

Selective oxidation of methanol to formaldehyde using modified iron-molybdate catalysts

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Methanol selective oxidation to formaldehyde over a modified Fe–Mo catalyst with two different stoichiometric (Mo/Fe atomic ratio = 1.5 and 3.0) was studied experimentally in a fixed bed reactor over a wide range of reaction conditions. The physicochemical characterization of the prepared catalysts provides evidence that $\text{Fe}_2(\text{MoO}_4)_3$ is in fact the active phase of the catalyst. The experimental results of conversion of methanol and selectivity towards formaldehyde for various residence times were studied. The results showed that as the residence time increases the yield of formaldehyde decreases. Selectivity of formaldehyde decreases with increase in residence time. This result is attributable to subsequent oxidation of formaldehyde to carbon monoxide due to longer residence time.

KEY WORDS: formaldehyde; iron-molybdate; methanol; residence time; selective oxidation.

1. Introduction

Methanol, one of the most important chemical intermediates, used in chemical industry. It is the starting material for the synthesis of various products such as hydrocarbons and oxidation product [1]. Formaldehyde production is the major one among the oxidation processes. Two processes are generally used in the industry to produce formaldehyde, both using methanol as the starting material [2]. The dehydrogenation of methanol-rich air mixture over silver catalyst and direct oxidation of methanol-poor air mixture over iron molybdate catalyst. Both processes are still in use [3] and the choice between silver and iron molybdate catalyst must be based not only on economic aspect but should also take into account the product end-use, size of plant and type of operation [4]. Silver catalyst has been used in the form of either a bulk metal or a dispersed metal supported on various supports. In general, the widely used pumice supported catalyst has a longer life than the bulk metal catalyst such as an electrolyte silver catalyst but gives a relatively low formaldehyde yield [5]. Silica–alumina supported catalysts have been found to exhibit a much higher catalytic activity even at a lower content of silver as compared to the pumice-supported catalyst. Electrolytic silver also showed promising results according to the recent study [6,7]. The silver containing

ceramics [8] showed good results. Silver with iodides [9] especially CH_3I as modifier the yield of formaldehyde and conversion of methanol was increased. Modified foam-silver catalyst also gives good results on dehydrogenation of methanol [10]. In comparison with catalysis over silver, the oxidation of methanol over Fe_2O_3 – MoO_3 is carried out at lower temperatures [11–17]. Modification in Fe_2O_3 – MoO_3 has been reported [16,17]. The catalyst prepared by sol-gel method seems to be more stable than the co-precipitated catalyst. The Fe_2O_3 – MoO_3 catalyst is less sensitive to contamination by normal methanol impurities and also provides very good selectivity to formaldehyde. The commercial synthesis of formaldehyde is by dehydrogenation and oxidation of methanol on metallic silver, operating at high temperature and in deficiency of air, or oxidation of methanol in considerable excess of air on metal oxide catalysts, operating at relatively low temperatures (493–723 K). The processes that use metal oxide as catalysts have, with respect to those using metallic silver, the advantages of higher yields in formaldehyde and complete methanol conversion. In consequence, one does not need to recover the unaltered methanol from the reaction products and aqueous solutions of formaldehyde that are substantially free from alcohol are obtained. A comparative study on the silver and iron molybdate catalyst on oxidative dehydrogenation of methanol to formaldehyde is given in table 1. The growing industrial importance of Mo–Fe oxide catalysts has led to good number of investigations. The literature

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Table 1
Comparative study of the activity and selectivity of silver and iron-molybdate catalysts for the selective oxidation of methanol to formaldehyde

Sl. No.	Catalyst	Reaction temperature	Conversion/Selectivity/Yield	Ref.
1	Silver on Pumice stone	973 K Gas Phase	75.0% yield	5
2	Silver on SiO ₂	913 K Gas Phase	85.5% yield 94.0% conv.	5
3	Electrolytic Silver	913 K Gas Phase	84.5% yield 93.6% conv.	5,6
4	Electrolytic Silver	923 K Gas Phase	88.0% selec.	7
5	Silver on Ceramics	893 K Gas Phase	89.3% yield 95.9% conv.	8
6	Silver with Iodides	873 K Gas Phase	95.0% selec. 98.0% conv.	9
7	Modified foam-Silver	823–923K Gas Phase	78.0% yield 96.5% selec.	10
8	Fe ₂ O ₃ -MoO ₃	483–498K Gas Phase	100% selec. 80.0% conv.	11,12, 13,14,15
9	Fe ₂ O ₃ -MoO ₃ on carbon fiber	513 K Gas Phase	98.0% conv 96.0% selec.	16
10	Fe ₂ O ₃ -MoO ₃ sol-gel method	625 K Gas Phase	98.0% conv. 66.0% selec.	17
11	Fe ₂ O ₃ -MoO ₃ modified	473 K Gas Phase	80.0% conv. 70.0% selec.	Present work

