

Mo/ γ -Al₂O₃-MgO as a Bifunctional Catalyst for Renewable Hydrogen Production from Steam Reforming of Glycerol

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Abstract. In this paper the catalytic steam reforming of glycerol to H₂ has been evaluated in the presence of Mo/ γ -Al₂O₃ and Mo/ γ -Al₂O₃-MgO in a fixed-bed microreactor at 700 °C. Physiochemical properties of the Mo catalysts were explored by various analytical techniques such as N₂ adsorption-desorption (BET), X-ray diffraction (XRD), X-ray fluorescence spectrum (XRF), Temperature-programmed reduction (TPR) and Transmission Electron Microscopy (TEM). Mo/ γ -Al₂O₃-MgO catalysts show promising results with higher glycerol conversion and higher H₂ selectivity as compared to Mo/ γ -Al₂O₃ catalysts. The Mo was found to be uniformly distributed on the surface of γ -Al₂O₃-MgO support and addition of MgO contents into γ -Al₂O₃ improves the dispersion of Mo on the surface of the support.

Introduction

Hydrogen has received a significant attention as a renewable energy carrier in the future. At present, almost 96% of the total commercial usable world's hydrogen is being produced from fossil fuel based stocks [1]. Renewable resources based technologies for hydrogen production are attractive options for the future due to carbon neutral nature with lesser effects on the global climate. Significant amount of glycerol is produced as a by-product during biodiesel synthesis from vegetable oil transesterification with alcohols such as methanol and bio-ethanol. Since the biodiesel production has increased to a great extent due to environmental concerns and increasing energy demand, the market price of glycerol has dropped rapidly. Therefore, the conversion of this surplus glycerol to high value-added product is highly desirable in the view of its oversupply to the market and comparatively low usage value [2-3].

Due to their high thermal stability, surface area and suitable number of acid/basic sites, mixed oxides have attracted much attention as a support materials for different applications in the recent years [4]. Moreover, mixed oxides are used as support materials to attain a high dispersion of active metal components and to avoid any sort of segregation of different phases which can be formed [5]. The strength and concentration of acidic sites of alumina (Al₂O₃) can be changed by introducing some basic elements. In order to neutralize the stronger acidic sites of Al₂O₃ and find supports with lower acidity and higher thermal stability, magnesium oxide (MgO) has been added to Al₂O₃ in some formulations. The basic character of MgO as well as the high specific surface and the stability of Al₂O₃ bring out promising combination for application as support in steam reforming [6]. In this paper the steam reforming of glycerol has been studied over Mo/ γ -Al₂O₃-MgO catalysts at 700 °C as potential catalyst for sustainable hydrogen production.

Methodology

Preparation of support and catalysts. γ -Al₂O₃-MgO mixed oxides support with different MgO loadings, Mo/ γ -Al₂O₃, and Mo/ γ -Al₂O₃-MgO catalysts were prepared by impregnation method [7]. An appropriate amount of Mg (NO₃)₂·6H₂O was first dissolved in deionized water, and pre-calcined γ -Al₂O₃ support was slowly added into the solution with constant stirring at room temperature for 5 h. The water was then evaporated completely at 70 °C. The solid paste was then dried at 110 °C for 12 h and finally calcined at 500 °C for 5 h. The MgO contents in γ -Al₂O₃-MgO supports were 5, 10, 15, 20 wt % with respect to γ -Al₂O₃. The γ -Al₂O₃-MgO supports were then impregnated with an appropriate amount of ammonium heptamolybdate tetrahydrate (NH₄)Mo₇O₂₄·4H₂O aqueous solution. The mixture was stirred for 5 h at room temperature after which the water was evaporated completely at 70 °C. The resulting solid catalysts were then dried at 110 °C for 12 h and subsequently calcined at 500 °C for 5 h. The Mo loading in all catalysts was 5wt % with respect to the support. The catalysts are denoted as S0, S5, S10, S15, and S20 depending on the contents of MgO in the γ -Al₂O₃-MgO supports.

