

메탄올로부터 포름알데히드 제조를 위한 Molybdenum oxide 의
부분산화 촉매 반응 연구

김태환*, 최정식¹, B. Ramachandra²
한국에너지기술연구원, ¹충남대학교 화학공학과, ²NITK(India)
(thkim@kier.re.kr*)

Molybdenum Oxide based Partial Oxidation Catalyst for the Preparation of Formaldehyde from Methanol

Tae-Hwan Kim*, Jung Sik Choi¹, B. Ramachandra²
Korea Institute of Energy Research (KIER), Dep. of Chem. Eng., ¹CNU, ²NITK (India)
(thkim@kier.re.kr*)

1. Introduction

Catalytic selective oxidation reactions belong to the most important processes. About one quarter of the value produced worldwide via catalytic reactions stems from partial oxidation reactions, and hence, they considerably contribute to the gross national products of industrialized countries. Thus, it is highly important to further develop not only the performance of such industrial processes but also the fundamental understanding of such multi element and multiphase catalysts, e.g. the role of each phase and their interaction under catalytic action. This information is prerequisite for future material science tailoring of molecularly defined selective catalysts. It may be anticipated that oxygen diffusivities are affected by the elemental compositions and the geometric structures of the catalyst phases. The real metal–oxygen stoichiometry and defect structure of molybdenum oxides thus may play an important role in selective partial oxidation reactions. It can be assumed that the degree of reduction, and hence, the presence of reduced surface metal centers, strongly affects the adsorption properties of hydrocarbons, and the C H bond activation. The electronic properties of reduced molybdenum oxides, i.e. high electron density at the surface, may effect the oxygen activation. X-ray diffraction XRD and transmission electron microscopy SEM literature provides about structural changes of molybdenum oxides as function of their degree of reduction. In the present paper the structure and activity of the catalyst towards the partial oxidation was studied.

2. Experimental

2.1. Preparation of catalysts

Catalyst was prepared based on [1]. Aqueous solutions of ammonium heptamolybdate (AHM), ammonium metatungstate (AMT), and ammonium metavanadate (AMV) having the respective transition metal concentrations were mixed in order to obtain the catalyst with a composition of Mo, W and V of 64, 9, and 27%, respectively. This solution was dried by evaporation and decomposed under nitrogen at 400°C. The bluish black compound was obtained. The thermal activation treatments have been carried out in a tubular furnace at 535°C in a flow of 100 ml/min pure nitrogen for 2 h.

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). EDX was done with a The XRD for the catalysts were obtained on Rigaku (D/Max2000-Ultima plus; X-ray radiation, CuK α). The FT-IR spectra were recorded with a Shimadzu 8900 spectrometer in the range of 1500-400cm⁻¹. For each analysis, 1mg of the sample was ground with 100mg of KBr and then pelleted (2000kg cm⁻²) to a disc 13mm 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 fixed quantity of the catalyst diluted with SiC 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 120°C. 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 of the prepared catalyst is 5.9g/m². This is in agreement with [2]. It was found that the thermal treatment has no effect on the surface area of the catalyst.

The scanning electron micrographs (Fig. 1) for the prepared catalyst show agglomerates of platelet-like crystallites of a few hundreds of nanometers in size. However, there remained parts of the sample, which still showed irregular particle shapes. The EDX analysis (Fig.2) gave the elemental distribution of Mo, V and W as 64.18, 28.10 and 7.72 w% respectively. These results are comparable with the weight of the precursor taken during the preparation. The mixed oxide characterized by an inhomogeneous elemental distribution on the length scale of few microns. It can be seen that the material is not well crystalline. This may be due to the different solubilities of the ammonium precursors led to elemental inhomogenities during the drying process.

The XRD pattern of the catalyst (Fig.3) can be understood as a mixture of a majority of nanocrystalline Mo₅O₁₄-type oxide with minor amounts of nanocrystalline MoO₃ and MoO₂-type material [2,3]. The FTIR pattern show that there exists a multi phase component like Mo(or V or W)-O- Mo bond [4].

3.2 Catalytic behavior

The results of conversion of methanol, selectivity and yield towards formaldehyde were studied in these conditions (MeOH, 0.04 ml/min; N₂, 80 sccm; O₂, 20 sccm). The selectivity of formaldehyde formation and conversion of methanol is shown in Fig.5. The yield of formaldehyde was shown in Fig.6.

4. Conclusion

The present work demonstrates that the mixed oxide catalyst with inhomogeneous nanocrystalline Mo₅O₁₄-type oxide with minor amount of MoO₃- and MoO₂-type material. The structural analysis suggests that the catalytic performance of the MoVW oxide catalyst in the partial oxidation of methanol is related to the formation of the Mo₅O₁₄ type mixed oxide.