survey reveals the fact that catalytic behavior of iron molybdate is mainly dependent on their Mo/Fe atomic ratio [18–25]. MoO₃ exhibits high selectivity, but has poor activity, where as Fe₂O₃ has poor selectivity for HCHO. The addition of Fe₂O₃ to MoO₃ leads to an increase in activity, proportional to iron content, up to a Mo/Fe atomic ratio 1.7 [18]. Further enrichment with iron leads to progressive decrease in activity. Iron molybdate [Fe₂(MoO₄)₃] is likely to be the active component of the catalyst [15,18,19,26]. Few researcher associate active sites with surface Mo atoms in octahedral coordination and such coordination is only achieved in Fe-defective iron molybdate [20,23]. This result agrees with the fact that maximum activity is found for catalyst with a Mo/Fe atomic ratio greater than the stoichiometric value. The presence of two terminal oxygen atoms double bonded to Mo in such coordination allows the reacting methanol molecules to be bonded simultaneously at two points to the surface. The hydrogen abstraction of the methanol hydroxyl

group produces metoxy species that are intermediate in formaldehyde formation. The role of Fe in iron molybdate catalysts would be to favor the transfer of O₂ and H₂O between the surface and the gas phase and to facilitate re-oxidation of reduced Mo [23,27]. It is reported that the presence of Fe³⁺ ions increases the concentration of methanol adsorption sites, consisting of an anion vacancy (acid site) and an O²⁻ (basic site). In the present investigation the activity of the modified Mo/Fe catalyst was studied for the different residence times.

2. Experimental

2.1. Preparation of catalysts

The catalyst was prepared based on the procedure given in [19]. The Mo/Fe catalyst with atomic ratios of 1.5 and 3.0 were prepared by co-precipitation from an aqueous solution of Fe(NO₃)₃·9H₂O and (NH₄)₆Mo₇O₂₄·4H₂O. Iron nitrate solution was slowly added to the cold solution of ammonium hepta molybdate acidified (pH = 2) with nitric acid under vigorous stirring. After total addition of iron solution, the precipitates were ripened in contact with mother liquors at 373 K for 3 h under stirring. During this period, the Mo/Fe = 1.5 yellowish precipitate changes to pale green color and dark yellow colored Mo/Fe = 3 was obtained. After ripening, the precipitates were filtered, dried at 393 K overnight, and calcined at 648 K for 10 h in airflow.

2.2. Characterization of catalysts

The BET surface area, pore size distribution and pore volume were measured with a Micrometrics ASAP-2010 apparatus. The morphology, chemical analysis and homogeneity of the prepared catalysts were examined by FE-SEM (LEO-1530FE). The XRD for the catalysts were obtained on Rigaku (D/Max2000-Ultima plus; X-ray radiation, Cu K α). The FT-IR spectra were recorded with a Shimadzu 8900 spectrometer in the range of 1200–400 cm⁻¹. For each analysis, 1 mg of the sample was ground with 100 mg of KBr and then pelleted (2000 kg cm⁻²) to a disc 13 mm in diameter.

2.3. Catalytic tests

The oxidation of the methanol was carried out in a fixed bed reactor at atmospheric pressure. The activity of the catalyst was examined by taking 11.2 g of catalyst. The feed concentration was prepared by taking oxygen (20 sccm), nitrogen (80 sccm) with different methanol flow rates. Methanol flow was varied (5.40–20.4 ml/h) in order to study its influence. The feed mixtures were prepared by injecting liquid methanol in to nitrogen flow with a precise 301 HPLC pump. To prevent the

polymerization of the formaldehyde, out lets were kept at 393 K. The data were obtained at 473 K. Analyses of the reaction products were done using online Shimadzu GC-2010 gas chromatograph with a thermal conductivity detector.

