

Titration of Active Sites for Partial Oxidation of Methanol over V_2O_5 / SnO_2 and MoO_3 / SnO_2 Catalysts by a Low-Temperature Oxygen Chemisorption Technique



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ABSTRACT

The amount of oxygen chemisorbed at -78°C on V_2O_5 / SnO_2 and MoO_3 / SnO_2 catalysts has been found to correlate directly with the conversion of methanol at 175°C . These catalysts have shown high selectivity for the formation of formaldehyde, selectivities being over 95% for V_2O_5 / SnO_2 and ca. 90% for MoO_3 / SnO_2 .

In studying the correlation between catalytic activity and physico chemical properties of a catalyst it is important to obtain information about the number and nature of active sites. Recently, the technique of low-temperature oxygen chemisorption (LTOC) has proved most suitable for the study of supported molybdena [1,2] and vanadia [3-5] catalysts. It has been demonstrated that specific information on the active surface area as well as dispersion of the supported molybdena and vanadia phases could be obtained from LTOC data. In this communication, we report the direct correlation between LTOC capacity of a series of SnO_2 supported V_2O_5 and MoO_3 catalysts and their catalytic activity for the partial oxidation of methanol. These catalysts, as well as the reaction, are very important from a commercial point of view, and are also reported to show high activity and selectivity for oxidation and ammoxidation of various other hydrocarbons [6,7].

The SnO_2 supported catalysts containing 0.5 to 5.5 wt.-% V_2O_5 or MoO_3 were prepared by the standard wet impregnation technique with the required amounts of aqueous ammonium metavanadate or ammonium heptamolybdate solutions. The impregnated samples were dried at 120°C for 12 h and calcined at 500°C for 6 h. The LTOC measurements were conducted on a standard static volumetric high-vacuum system. Prior to the adsorption measurements,

the catalyst samples were reduced in flowing hydrogen at 500°C for 6 h. Experimental details on the LTOC technique have been given elsewhere [4]. Chemisorption of oxygen was determined as the difference between two oxygen adsorption isotherms at -78°C. Activity measurements were conducted on a flow micro reactor operating under normal atmospheric pressure and interfaced using a 6-way gas sampling valve with a gas chromatograph. For each run about 0.5 g of catalyst was loaded in a Pyrex glass reactor of 10 mm I.D. and the activities were measured at 175°C. An average catalyst particle size of less than 0.5 mm was chosen so as to eliminate mass transfer effects. The feed gas consisted of 72, 24 and 4% by volume of nitrogen, oxygen and methanol vapour, respectively. Analysis of the reaction products indicated formation of mainly formaldehyde and some dimethyl ether with small traces of methyl formate, carbon monoxide and carbon dioxide respectively.

The total conversion of methanol was plotted as a function of oxygen uptake in Fig. 1, which clearly demonstrates that methanol oxidation activity is directly proportional to the amount of oxygen chemisorbed at -78°C. The two series of catalysts, V_2O_5/SnO_2 and MoO_3/SnO_2 , are represented by two different correlation lines. It is important to note from Fig. 1 that the correlation line representing the V_2O_5/SnO_2 catalysts has a three times higher slope than that representing the MoO_3/SnO_2 catalysts. This implies that the V_2O_5/SnO_2 catalysts have circa three times higher activity per unit of chemisorbed oxygen than the MoO_3/SnO_2 catalysts. In other words, the activity per site on the V_2O_5/SnO_2 catalysts is three times higher than that on the MoO_3/SnO_2 catalysts.

Composition, oxygen uptakes, activity and selectivities of various catalysts are shown in Table 1. As can be seen from Table 1, the oxygen uptake increases

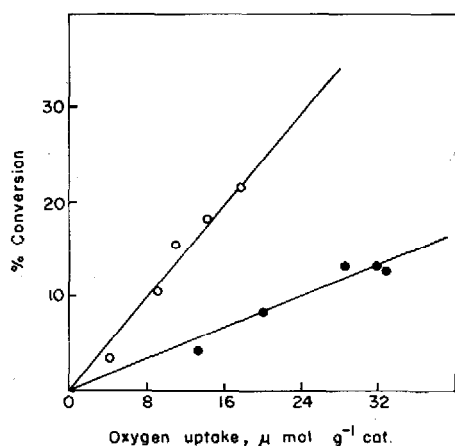


Fig. 1. Methanol oxidation activity at 175°C plotted as a function of oxygen uptake at -78°C. (○) V_2O_5/SnO_2 ; (●) MoO_3/SnO_2 catalysts. (The support also shows a small activity and uptake; this was corrected before reporting the results.)

