Elucidation of Mo-species in Mo-Silicalite-1 (MoS-1) molecular sieves through oxidative dehydrogenation of ethanol.

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Abstract: Whenever a metal incorporated materials are synthesized, it invariably requires instrumental techniques, like FTIR, laser Raman Spectroscopy, TEM, ESCA, NMR, etc., combined with computer modeling to establish the nature of metallic species present in the sample. In this paper, a very well known reaction, namely, oxidative dehydrogenation of ethanol is carried out over Mo-silicate-1 samples. From literature, it is understood that the product distribution of the above reaction is very much specific, which depends on the nature of the active sites present in the catalyst. Hence, by analyzing the selectivity of the products in the above reaction over Mo-silicalite samples, an attempt to deduce the nature of Mo-species is presented.

Introduction

Eco-friendly zeolite catalysts are replacing the hazardous conventional catalysts, especially in the arena of petrochemicals. The replacement of Si and Al ions in zeolite framework, namely isomorphous substitution was given special attention for the past two decades, which lead to the synthesis of TS-1, TS-2, and other novel catalysts. Establishment of the presence of metal ions in the framework has always been a challenge for the scientists.

Ethanol oxidation over Mo supported catalysts have been carried out by some workers [1-4]. Tatibouet *et.al.* has carried out ethanol oxidation over MoO_3 crystals prepared by sublimation [1]. They have proved that the -M=O sites were responsible for acetaldehyde formation. It has been established by Iwasawa *et. al.* that the Mo dimers were the active centers for ethanol oxidation over Mo supported catalyst [2]. It was concluded latter that the reaction proceeds through the formation of an ethoxide type intermediate [3]. The formation of two types of ethoxide intermediates over -M=O and Mo-O-Mo sites were reported by some authors, based on *in situ* laser Raman studies [4]. Hence, the oxidative dehydrogenation of ethanol can be used for determining the nature of species present in Mo-silicalite-1 samples. The product distribution is compared simultaneously with that of impregnated samples from literature [4].

Experimental

In a typical synthesis, the silica source (tetraethylorthosilicate, Aldrich) was added to the organic template (tetrapropylammonium hydroxide, Aldrich) with stirring. After 15 minutes, molybdenum source (ammonium heptamolybdate, LOBA, India) dissolved in minimum quantity of water was added drop wise to the above mixture with continuous stirring for 30 minutes. The final clear solution was transferred to a stainless steel autoclave with teflon lining and kept in a static air oven maintained at 443 K for 24 h. The crystalline material was separated by centrifugation. The material was calcined at 783 K for 8 h and labeled as MoS-1(n), where n represents its Si/Mo ratio. The typical composition of the synthesis gel used in the synthesis of MoS-1(71) sample is given below.

$$\mathbf{SiO_2 : Template : MoO_3 : H_2O}$$
$$\mathbf{1 \;:\; 0.326 \;:\; 0.02 : 24.33}$$

Powder X-ray diffraction data for the calcined samples were collected using a computer-automated diffractometer (Rigaku; Model D-MAX III VC). Data were recorded in the 2θ range of 5 to 50° at a scan rate of 0.5° /min using silicon as the internal standard. The XRD profiles of the calcined MoS-1 samples match well with that of silicalite-1 (MFI) structure [5]. No impurity phase of MoO_3 was observed. The bulk chemical analysis of silica and molybdenum was carried out using AAS.

The oxidative dehydrogenation of ethanol over MoS-1 samples was carried out in a fixed bed glass reactor (1.9 cm i.d., down flow mode), followed by a spiral condenser and a gas-liquid separator. Proper mass balance was done after analyzing both the gas and the liquid products using HP-5880A gas chromatograph fitted with a capillary column (50m X 0.2 mm). The reactor was charged with 2.0 g of the catalyst (12-14 mesh, ASTM). Ceramic beads were used in the pre-heating zone. The experiments were carried out at different temperatures. The alcohol/oxygen ratio was maintained well below the explosion limit (1.52 vol. %). Under experimental conditions, only a negligible amount of CO_2 (0.5 - 1.2 %) was produced.

Results and discussion

Oxidative dehydrogenation of Ethanol

Conversion of ethanol over MoS-1(71) (the number inside the parenthesis represents Si/Mo ratio) at different temperatures are presented in Table 1. As temperature increases the conversion was found to increase. Maximum selectivity of acetaldehyde was observed at 630 K. Beyond this temperature, polymer and cracked products (others) were formed to a greater extent.

Table 1—Oxidation of ethanol over MoS-1 (71) : Conversion and Product distribution

Temperature	Conversion	Selectivity, %				
K	%	C_2H_4	CH_3CHO	CH_3COOH	Ether	Others
573	19.9	10.1	67.8	3.4	13.6	5.1
600	28.9	7.9	74.8	2.0	9.4	5.9
630	32.2	4.3	85.7	-	3.0	7.0
655	35.8	2.6	69.2	-	6.1	22.1
680	40.9	0.9	59.5	-	4.0	35.6

Product distribution and conversion under similar process conditions, over MoS-1 with different Si/Mo (mole) ratios are presented in Table 2 (temperature being constant, 630 K). As the Mo content was increased, the total conversion and the acetaldehyde selectivity were found to increase, since, the active -M=O sites were available for the reaction.