The conversion of methanol and the selectivity of the formaldehyde are calculated by the following equations.

$$\text{Conversion} = \frac{C_{\text{MeOH}_{in}} - C_{\text{MeOH}}}{C_{\text{MeOH}_{in}}} \quad (1)$$

$$\text{Selectivity} = \frac{C_{\text{HCHO}}}{C_{\text{MeOH}_{in}} - C_{\text{MeOH}}} \quad (2)$$

3. Results and discussion

3.1. Characterization of catalysts

The BET surface area for the modified Mo/Fe = 1.5 is $2.0 \text{ m}^2 \text{ g}^{-1}$ and for the Mo/Fe = 3.0 it is $3.2 \text{ m}^2 \text{ g}^{-1}$. This is in agreement with [1,31]. This shows that the surface area of the prepared catalyst increases with Mo content in the bulk. The Mo/Fe = 3.0 has lower surface area than the conventional catalyst of the same ratio, which can be attributed to a less content of the Mo in the bulk due to the treatment with nitric acid.

The scanning electron micrographs (figures 1 and 2) for the prepared catalyst show ordered *lamellae* morphology. The morphological appearance is in accordance with surface area of the catalyst [23]. It can be seen from the figure that no fiber-like material, usually assignable to the MoO_3 phase [15,23,28], was found in the prepared catalysts, which is a good indication that no phase segregation occurred during the precipitation and calcination steps. The segregation of MoO_3 is a frequent and adverse occurrence during the preparation of iron molybdenum mixed oxides. In fact, such an occurrence must be prevented because the MoO_3 phase is much less active for the selective oxidation of methanol than iron molybdate. Moreover, segregation

of MoO_3 can lead to a Fe-rich phase that promotes total oxidation of methanol [29].

The XRD of prepared catalysts (figure 3) shows that the stoichiometric phase is better crystallized than the catalyst with molybdenum excess. This result confirms that stoichiometric mixed oxide display a higher crystallinity than mixed oxide with molybdenum excess. This result agrees with the fact that molybdenum excess retards the crystallization of $\text{Fe}_2(\text{MoO}_4)_3$ [18].

The FT-IR spectra of the prepared catalysts (figures 4 and 5) confirms the molybdenum excess in the Mo/Fe = 3.0. A narrow band of catalysts at 990 cm^{-1} and a broad band at 624 cm^{-1} characteristic of MoO_3 [15,20,23,30]. The weak and narrow band that appears at 960 cm^{-1} can be assigned to Fe–O–Mo bond vibration [30]. The broad band in the range $700\text{--}900 \text{ cm}^{-1}$ can be ascribed to tetrahedral species of Mo in $\text{Fe}_2(\text{MoO}_4)_3$ [20].

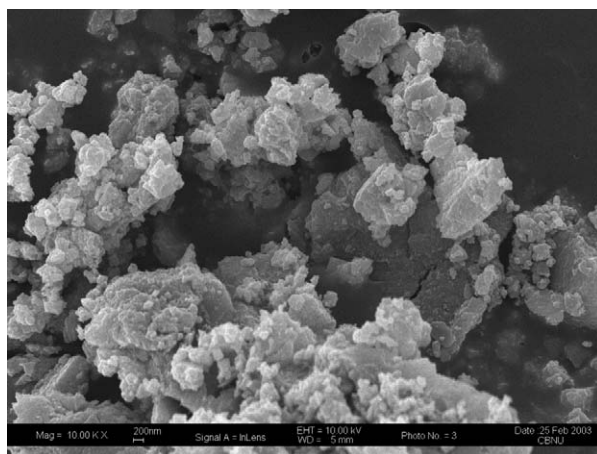


Figure 2. SEM image of Mo/Fe = 3.0 catalyst.

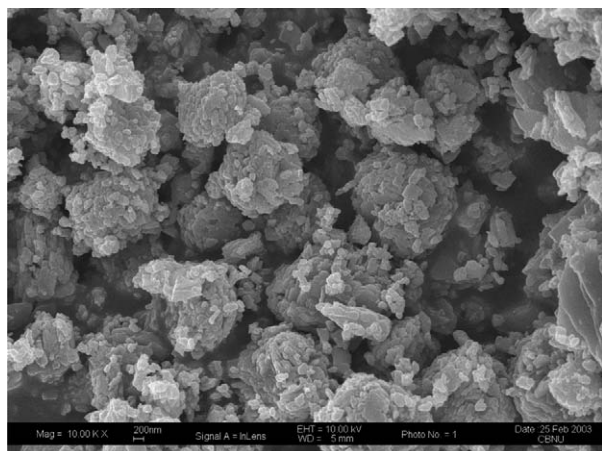


Figure 1. SEM image of Mo/Fe = 1.5 catalyst.

