산처리한 **Iron-Molybdate** 촉매를 이용한 메탄올의 포름알데히드 부분산화반응 연구

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Partial oxidation of methanol to formaldehyde using acid treated Iron-Molybdate catalysts

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1. Introduction

Formaldehyde is one of the important basic chemicals and is required for the manufacture of a number of industrial and consumer products. Two processes are generally used in the industry to produce formaldehyde, both using methanol as the starting material [1]. The dehydrogenation of methanol–rich air mixture over silver catalyst operating at high temperature and direct oxidation of methanol–poor air mixture over iron molybdate catalyst operating at relatively low temperatures (493−723K). The processes, which 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 dose not need to recover the unaltered methanol from the reaction products and aqueous solutions of formaldehyde, which are substantially free from alcohol, are obtained. The growing industrial importance of Mo-Fe oxide catalysts has led to good number of investigations.

In the present investigation the activity of the prepared Mo-Fe catalyst was studied for the conversion of methanol and selectivity towards formaldehyde for various residence times.

2. Experimental

2.1. Preparation of catalysts

The catalyst was prepared based on the procedure given in [2]. The Mo-Fe catalyst with atomic ratios of 1.5 and 3.0 were prepared by co-precipitation from an aqueous solution of $Fe(NO_3)_3.9H_2O$ and $(NH_4)_6Mo_7O_{24}$.Iron nitrate solution was slowly added to the cold solution of ammonium hepta molybdate acidified with nitric acid under vigorous stirring. After total addition of iron solution, the precipitates were ripened in contact with mother liquors at 371K 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 391K 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, CuKα).

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 fixed quantity of the catalyst and variable reaction conditions. 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. Analyses of the reaction products were done using online Shimadzu GC-2010 gas chromatograph with a thermal conductivity detector.

3. Results and discussion

3.1. Characterization of catalysts

The BET surface area for the acid treated Mo/Fe=1.5 is 2.0 m^2/g and for the Mo/Fe=3.0 it is 3.2 m^2/g. This is in agreement with [2,3]. 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 (Fig. 1,2) for the prepared catalyst show an ordered *lamellae* morphology. The morphological appearance is in accordance with surface area of the catalyst [4]. It can be seen from the figure that no fiber-like material, usually assignable to the MoO_3 phase [5], 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 [6]. The FT-IR spectra of the prepared catalysts (figure not shown) confirms the molybdenum excess in the Mo/Fe=3.0. A narrow band of catalysts at 990cm^{-1} and a broad band at 624 cm^{-1} characteristic of MoO_3 [2,4,7,8].]. The broad band in the range 700–900 cm^{-1} can be ascribe to tetrahedric species of Mo in $Fe_2 (MoO_4)_3$ [7]. The weak and narrow band that appears at 960 cm^{-1} can be assigned to Fe–O–Mo bond vibration [8].

3.2. Catalytic behavior

The results of conversion of methanol and selectivity towards formaldehyde for various residence times were studied. The yield of formaldehyde for various residence times was also examined. Figure 3 shows the conversion of methanol for various residence times, viz. 22.26, 44.53 and 84.11 g_{cat} h mol_{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. The selectivity of formaldehyde formation for various residence times is presented in Figure 4. 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 5, 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.

4. Conclusion

The present work demonstrates that the acid treated 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 $Fe_2(MoO_4)_3$ phase would be the active phase of the catalyst. 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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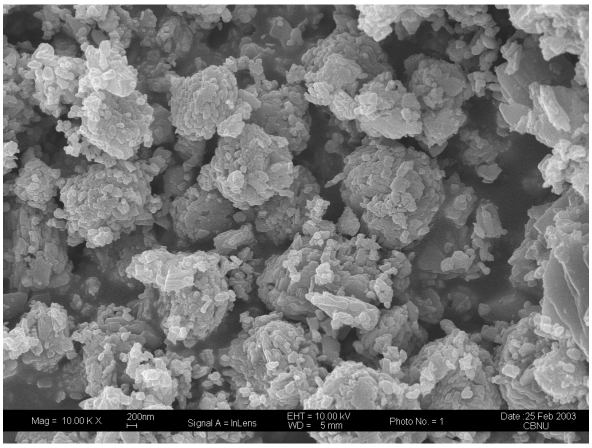

Fig. 1. SEM image of Mo/Fe=1.5 catalyst.