Table 2—Oxidation of ethanol: Conversion and Product distribution over Mo-silicalite-1 (MoS-1) with different Si/Mo ratio at 630 K.

Sample	Si/Mo	MoO_3	Conv.	Selectivity, %				
	(mole)	Wt.%	%	C_2H_4	CH_3CHO	CH_3COOH	Ether	Others
MoS-1	71	3.25	32.2	4.3	85.7	-	3.0	7.0
MoS-1	90	2.62	13.8	2.6	83.0	2.6	10.4	1.4
MoS-1	137	1.71	7.31	14.5	63.6	4.6	15.6	1.7

It is understood from the literature, that, Mo-O-R (R = Si, H) sites are responsible for the formation of ether [3]. As the Mo content was decreased (sample MoS-1(137)), the polyanions with Mo-O-Mo bridging does not form at the surface of the catalyst, on the other hand, more amount of Mo-O-H,Si (octahedral Mo at the surface) sites should have access for the reaction, leading to the formation of more amount of ether. It is clear from Table-2, more amount of acetaldehyde was produced over MoS-1(71). The MoS-1 with Si/Mo = 90, gave good selectivity (80-87 %). The MoS-1 sample with Si/Mo = 137, gave very low conversion/selectivity towards acetaldehyde (63 - 70 %), producing more amount of ether. In short, the sample with higher and lower Mo content did not give good yield of acetaldehyde throughout the temperature range. This can be attributed to the fact that the higher loading leads to the deposition of polyanions at the surface, which favors the formation of polymer and cracked products. On the other hand, at low Mo content, the distinct Mo-O-Si,H sites favors the formation of ether (MoS-1 (137)). Hence, the MoS-1 with moderate Si/Mo ratio of 90, which possesses well-dispersed -Mo=O sites give good selectivity towards acetaldehyde at low and higher temperatures.

Table 3—Oxidation of ethanol: Conversion and Product distribution over MoS-1 and MoO_3/SiO_2 catalysts.

Sample	MoO_3	Temp.	Conv.	Selectivity, %				
	Wt.%	K	%	C_2H_4	CH_3CHO	CH_3COOH	Ether	Others
MoO_3/SiO_2*	1.0	575	2.4	3	81.0	14	2	-
MoS-1	2.62	573	11.2	1.9	81.3	3.6	11.3	1.9
MoO_3/SiO_2*	9.0	563	42.7	4.0	72.0	7	4	13.0#

* Values taken from Ref. No. 4 for comparison

\# Includes ethyl acetate and CO_2.

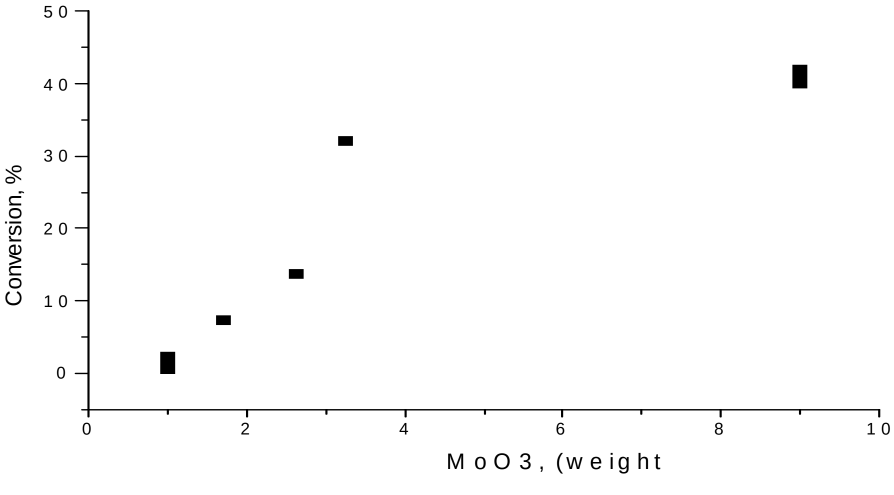

Fig. 1—Total conversion of ethanol over MoS-1 with different Mo content (630K), Values of 1 wt.% and 9wt.% MoO_3 is taken from Ref. No.4.

The conversions of ethanol over MoS-1 with different Si/Mo ratio were found to be directly proportional to Mo content and match well with that reported by earlier workers [4] (Fig.1). Even though, more amount of ether was produced over MoS-1 (90), the selectivity towards acetaldehyde was better compared to MoO_3/SiO_2 catalyst. The higher selectivity of acetic acid over MoO_3/SiO_2 proves the deposition of polyanions over silica, whereas production of ether over MoS-1(90) indicates the presence of Mo-O-R (R=Si, H) sites (defect sites). This proves that the Mo-species present in MoS-1 samples are entirely different to that of the impregnated analogues.

Conclusions

Mo-silicalite-1 was synthesized hydrothermally. The oxidative dehydrogenation of ethanol over Mo-silicalite-1 samples revealed that, when Mo concentration was increased, deposition of Mo at the surface in the form of polyanions takes place. The MoS-1 samples were found to give better activity compared to MoO_3/SiO_2 catalyst from literature.

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