and a spot of it was settled on the TLC paper by means of a capillary tube and at the time a spot of evidence (containing a drop of benzaldehyde and 4 drops of ethyl acetate) was also settled on TLC paper. At first, these two spot were aligned and

then TLC paper was located into the solution containing 3 drops of ethyl acetate and 7 drops of hexane-n (the solution was absorbed by TLC paper). Then prepared paper was exposed to UV light lamp. The locations of sample and control spot were recorded and the procedure was repeated until the spot of the test solution and the control spot were aligned at the end. This means that benzyl alcohol is completely oxidized to benzoaldehyde and the duration is a measure of oxidation rate. Upon analyzing the results, the best molar ratio of  $Mn^{2+}/Co^{2+}$  was 1:1.

### Assessment of the optimum mass percent of nano- $Al_2O_3$

The experiment was repeated with various mass percents of nano-  $Al_2O_3$  and the optimum mass percent was 15% of  $Al_2O_3$ .

## RESULTS AND DISCUSSION

The results of experiments for evaluating the optimum ratio are given in tables 1 and 2.

In order to represent the experimental results (tables 2) in a suitable fashion, we constructed a diagram where vertical axis shows the transformation fraction or efficiency and horizontal axis shows the transformation time for benzyl alcohol transformation to Benzoaldehyde (Fig. 1). As illustrated in this diagram, at 35 minutes we have optimum efficiency percent equal to 98%, it means that after 35 minutes almost all Benzyl alcohol is transformed to Benzoaldehyde and this optimum state is related to molar ratio of (1:1) for  $Mn^{2+}/Co^{2+}$  (tables 2).

In Table 3, the results related to the optimum mass percent of the involved substances are gathered. In Fig. 2, efficiency of prepared catalysts is plotted against the mass percent of nano  $Al_2O_3$  (see tables 4).

**CONCLUSION**

The nano catalysts containing  $Mn^{2+}/Co^{2+}$  on nano  $Al_2O_3$  basis were prepared and the optimum ratio of  $Mn^{2+}/Co^{2+}$  with different molar ratios was determined. It was found that the molar ratio of (1:1) of  $Mn^{2+}/Co^{2+}$  is an optimum ratio.

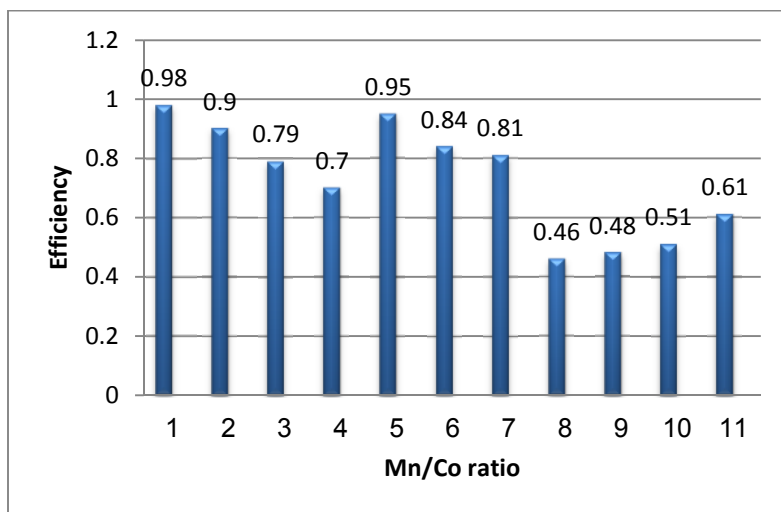
In addition, we found that the mass percent of 15% of  $Al_2O_3$  powder is a best one and the 98% efficiency was obtained after 35 minutes for transforming Benzyl alcohol to Benzaldehyde.

