Partial oxidation of methanol to formaldehyde on Molybdenum based mixed oxide catalyst

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Molybdenum based mixed oxide containing $Mo_{0.65}V_{0.25}W_{0.10}$ was investigated for the partial oxidation of methanol. The structural property and catalytic activity of the mixed oxide catalyst was studied by surface area (BET), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), Fourier transform infra-red spectroscopy (FTIR) and X-ray diffraction (XRD). The thermal activation of the catalyst resulted increase in the conversion of methanol and the selectivity to formaldehyde. The thermal activation of the MoVW mixed oxide in nitrogen atmospheres induces partial crystallization of a Mo_5O_{14}-type oxide at 813 K. The SEM images of the thermally activated catalyst show needle like particles. These particles were agglomerates of platelet-like crystallites of a few hundreds of nanometers in size. SEM and EDX techniques show that the mixed oxide is characterized by an inhomogeneous elemental distribution on the length scale of a few microns. XRD of the thermally activated catalyst showed a nanocrystalline material identified as a mixture of Mo_5O_{14}, MoO_3 and MoO_2-type MoVW oxides. The catalytic activity of the MoVW mixed oxide show a good conversion of methanol and selectivity to formaldehyde.

KEY WORDS: formaldehyde; methanol; mixed oxide; partial oxidation.

1. Introduction

Formaldehyde is a well-established raw material for the manufacture of a large number of important industrial and consumer products. It is produced industrially by methanol oxidation, two processes are generally used in the industry to produce formaldehyde, both using methanol as the starting material; (i) The dehydrogenation of methanol-rich air mixture over silver catalyst and (ii) direct oxidation of methanol-poor air mixture over iron molybdate catalyst.

Nowadays both processes are still in use and the choice between silver and iron-molybdate catalysts is based not only on economical aspects but also in the product end-use, size of the plant and type of operation [1]. The literature survey on Silver catalyst [2–7] and iron-molybdate [8–15] mixed oxide gave an idea of the advantage and disadvantage of the above catalysts. Transition metal oxides show a broad structural variety due to their ability to form phases of varying metal to oxygen ratios reflecting multiple stable oxidation states of the metal ions [16–18]. Metal oxides exhibiting strong crystallographic anisotropy may show differing catalytic properties for different exposed crystal faces. One possible reason responsible for surface structure sensitivity may be the differently strong M=O bonds at the dif-

ferent surface planes. The stronger the M=O bond the more basic is its function with respect to hydrocarbon activation. Compound sensitivity can be expected in addition to this surface structure sensitivity, i.e. of all possible oxides with the overall composition $Mo_wV_{w-x}W_{w-y}O_z$ here may only be one single oxide which exhibits the highest catalytic selectivity and activity. This compound sensitivity may result from its special geometric, electronic or lattice diffusion properties providing selective active sites, an optimum match of catalyst and substrate electronic states and fast red-ox kinetics.

Structure and compound sensitivity for oxidation reactions serve as for the development and fundamental understanding of catalysts and their catalytic properties [19]. Currently, MoVW-supported catalysts are used in industry for the synthesis of acrylic acid [20–24]. Some researchers [25] have been studied the MoVW mixed oxide catalyst with different concentration of the metals for the acrolein oxidation. Since methanol is very reactive and because the possible reaction products are linked to different reaction channels, the conversion of methanol to formaldehyde was used as a test reaction to investigate the catalytic properties of the mixed oxide. Pure MoO_3 catalysts exhibit high selectivity to formaldehyde. The rate-determining step was identified to be the hydrogen abstraction from the methyl group. Mo=O double bonds were suggested to be active for the formaldehyde formation, while bridged Mo–O–Mo sites

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lead to dimethyl ether. In this respect, it is interesting to note that the oxygen exchange capabilities of the different Mo–O bonds in MoO_3 depend on the Mo–O bond order. The real metal–oxygen stoichiometry and defect structure of molybdenum oxides thus may play an important role in selective partial oxidation reactions.

In this paper, the preparation, characterization and the catalytic performance of the $Mo_{0.65}V_{0.25}W_{0.10}O_x$-mixed oxide as a partial oxidation catalyst for the methanol to formaldehyde reaction was studied.

