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Synthesis and characterization of nanocrystalline Mo–V–W–Fe–O mixed oxide catalyst and its performance in selective methanol oxidation

Badekai Ramachandra Bhat,[a,*] Jung-Sik Choi,[b] and Tae-Hwan Kim[c,*]

[a]*Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Srinivasanagar, Mangalore 575025, India*
[b]*Department of Chemical Engineering, Chungnam National University, Yusong-gu, Daejeon, South Korea*
[c]*Korea Institute of Energy Research (KIER), P.O. Box No. 103Yusong-gu, Daejeon, South Korea*

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A mixed oxide catalyst containing Mo, V, W and Fe with the composition of 63, 23, 09 and 06 wt% respectively for the selective oxidation of the methanol to formaldehyde is in reported in this paper for the first time. The characterization of the catalyst was done using BET surface analysis, X-ray diffraction (XRD), Infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX). The mixed oxide after calcination at 673 K in N_2 which was subjected for the thermal activation in N_2flow at 813 K was used for the methanol selective oxidation. The thermal treatment shows enhanced catalytic performance. Thermal activation of the nanocrystalline $Mo_{0.63}V_{23}W_{0.09}Fe_{0\cdot06}O_x$precursor oxide in nitrogen atmospheres induces partial crystallization of a Mo_5O_{14}-type oxide only in a narrow temperature range up to 813 K. XRD showed that the thermally activated mixed oxide consists of a mixture of a majority of crystalline Mo_5O_{14}-type oxide and of small amounts of crystalline MoO_3-type and MoO_2-type oxides. The structural analysis suggests that the improvement of the catalytic performance of the MoVWFe oxide catalyst in the selective oxidation of methanol is related to the formation of the catalytic active site such as Mo_5O_{14}-type mixed oxide.

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

1. Introduction

Formaldehyde is one of the most important basic chemicals and is required for the manufacture of a large number of industrial and consumer products. It is the most important industrially produced aldehyde [1].Two processes are generally used in the industry to produce formaldehyde, both using methanol as the starting material [2]: (i) dehydrogenation of methanol-rich air mixture over silver catalyst and (ii) direct oxidation of methanol-poor air mixture over iron molybdate catalysts. Now a days, both processes are still in use and the choice between silver and iron molybdate catalysts must be based not only on economic aspects but should also take into account the product end- use, size of the plant and type of operation. In comparison with catalysis over Ag [3–8], the oxidation of methanol over Fe_2O_3–MoO_3 [9–16] is carried out at lower temperatures, the catalyst is less sensitive to contamination by normal methanol impurities and also provides good selectivity to formaldehyde [1, 2]. 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 [17]. Metal oxides exhibiting strong crystallographic anisotropy may show differing catalytic properties for differently exposed crystal faces. One possible reason for surface structure sensitivity may be the differently strong M = O bonds at the different surface planes. The stronger the M = O bond the more basic is its function with respect to hydrocarbon activation. Structure and compound sensitivity for oxidation reactions serve the development and fundamental understanding of catalysts and their catalytic properties [18]. The behavior of the catalysts in general in the process in which they are used, and that of the metal oxide catalysts in particular, depends on their chemical composition and their structural characteristics, the latter depending in turn on the process selected for the preparation of said catalysts. Because 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.

This paper, studies the synthesis, characterization and the catalytic performance of the $Mo_{0.63}V_{23}W_{0.09}Fe_{0\cdot06}O_x$-mixed oxide as a selective oxidation catalyst for the methanol to formaldehyde reaction.