Characterization of samples. The N₂ physisorption was carried out at -196 °C on a Micromeritics ASAP 2020 system where the samples were degassed at 160 °C for 4 h prior to measurement. S_{BET} was obtained by Multi-point Brunnauer-Emmet-Teller method (BET) while average pore diameter by BJH method using the desorption branch of the isotherm. X-ray diffractions (XRD) of the catalysts was performed on JEOL JDX-3530M X-ray Diffractometer (XRD) with Mn filtered Cu-K α radiations. Elemental analysis was carried out on Bruker S4 PIONEER X-ray Fluorescence Spectroscopy (XRF) using Ru target and 4 kW maximum power.

Activity of Catalysts. Steam reforming of glycerol for hydrogen production was carried out in a fixed-bed microreactor at 700 °C using 0.3 g catalyst with steam to glycerol ratio of 4:1 (wt/wt) and steam to argon (Ar) ratio of 1:6 (vol/vol). The gaseous products (H₂, CH₄, CO₂, CO) were analyzed with online gas chromatograph (GC) (Agilent 7890A GC System) equipped with thermal conductivity detector (TCD) and fitted with TDX-01 column using Ar as a carrier gas.

Results and Discussion

Textural Properties. The surface area, pore volume and average pore diameter for Mo-supported catalysts are summarized in Table 1. It can be seen that the surface area, pore volume and average pore diameter gradually decreases as the MgO loading increases with Mo/ γ -Al₂O₃-20% MgO catalyst shows the lowest surface area. This decrease in the surface area, pore volume and mean pore diameter may be due to the (i) plugging of the some pores with metal oxide species and, (ii) some solid reactions between the oxides on support surface.

Table 1. Textural properties of Mo based catalysts.

Catalysts	S _{BET} (m ² g ⁻¹)	V _P (cm ³ g ⁻¹)	D _P (nm)
γ -Al ₂ O ₃	186	0.241	7.8
Mo/ γ -Al ₂ O ₃	181	0.197	7.7
Mo/ γ -Al ₂ O ₃ -5% MgO	165	0.169	7.1
Mo/ γ -Al ₂ O ₃ -10% MgO	149	0.160	6.6
Mo/ γ -Al ₂ O ₃ -15% MgO	140	0.149	5.9
Mo/ γ -Al ₂ O ₃ -20% MgO	131	0.138	4.8

X-Ray Diffraction Patterns. The X-Ray diffraction patterns for Mo supported catalysts (Fig. 1) show the absence of MgO diffraction peaks at lower loading of MgO which indicates that the γ -Al₂O₃ structure remains intact. However, diffraction peaks attributed to MgO phase are observed at $2\theta = 42.75^\circ$ and 62.11° when high loading of MgO was incorporated to the γ -Al₂O₃. The absence of Mo diffraction peaks may indicate that the oxide is highly dispersed on the surface of all supports [8-9].

Temperature Programme Reduction. The TPR profiles of Mo supported catalysts are shown in the Fig. 2. In general, two reduction peaks are observed at 535 and 971 °C which may be attributed to the reduction of Mo oxide species. The first peak is attributed to the reduction of Mo^{+6} to Mo^{+4} species of polymeric Mo structures. It has been reported that poly-molybdate species possess less polarized bonds and therefore, reduce more easily as compared with the species directly bonded to the alumina [10-11]. The second peak is attributed to further reduction of Mo species produced during the reduction in the first stage, together with the partial reduction of support strongly interacting with coordinated tetrahedral Mo species (Mo^{+3} to Mo^{+2}) [12]. Furthermore, it can be seen from Table 2 that the reduction temperature increases as the MgO contents was increased. This increase in reduction temperature indicates a strong metal-support interaction. The strong metal-support interaction is attributed to the poor electronegativity of Mg^{+2} ions in mixed oxides of $\gamma\text{-Al}_2\text{O}_3\text{-MgO}$, leading to weak Mg-O bond. Thus, the coordination ability of oxygen of $\gamma\text{-Al}_2\text{O}_3\text{-MgO}$ support to Mo metal is higher resulting in strong metal-support interaction and therefore resulted in an increase in the reduction temperature of Mo on $\text{Al}_2\text{O}_3\text{-MgO}$ mixed oxide [13].