2. Experimental

2.1. Preparation of catalysts

Catalyst was prepared based on [26]. 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 65, 10 and 25%, respectively. This solution was dried by evaporation and decomposed under nitrogen at 673 K. The bluish black compound was obtained. The thermal activation treatments have been carried out in a tubular furnace at 813 K 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 Hitachi S-4700 FE SEM with EDX facilities. The XRD for the catalysts were obtained on Rigaku (D/Max2000-Ultima plus; X-ray radiation, $CuK\alpha$). The FT-IR spectra were recorded with Nicolet Magna IR 550 in the range of 1400–400 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 partial oxidation of the methanol was carried out in a fixed bed reactor at atmospheric pressure. The activity of the catalyst was examined by taking 10 g of the 80 w% of the catalyst prepared with SiC. The methanol to oxygen ration was kept at 1.47 and the nitrogen gas was kept at 60 sccm.The temperature of the reactor was varied in the range of 573–673 K. 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, outlets were kept at 393 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.

$$\text{Conversion} = \frac{C_{MeOH_{in}} - C_{MeOH}}{C_{MeOH_{in}}} \qquad (1)$$

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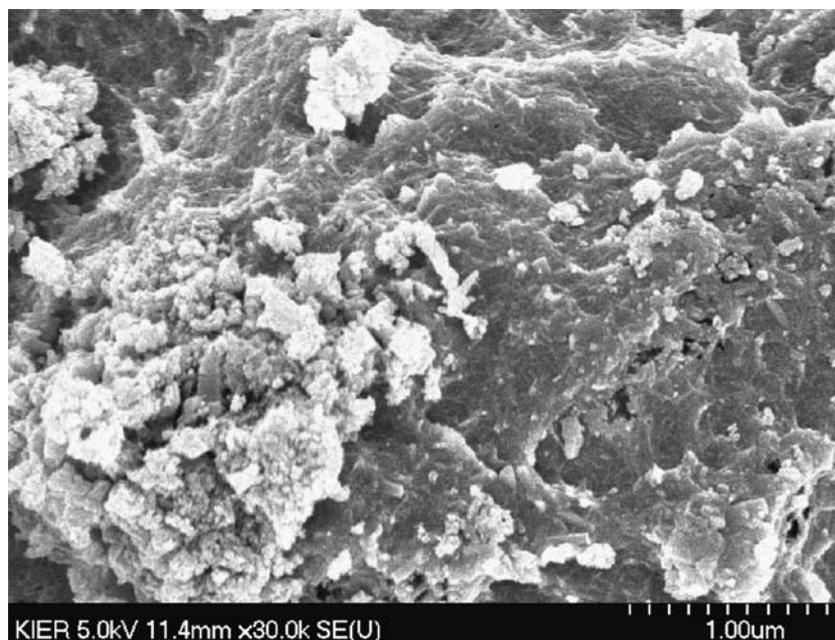

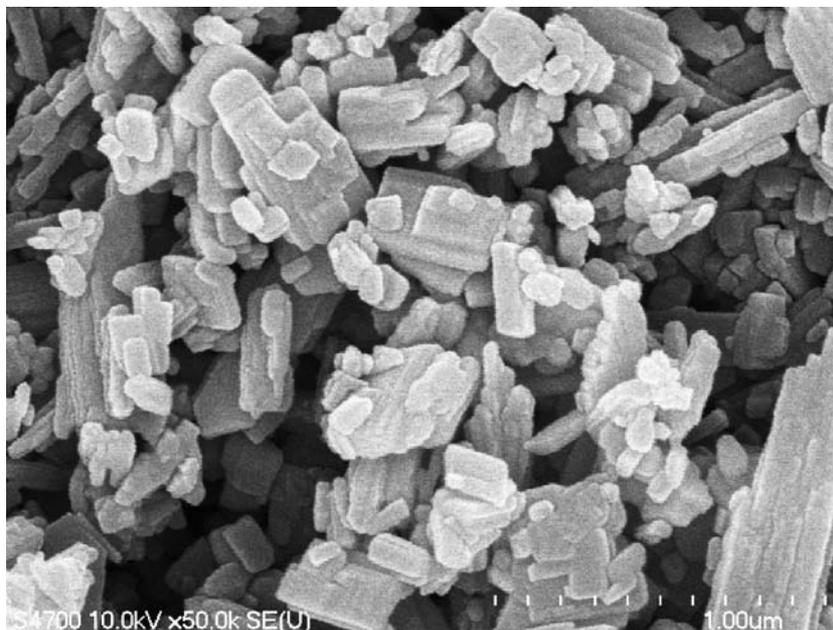Figure 1. SEM image of the calcined MoVW catalyst.