*To whom correspondence should be addressed.
E-mails: chandpoorna@yahoo.com; thkim@kier.re.kr

2. Experimental

2.1. Preparation of catalyst

Aqueous solutions of ammonium heptamolybdate (AHM), ammonium metatungstate (AMT), ammonium metavanadate (AMV) and ferric nitrate nona hydrate (FN) having the respective transition metal concentrations were mixed in order to obtain the catalyst with a composition of Mo, W, V and Fe of 63, 9, 23 and 6 wt.%, respectively. This solution was dried by evaporation and decomposed under nitrogen at 673 K. The greenish black compound was obtained. The thermal activation treatments have been carried out in a tubular furnace at 813 in a flow of 100 mL/min pure nitrogen for 2 h.

2.2. Characterization of catalyst

The BET surface area was measured with a Micrometrics ASAP-2010. 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, CuKα). The FT-IR absorbance was recorded with Nicolet Magna IR 550 in the range of 1400–400 cm^{-1}.

2.3. Catalytic test

The selective 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 wt.% of the catalyst prepared with SiC. The methanol to oxygen ratio was kept at 1.47 and the nitrogen gas flow was fixed 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 into nitrogen flow using a precise 301 HPLC pump. To prevent the polymerization of the formaldehyde, outlets were kept at 398 K. Analyses of the reaction products were done using online Shimadzu GC-2010 gas chromatograph. The instrument was enabled with a thermal conductivity detector (TCD) and a column Hayesep T at 423 K for analyzing HCHO, CH_3OCH_3, H_2O, CH_3OH, $HCOOCH_3$ and $CH_2(OCH_3)_2$.

3. Results and discussion

3.1. Characterization of catalyst

The BET surface area of the prepared catalyst is 3.4 m^2/g. It was found that the thermal treatment has no effect on the surface area of the catalyst. The scanning electron micrograph (Figures 1, 2) for the calcined sample is not a good crystalline one, where as thermally activated catalyst show spherical particles. These particles were agglomerates of platelet-like crystallites of a few hundreds of nanometers in size. However, there

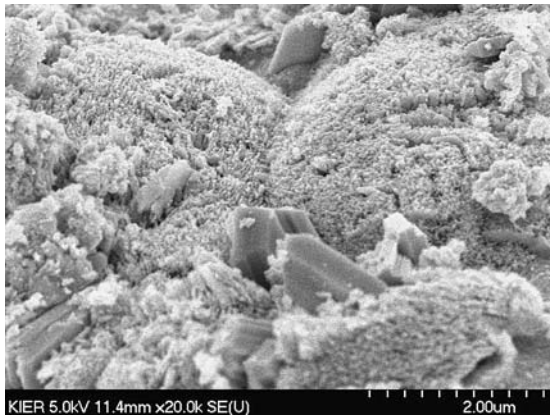

Figure 1. SEM image of the calcined catalyst.

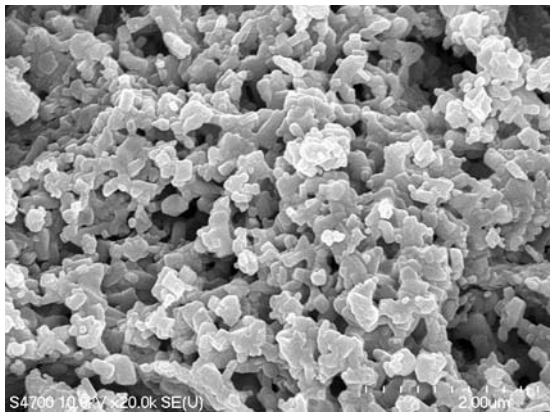

Figure 2. SEM image of the catalyst activated at 813 K.

remained parts of the sample, which still showed irregular particle shapes. The EDX analysis (Figure 3) gave the elemental distribution of Mo, V, W and Fe as 58.74 wt.% (48.35 a%), 24.82 wt.% (38.48 a%), 10.22 wt.% (4.39 a%), and 6.21 wt.% (8.78 a%) respectively. In summary, SEM and EDX techniques

