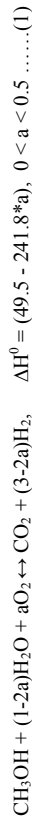


Hydrogen Production Via Oxidative Steam Reforming of Methanol over Cu/Ce(or Cr)/Al Oxide Catalysts

Sanjay Patel¹ and K. K. Pant^{2*}
^{1,2} Indian Institute of Technology, Chemical Engineering Department Hauz Khas
 New Delhi-11006 (India)
 *kkpant@chemical.iitd.ac.in, sanjay9patel@yahoo.com

Introduction

The realistic alternative to the conventional combustion engine of automobile carriers can be a fuel cell, which does not emit the toxic pollutants at tail pipe. The hydrogen required for the functioning of fuel cell can either be stored in pressurized tank or generated on-board using liquid hydrogen carrier such as methanol that offers several advantages [1,2]. The use of pressurize hydrogen has some technical and economical problem. Therefore present study has been carried out to produce hydrogen from methanol with high yield and low CO selectivity by developing appropriate catalyst and optimizing process parameters. The oxidative steam reforming of methanol [Reaction (1)], combination of steam reforming (SRM) and partial oxidation (POM), was carried out over different CuCrAl and CuCeAl catalysts.



Although Cu/Zn/Al₂O₃ based catalysts have been studied and reviewed for OSRM, the catalyst giving low CO formation and consistent performance needs to be developed, which was the motive of present study.

Materials and Methods

Cu-Ce-Al-oxide catalysts were prepared by the co-precipitation method from nitrate salts as mentioned in our previous work [3]. The pre-reduction of catalysts was carried out in-situ using 10 % hydrogen and 90 % nitrogen mixture stream with a heating rate of 5 °C min⁻¹ and dwelling at 200 °C for 2 h for Cu-Ce-Al-oxide catalysts. The dwelling temperature for Cu-Cr-Al-oxide catalysts was maintained at 240 °C. Surface area and pore volume of the catalysts were measured by BET method using N₂ adsorption isotherm recorded at -196 °C using a Micromeritics ASAP 2010 analyzer. Different crystalline phases of catalysts were identified by X-ray powder diffraction (XRD) using Philips X'PERT PW1827/21 powder diffractometer. Temperature programmed reduction was carried out using Micromeritics 2720 TPD/TPR analyzer.

Results and Discussion

Chemical composition, surface area and activities of different catalysts are listed in Table 1. It can be seen that an excessive CuO loading onto catalysts resulted in a decrease in surface area. XRD patterns (Fig. 1) revealed that on the reduction of catalyst copper oxide reduced to the copper while cerium oxide and aluminum oxide remained in oxide form only. The TPR profiles indicated Cu-Ce-Al-oxide catalysts could be reduced at lower temperature compared to Cu-Cr-Al-oxide catalysts. The methanol conversion for different catalysts as a function of temperature is shown in Fig. 2 at contact time 17 kg_{cat} s mol⁻¹. Among Cu-Cr-Al-oxide catalysts maximum methanol conversion 86% was obtained with the 2CuCrAl

(Cu/Cr/Al: 30/10/60) catalyst at 260 °C. Catalysts modified by CeO₂ showed significant enhancement not only in terms of methanol conversion but also in terms of H₂ production rate and minimization of CO formation. The methanol conversion and H₂ rate increased up to 0.3 O/M, after reaching to the limiting value it decreased with further increase in the O/M ratio.

Table 1. Physicochemical of catalysts.

Abbreviation	1CuCrAl	2CuCrAl	1CuCeAl	2CuCeAl	3CuCeAl
	Cu/Cr/Al	Cu/Cr/Al	Cu/Ce/Al	Cu/Ce/Al	Cu/Ce/Al
Composition, mol%	20/10/70	30/10/60	20/10/70	30/10/60	40/10/50
S _{BET} , m ² g ⁻¹	41	62	66	78	34
Pore volume, cm ³ g ⁻¹	0.18	0.17	0.19	0.27	0.14
% CH ₃ OH conversion	41	62	49	81	29
H ₂ rate, mmol s ⁻¹ kg _{cat} ⁻¹	89	134	118	158	64
CO outlet ^a , ppm	810	740	690	650	680

^aT=260 °C, W/F=15 kg_{cat} s mol⁻¹, S/M=1.5 M, O/M=0.2 M, P=1 atm.

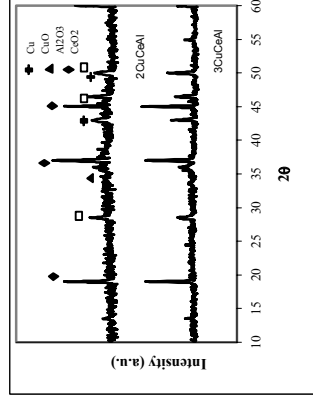


Figure 1. X-ray Diffraction patterns of reduced fresh catalysts.

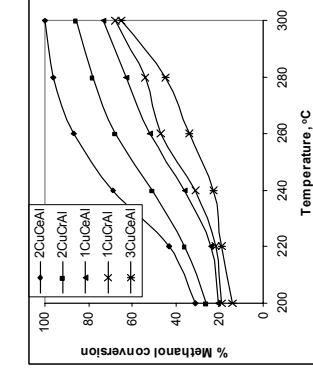


Figure 2. Comparison of catalytic activity.

In the present study the 2CuCeAl catalyst exhibited consistent performance for which methanol conversion decreased by the magnitude of 3% over the period of 60 h run-time.

Significance

The catalyst 2CuCeAl (Cu/Ce/Al:30/10/60) has been found effective for the production of hydrogen by oxidative steam reforming of methanol in terms of maximization of hydrogen production with minimum CO formation for PEM fuel cell applications. Optimum operating conditions, W/F=19 kg_{cat} s mol⁻¹, T=280 °C, O/M molar ratio=0.25-0.3 and S/M molar ratio=1.4, could be suggested to obtain the high methanol conversion and hydrogen production rate. Incorporation of ceria increased the durability of catalysts by providing thermal stability and coke gasification to minimize the sintering and coking respectively.

References

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