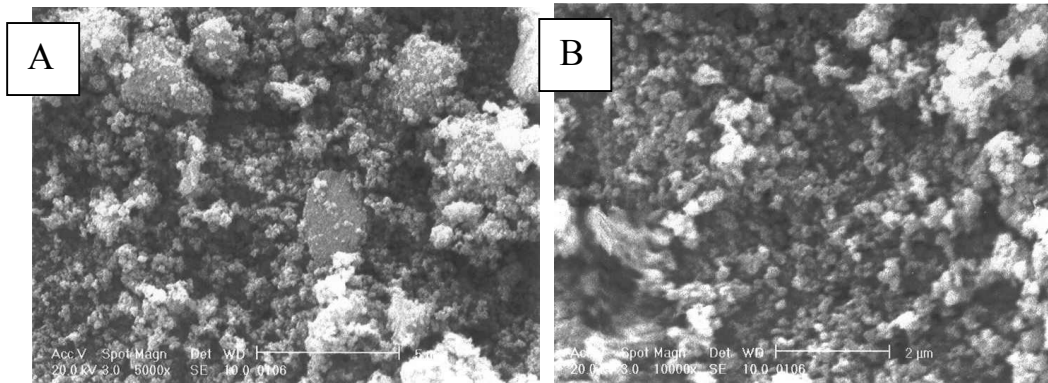
Acknowledgements

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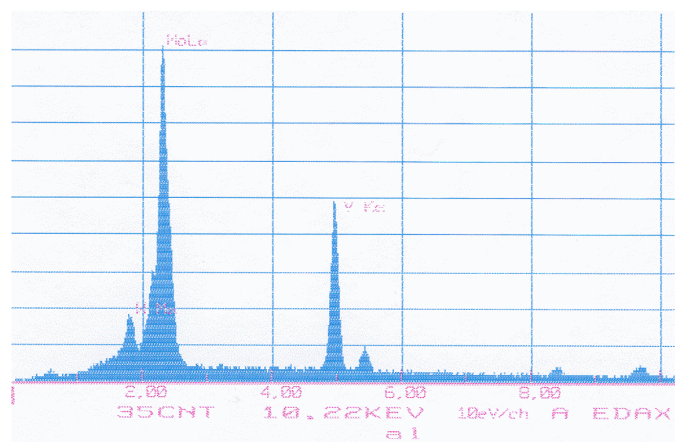
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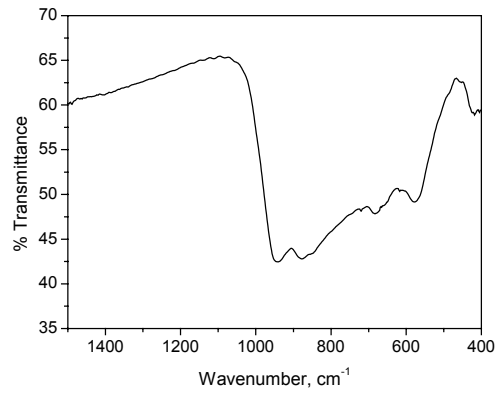
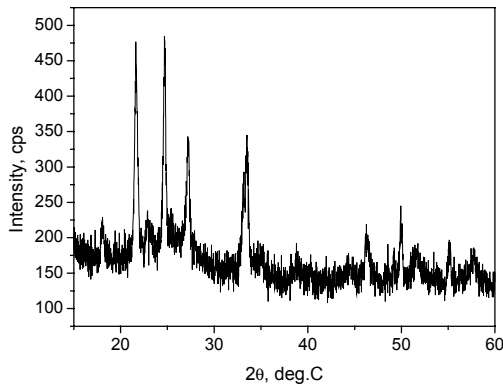
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[Fig. 1] SEM images of Mo-W-V catalysts
(A, 5 K; B, 10K)

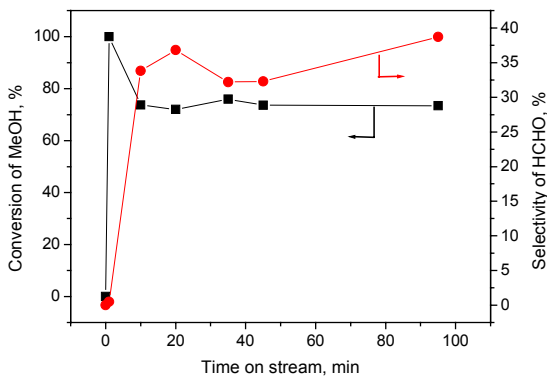


[Fig.2] EDX analysis of Mo-W-V catalyst.

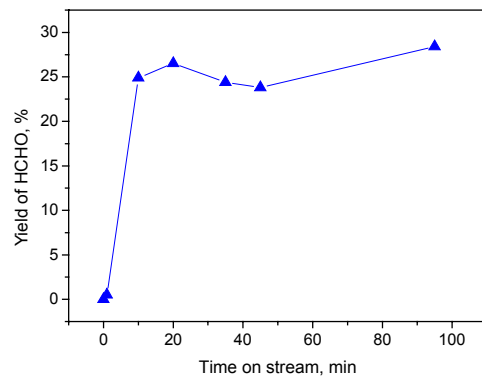


[Fig. 3] The XRD patterns of Mo-W-V catalyst

[Fig. 4] FT-IR result of Mo-W-V catalyst.



[Fig. 5] MeOH conversion and HCHO selectivity through the time



[Fig. 6] HCHO yield through the time