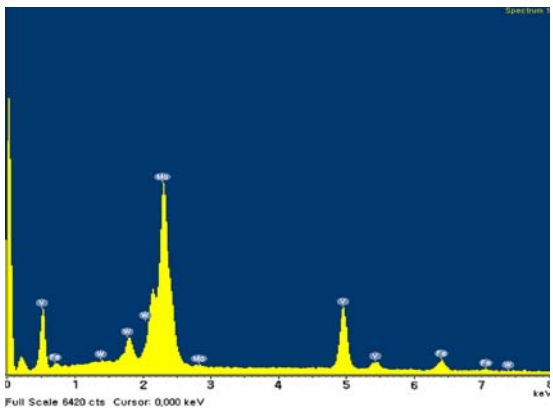

Figure 3. EDX analysis of the thermally activated MoVWFe-mixed oxide catalyst.

show that the mixed oxide is 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 leading to elemental inhomogenities during the drying process. The thermal activation led to the formation of regular particle shapes pointing to crystallization. The XRD pattern of the catalyst samples (Figure 4) at different temperatures shows that thermal activation of the catalyst at 813 K is best crystallized compared to other samples. The sample decomposed during activation at 833 K shows that the thermal activation is possible only in a small temperature range between about 800 and 820 K in inert gas. At activation temperatures above 820 K, the Mo_5O_{14}-type phase increasingly take disproportionate forms as $MoO_3$and MoO_2-type oxides. It is evident that thermal activation has lead to crystallization of the sample. The peaks show that the catalyst is a mixture of a majority of nanocrystalline Mo_5O_{14}-type oxide with minor amounts of nanocrystalline $MoO_3$and MoO_2-type material [19, 20]. The FT-IR pattern (Figure 5) showing the absorption at 711cm^{-1}suggests that there exists a multi phase component like Mo (or V or Fe or W)-O- Mo bond [21]. The somewhat broad band at 860 cm^{-1} is attributable to the tetrahedral coordination of the oxygen atoms with respect to the metal atoms [22].

Mo_5O_{14} tolerates the incorporation of considerable amounts of V and W. Stoichiometries of such phases were reported to be $(Mo_{0.92}V_{0.08})$ O_{14} or $(Mo_{0.75}W_{0.25})O_{14}$, respectively [23]. Especially, the incorporation of W favors the formation of Mo_5O_{14}-type oxides comparable with the results on Ta and Nb incorporation [24, 25]. Tungsten and vanadium, thus, act as structural promoters enhancing, and stabilizing the formation of the Mo_5O_{14}-type phase. It is known that only 2 to 12% V lead to a stabilization of the Mo_5O_{14}- type oxide [26, 27]. The MoVW catalyst however contains 23% vanadium more than the structure can tolerate according to literature. It is known on the other hand that Mo_5O_{14} tolerates the incorporation of up to 25% W [23, 24, 27]. The 9% W found in the Mo_5O_{14}-type catalyst hence lead to stabilization of this phase. Alternatively, the role of W, V and Fe may also be discussed in view of lattice oxygen defects. The incorporation of oxygen defects into MoO_3 leads to a contraction of the c-axis [27, 28], thereby affecting extended regions within the crystal lattice. In light of this important role of W and V promotors for the stabilization of the Mo_5O_{14}-type mixed oxide, it may be understood why W and V are of paramount importance to the catalytic function.

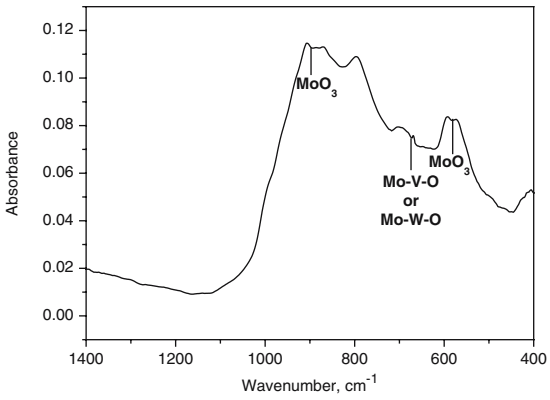

Figure 5. FT-IR pattern of the MoVWFe catalyst activated at 813 K.