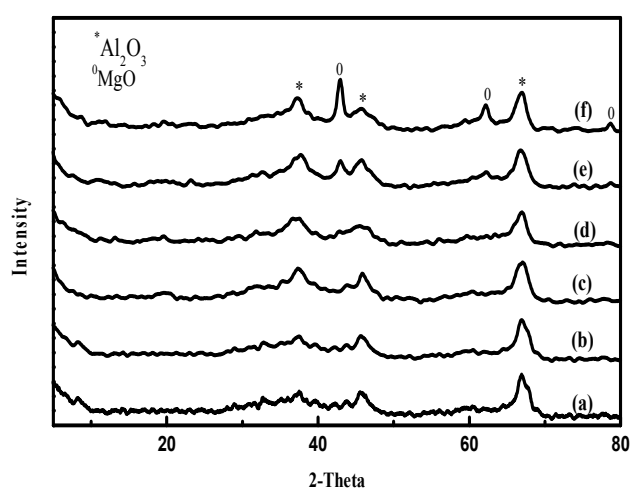


Fig 1. Diffraction patterns of (a) $\gamma\text{-Al}_2\text{O}_3$ (b) $\text{Mo}/\text{Al}_2\text{O}_3$ (c) $\text{Mo}/\text{Al}_2\text{O}_3\text{-5\% MgO}$ (d) $\text{Mo}/\text{Al}_2\text{O}_3\text{-10\% MgO}$ (e) $\text{Mo}/\text{Al}_2\text{O}_3\text{-15\% MgO}$ (f) $\text{Mo}/\text{Al}_2\text{O}_3\text{-20\% MgO}$.

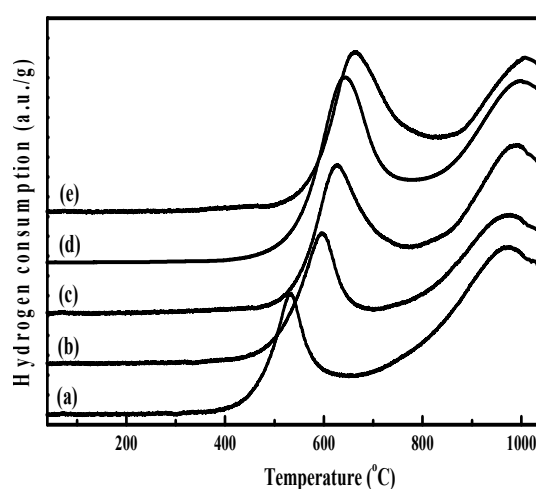


Fig 2. TPR profile of (a) $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ (b) $\text{Mo}/\gamma\text{-Al}_2\text{O}_3\text{-5\% MgO}$ (c) $\text{Mo}/\gamma\text{-Al}_2\text{O}_3\text{-10\% MgO}$ (d) $\text{Mo}/\gamma\text{-Al}_2\text{O}_3\text{-15\% MgO}$ (e) $\text{Mo}/\gamma\text{-Al}_2\text{O}_3\text{-20\% MgO}$.

Moreover, it has been reported that strong interaction between Mo and support leads to the formation of more than one type of Mo^{+6} species. The less polarized bonds of polymolybdates are more easily reduced than those of the species directly bonded to alumina [14]. The electronegativity of metal ions present in Al_2O_3 is stronger as compared to the mixed oxides, thus the interaction between Mo species and support is weaker as compared to the $\gamma\text{-Al}_2\text{O}_3\text{-MgO}$ leading to reduction at lower temperature.

XRF. The XRF elemental analysis results for Mo supported catalysts are given in the Table 3. It can be seen that the Mo and Mg content detected are in close agreement with the theoretical value. This shows that Mg has been successfully incorporated into $\gamma\text{-Al}_2\text{O}_3$ to form mixed oxides support and Mo has been successfully loaded as the active metal to form Mo supported catalysts.

H_2 production. The catalytic performance of Mo supported on $\gamma\text{-Al}_2\text{O}_3$ modified with various amounts of MgO in the steam reforming of glycerol for hydrogen production is depicted in Fig. 3. It can be seen that increases in the MgO contents in the mixed oxide support resulted in an increased in the hydrogen production. The results demonstrated that the catalyst modified with 15 wt% MgO contents show the highest hydrogen production with lower CH_4 , CO_2 and CO produced.