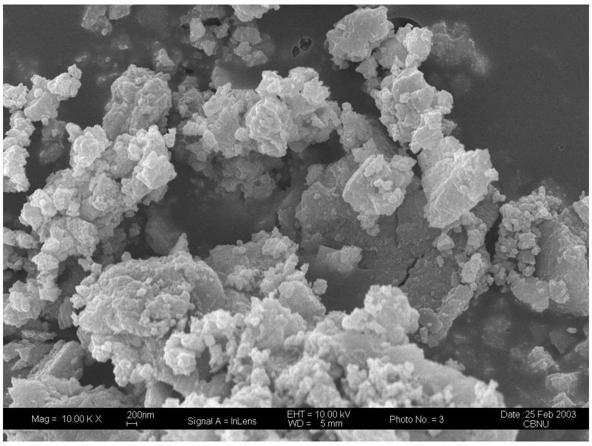

Fig. 2. SEM image of Mo/Fe=3.0 catalyst.

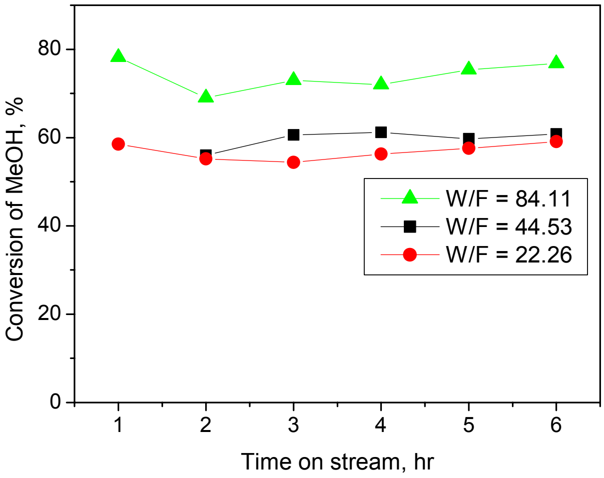

Fig. 3. Conversion of MeOH with three different W/F conditions

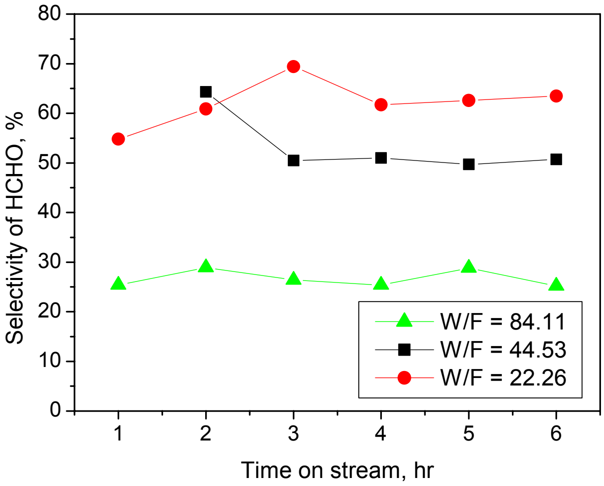

Fig. 4. Selectivity of HCHO with three different W/F conditions

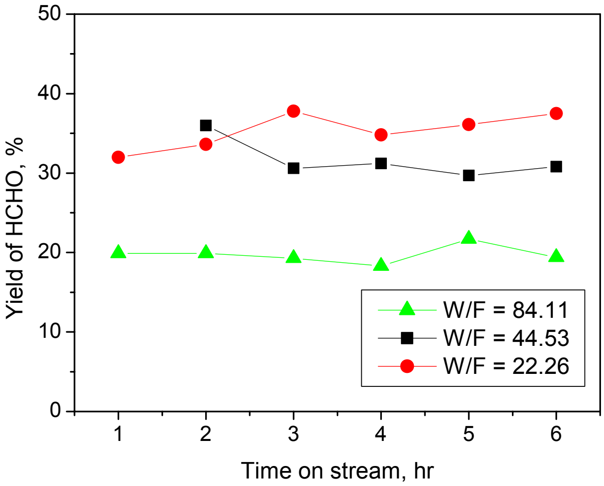

Fig. 5. Yield of HCHO with three different W/F conditions