3.2. Catalytic behavior

The results of conversion of methanol, selectivity and yield towards formaldehyde were studied in various reaction conditions. The selectivity of formaldehyde formation and conversion of methanol before and after the activation of the catalyst is shown in figure 6. The yield of formaldehyde with activated and untreated catalyst is shown in figure 7. It is well evident that the activity of the catalyst has been increased by the thermal treatment and during that process the amount of nanocrystalline Mo_5O_{14}-type oxide has been increased

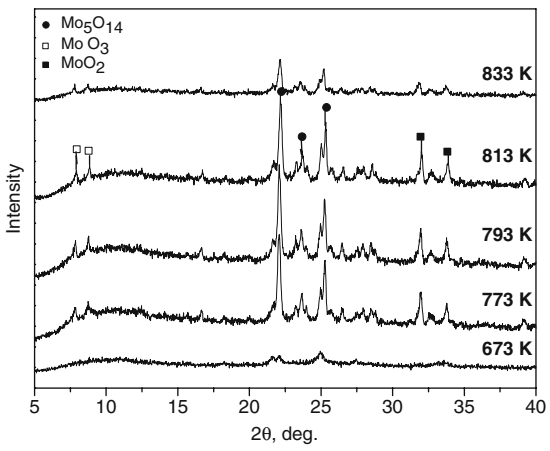

Figure 4. XRD analysis of the catalyst at different temperatures.

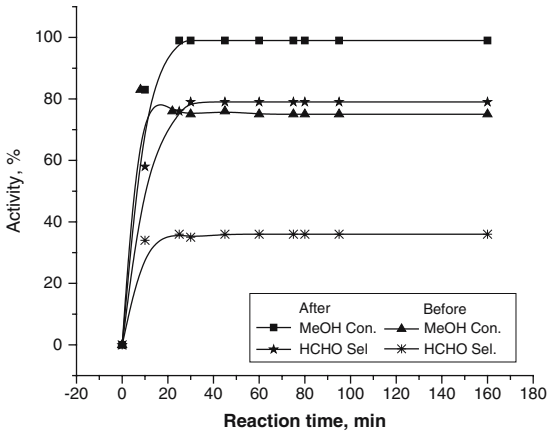

Figure 6. Conversion of methanol and Selectivity of formaldehyde at 640 K with before and after activation.

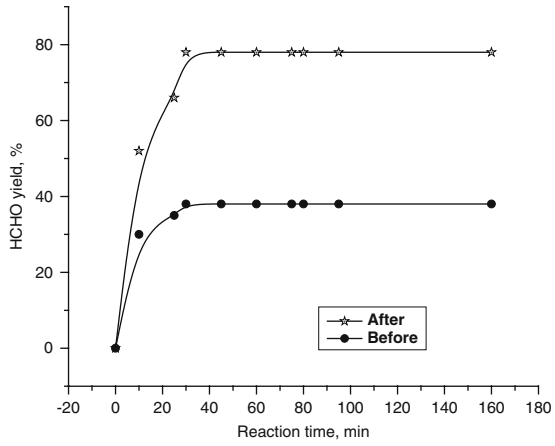

Figure 7. Yield of formaldehyde with MoVWFe catalyst before and after activation.

which contributes to the catalytic performance of the above catalyst.

4. Conclusion

The present work demonstrates that the mixed oxide catalyst with inhomogeneous nanocrystalline Mo_5O_{14}-type oxide with minor amount of MoO_3-and MoO_2-type material. The thermal activation of the catalyst leads to better crystallization of the sample. The structural analysis suggests that the catalytic performance of the MoVWFe mixed oxide catalyst in the selective oxidation of methanol is related to the formation of the Mo_5O_{14} type mixed oxide.

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