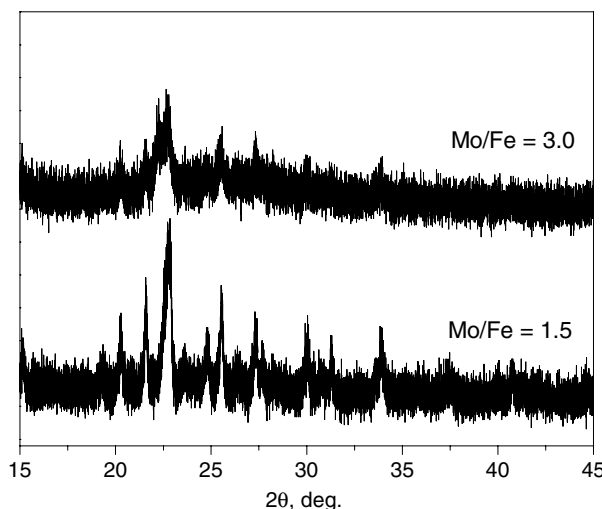


Figure 3. Modified Mo/Fe catalysts with HNO_3 (Mo/Fe = 1.5 ; Mo/Fe = 3.0).

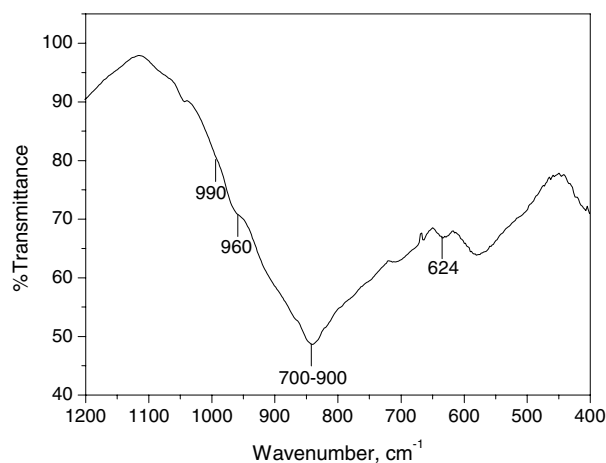


Figure 4. Analysis of FT-IR with modified Mo/Fe = 1.5 catalyst.

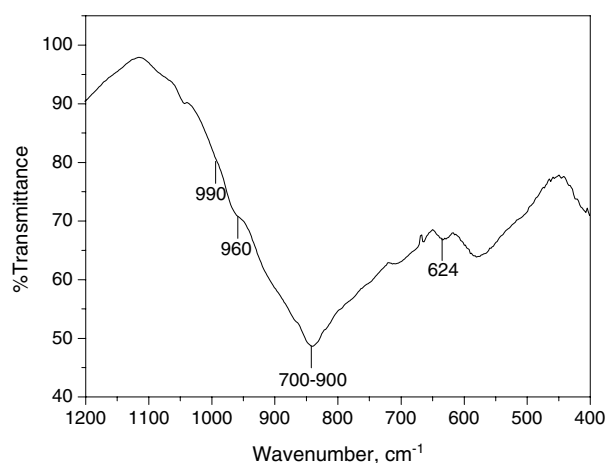


Figure 5. Analysis of FT-IR with modified Mo/Fe = 3.0 catalyst.

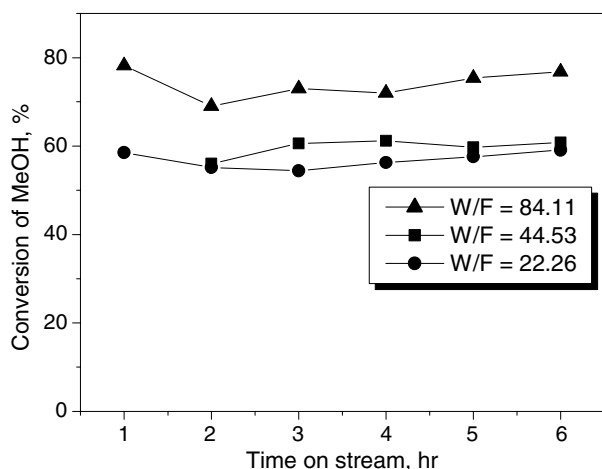


Figure 6. Conversion of MeOH with three different W/F conditions.