Table.2. TPR data for Mo/ γ -Al₂O₃ and Mo/ γ -Al₂O₃-MgO with varying MgO loadings

Catalysts	Reduction Temperature (°C)	
	Peak 1	Peak 2
Mo/ γ -Al ₂ O ₃	535	971
Mo/ γ -Al ₂ O ₃ -5% MgO	596	975
Mo/ γ -Al ₂ O ₃ -10% MgO	627	990
Mo/ γ -Al ₂ O ₃ -15% MgO	644	997
Mo/ γ -Al ₂ O ₃ -20% MgO	664	1004

Table. 3. Elemental analysis as measured by XRF

Catalysts	Percentage (%)		
	Mo	Al	Mg
Mo/ γ -Al ₂ O ₃	4.77	50.81	-
Mo/ γ -Al ₂ O ₃ -5% MgO	4.83	50.05	4.68
Mo/ γ -Al ₂ O ₃ -10% MgO	4.87	47.42	9.77
Mo/ γ -Al ₂ O ₃ -15% MgO	4.91	45.11	14.81
Mo/ γ -Al ₂ O ₃ -20% MgO	4.95	41.98	19.30

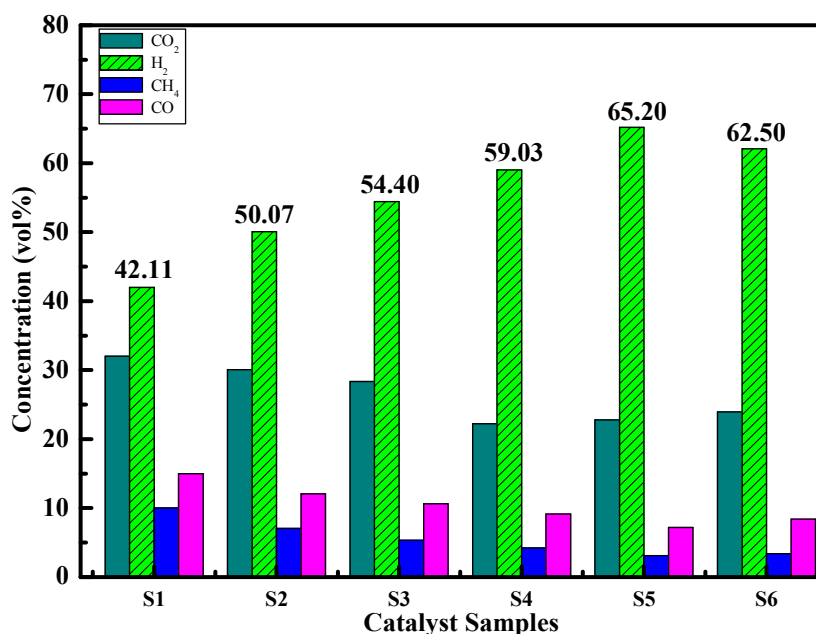


Fig 3. Concentration of gaseous products from the steam reforming of glycerol where (S1) γ -Al₂O₃, (S2) Mo/ γ -Al₂O₃, (S3) Mo/ γ -Al₂O₃-5% MgO, (S4) Mo/ γ -Al₂O₃-10% MgO, (S5) Mo/ γ -Al₂O₃-15% MgO and (S6) Mo/ γ -Al₂O₃-20% MgO.

However, when the MgO contents was further increased to 20%, hydrogen production decreased. MgO has basic character and therefore modified the acidic nature of γ -Al₂O₃ providing suitable number of acid/base sites. Basic oxides such as MgO are incorporated into the catalyst support to lower the support acidity and higher metal dispersion [19]. These acid/base sites play important role in controlling side reactions during steam reforming of glycerol and improve the steam activation. The good performance of Mo/Al₂O₃-15% MgO catalyst may be attributed to the suitable number of acid/basic sites thus resulting in maximum hydrogen production during the steam reforming of glycerol. However, catalyst with 20 wt% MgO showed decrease in the hydrogen production since additional 5% of MgO incorporated to the Al₂O₃ could have decreased the number of acid sites to an

extent which resulted in a decreased in the catalytic performance for hydrogen production during the steam reforming of glycerol.

Conclusions

Catalyst with suitable number of acid/base sites can improve the catalytic performance for hydrogen production. Incorporation of high contents of MgO into the support leads to a decrease in the acid site and an increase in the basic site thus decreases the hydrogen production.

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