**Table 1.** The weights of related substances for estimating the optimum ratio of  $Mn^{2+}/Co^{2+}$

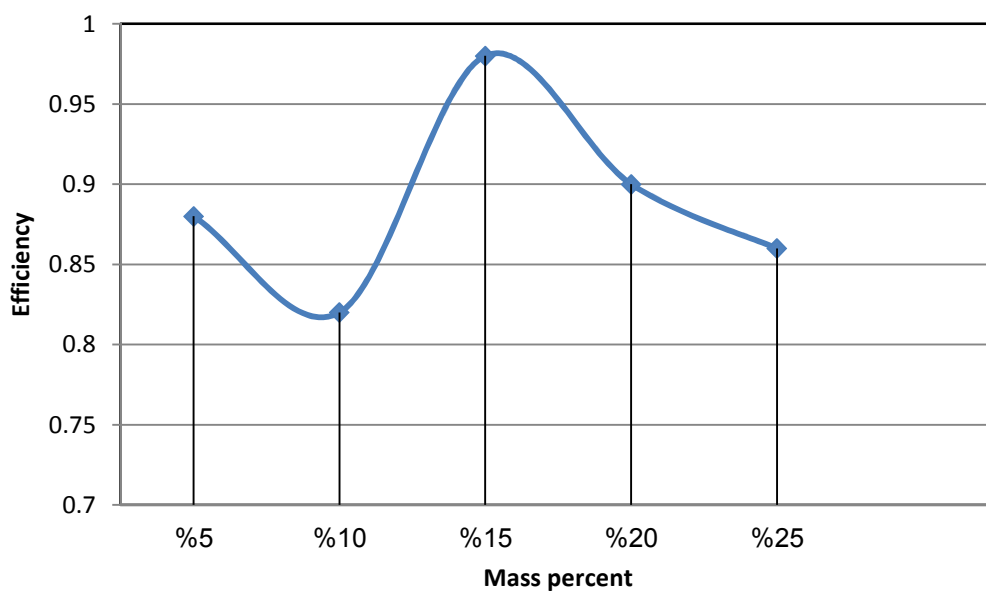
Ratio of Mn/Co	Co(g)	Mn(g)	$Al_2O_3$ (g)	$Na_2CO_3$ (g)
Mn/Co1-1	7.26	6.28	2.02	0.5
Mn/Co1-2	3.64	6.28	1.46	0.5
Mn/Co1-3	1.82	6.28	1.21	0.5
Mn/Co1-4	0.91	6.28	1.078	0.5
Mn/Co1-5	0.455	6.28	1.01	0.5
Mn/Co1-6	0.0156	6.28	0.98	0.5
Mn/Co2-1	7.26	3.135	1.56	0.5
Mn/Co3-1	7.26	1.567	1.32	0.5
Mn/Co4-1	7.26	0.783	1.2	0.5
Mn/Co5-1	7.26	0.391	1.15	0.5
Mn/Co6-1	7.26	0.2	1.12	0.5

**Table 2.** The optimum time and transformation fraction in order to determine optimum ratio of  $Mn^{2+}/Co^{2+}$

Ratio of Mn/Co	Time(min)	Conversion %
Mn/Co1-1	35	98
Mn/Co1-2	100	90
Mn/Co1-3	165	79
Mn/Co1-4	255	70
Mn/Co1-5	65	95
Mn/Co1-6	125	84
Mn/Co2-1	140	81
Mn/Co3-1	81	46
Mn/Co4-1	624	48
Mn/Co5-1	440	51
Mn/Co6-1	400	61



**Fig. 1.** Transformation fraction for transformation Benzyl alcohol to Benzaldehyde respect to  $Mn^{2+}/Co^{2+}$  ratio.



**Fig. 2.** The transformation fraction or efficiency against to the mass percent of nano  $Al_2O_3$  basis.

**Table 3.** The amount of involved materials and mass percent of nano-  $Al_2O_3$  basis

$Al_2O_3$ Weight%	$Co^{2+}$ (g)	$Mn^{2+}$ (g)	$Al_2O_3$ (g)	$Na_2CO_3$ (g)
5%	7.26	6.28	0.68	0.5
10%	7.26	6.28	1.35	0.5
15%	7.26	6.28	2.02	0.5
20%	7.26	6.28	2.7	0.5
25%	7.26	6.28	3.38	0.5

**Table 4.** The optimum time  $\tau$  mass percent of  $\text{Al}_2\text{O}_3$  and conversion%

$\text{Al}_2\text{O}_3$ Weight%	$t_{\text{opt}}$ (mine)	conversion%
5%	98	88%
10%	170	82%
15%	35	98%
20%	80	90%

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