3.2. Catalytic behavior

The results of conversion of methanol and selectivity towards formaldehyde for various residence times

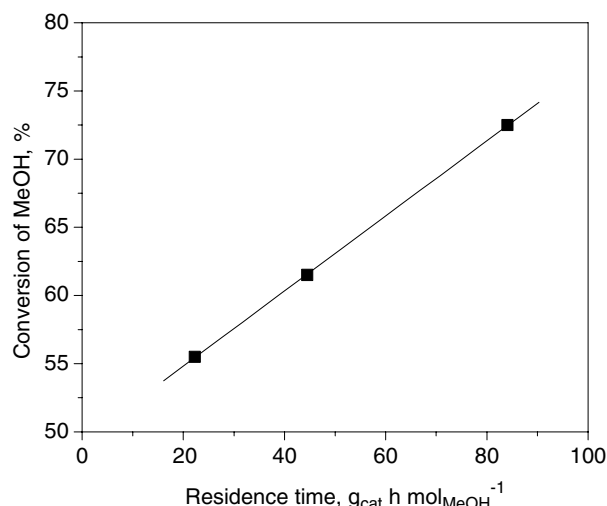


Figure 7. Conversion of MeOH with residence time.

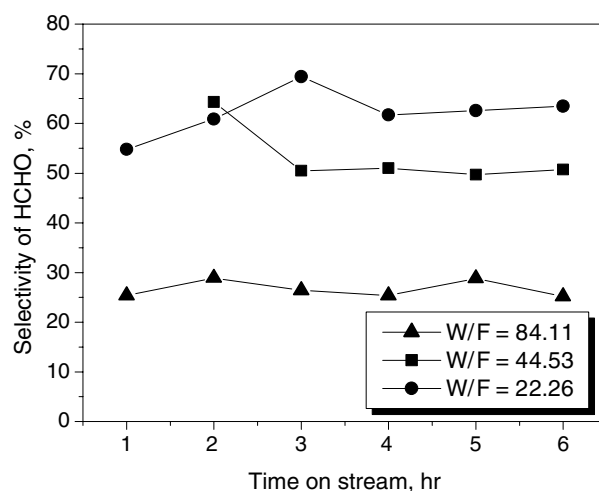


Figure 8. Selectivity of HCHO with three different W/F conditions.

were studied. The yield of formaldehyde for various residence times was also examined. Figure 6 shows the conversion of methanol for various residence times, viz. 22.26, 44.53 and $84.11 \text{ g}_{\text{cat}} \text{ h mol}_{\text{MeOH}}^{-1}$. It can be seen that as the residence time increases the conversion of methanol also increases. The increase in the conversion of methanol follows linear dependence on residence time as evident by Figure 7. The selectivity of formaldehyde formation for various residence times is presented in Figure 8. It can be seen that as the residence time increases the selectivity of formaldehyde decreases. This is due to the subsequent oxidation of formaldehyde to carbon monoxide, due to longer residence times. From Figure 9, the yield of formaldehyde for various residence times gives the idea that as the residence time increases the yield of formaldehyde decreases. This is due to the subsequent oxidation of formaldehyde to carbon monoxide, due to longer residence times.

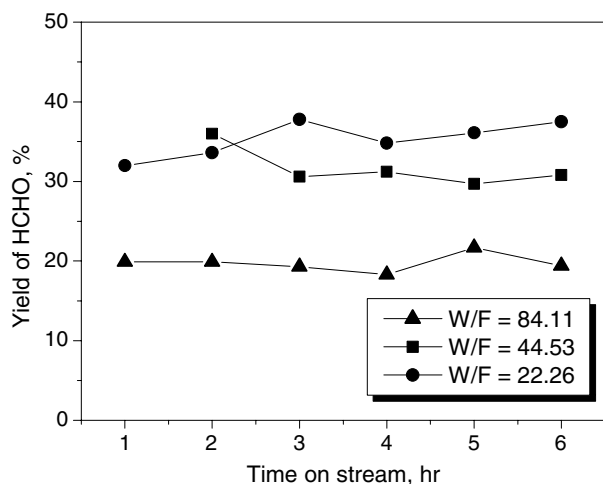


Figure 9. Yield of HCHO with three different W/F conditions.

4. Conclusion

The present work demonstrates that the modified Mo/Fe = 3.0 catalyst show a ordered lamellae and the results of the catalytic tests evidence that the activity is not affected by modification, suggesting that the $\text{Fe}_2(\text{MoO}_4)_3$ phase would be the active phase of the catalyst. Linearity was observed in conversion of methanol with residence time. However the increase in residence time decreases the selectivity of formaldehyde. This is due to the subsequent oxidation of formaldehyde to carbon monoxide, due to longer residence times.

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