Figure 2. SEM image of the thermally activated MoVW catalyst.

3. Result and discussion

3.1. Characterization of the catalyst

The BET surface area of the prepared catalyst is 5.9 g/m^2. Thermal treatment does not affect the surface area of the prepared catalyst. The SEM image was taken for both calcined and thermally activated samples. The calcined sample (figure 1) reveals that the sample is almost amorphous in nature, were as thermally activated sample show needle like particles. These particles were agglomerates of platelet-like crystallites (figure 2) of a few 100s of nanometers in size. However, there remained parts of the sample, which still showed irregular particle shapes. The SEM and EDX techniques show that the mixed oxide is characterized by an inhomogeneous elemental distribution on the length scale of few microns. The elemental distribution is homogeneous on the submicron scale. 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 thermal activation of the sample lead to formation of regular particle shapes pointing to crystallization. Elemental distribution X-ray analysis of the mixed oxide catalyst (figure 3) gave the elemental distribution of at Mo, V and W as 64.91 w% (55.73 a%), 24.42 w% (39.49 a%) and 10.67 w% (4.78 a%). This is in agreement with the weight of the precursor taken during the preparation of
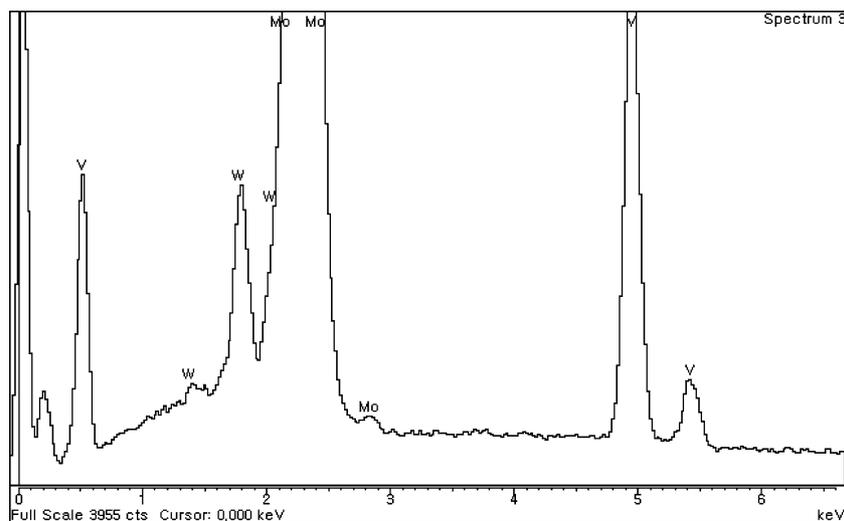

Figure 3. EDX analysis of the activated MoVW catalyst.

the catalyst. The XRD pattern of the catalyst (figure 4) shows that the mixed oxide is almost amorphous in nature as seen from the calcined sample. The thermally activated sample shows that the crystallinity has increased after the thermal treatment at 813 K [27]. XRD peaks confirm that the mixed oxide catalyst contains a mixture of a majority nanocrystalline Mo_5O_{14}-type and a minority of nanocrystalline MoO_3 and MoO_2-type oxides. The XRD pattern of the mixed oxide above 833 K shows that catalyst under goes decomposition.

FTIR (figure 5) pattern shows that there exits a multi phase component like Mo (or V or W)-O-Mo bond [28].

3.2. Catalytic behavior

The selectivity of the formaldehyde and the conversion of the methanol are studied before and after the thermal activation of the mixed oxide catalyst at 623 K. The obtained results were compared as shown in the
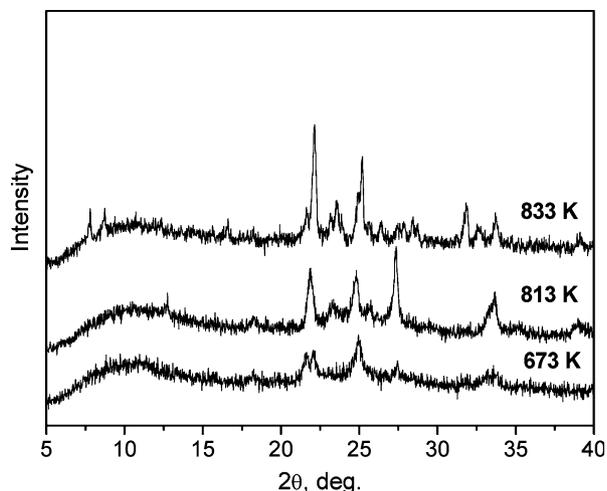
figure 6. Yield of formaldehyde is shown for the calcined and thermally activated catalyst in the figure 7. From these results it is very much evident that the thermal treatment of the catalyst has led to the formation of the active site responsible for the partial oxidation of the methanol to formaldehyde.

4. Conclusion

The mixed oxide is characterized by an inhomogeneous elemental distribution on the length scale of few microns. The elemental distribution is homogeneous on the submicron scale. 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 thermal activation of the sample lead to formation of regular particle shapes pointing to crystallization. XRD of the thermally activated catalyst showed a nanocrystalline material
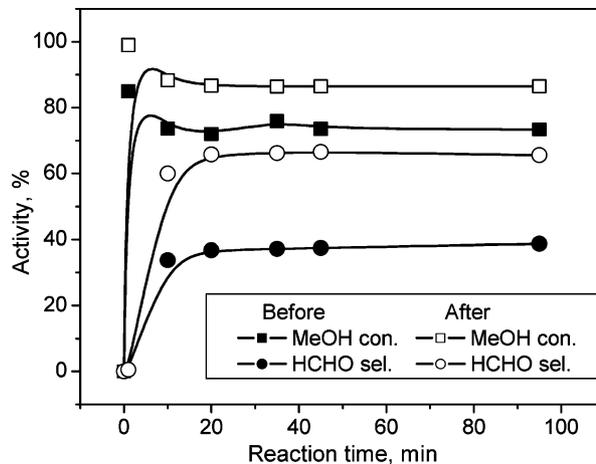

Figure 4. XRD pattern of the catalyst activated at different temperatures.

Figure 6. Catalytic activity at 623 K.

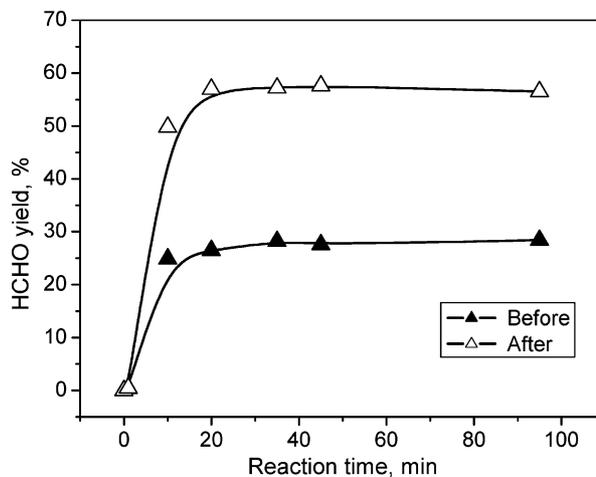Figure 5. FT-IR spectra of the activated catalyst.

Figure 7. Yield of formaldehyde obtained before and after the thermal treatment of catalyst.

identified as a mixture of Mo_5O_{14}, MoO_3 and MoO_2-type MoVW oxides. The catalytic activity of the MoVW mixed oxide was increased marginally by the thermal treatment of the catalyst due to the formation of catalytic active sites.

Acknowledgments

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