TABLE 1

Composition, oxygen uptake, activity and selectivities of various catalysts

Catalyst code	Composition ^a (wt.-%)		Oxygen uptake ($\mu\text{mol g}^{-1}$ cat.)	BET surface area ^b ($\text{m}^2 \text{g}^{-1}$)	Total methanol conversion (%)	Selectivity (%)	
	V ₂ O ₅	MoO ₃				HCHO	CH ₃ OCH ₃
VS-1	1.1	—	8.9	28	10.6	97.5	0.9
VS-2	2.2	—	14.0	26	18.0	95.8	1.8
VS-3	3.2	—	17.4	29	21.8	96.8	1.3
VS-4	4.3	—	10.8	28	15.8	97.6	2.0
VS-5	5.4	—	4.5	25	3.8	96.3	3.1
MS-1	—	0.5	13.1	29	4.2	90.1	6.8
MS-2	—	1.0	20.0	28	8.4	92.0	6.1
MS-3	—	2.0	28.6	27	13.1	90.2	7.9
MS-4	—	3.0	31.9	27	13.2	88.1	9.1
MS-5	—	5.0	32.6	24	12.6	86.3	9.8

^aThe balance is SnO₂.^bDetermined by nitrogen adsorption at -196°C by taking 0.162 nm^2 as the area of cross-section of nitrogen.

as the V₂O₅ or MoO₃ loading increases, reaches a maximum and then declines or levels off with further loading. The saturation loading is an indication of completion of monolayer coverage of active support surface by vanadium and molybdenum oxide phases having values of 3.2 and 3 wt.-% respectively. Very similar results were also reported earlier with vanadia and molybdena catalysts when supported on Al₂O₃ and SiO₂ [2-5]. Those results were explained in terms of 'patchy' monolayer models of vanadium and molybdenum oxide phases respectively by Nag et al. [3] and Nag [8]. Based on those results it was also clearly demonstrated that the coordinately unsaturated sites (CUS) of the reduced vanadium or molybdenum oxide patches are the exact locations for the dissociative chemisorption of oxygen at -78°C . It is to be true from the present study and also from an earlier report [3] that is mainly the specific surface area of the support that determines monolayer concentration of the active component and the strength of interaction between the support and the active component governs the dispersion and hence oxygen uptake capacity.

Recently, in a series of papers Machiels et al. [9] have proposed a mechanism for the methanol oxidation process, which involves the dissociative adsorption of CH₃OH (CH₃O⁻ + H⁺) to form surface methoxide ions. The next step in the catalytic cycle is the abstraction of a methyl hydrogen by a surface oxygen. This is followed by a rapid intramolecular rearrangement and the desorption of formaldehyde as well as other products. This mechanism has also been widely accepted [10]. The strong correlation as observed in Fig. 1 indi-

cates clearly that the CUS are the exact locations for the initial dissociative adsorption of methanol, where oxygen too adsorbs selectively at -78°C . Hence, a direct correlation between oxygen uptake and the total activity for the partial oxidation of methanol instead of a particular product selectivity is observed.

As a consequence of the Mars and Van Krevelen mechanism [11], catalytic properties have been shown to depend on the nature and mobility of surface oxygen species, on electron transfer capability which facilitates the redox process during the catalytic reaction and also on geometric considerations, particularly the distance between active cations. It appears from the present study that all these factors are favourable in the case of $\text{V}_2\text{O}_5/\text{SnO}_2$ catalysts resulting in higher activity and selectivity for the reaction of methanol to formaldehyde even though the sites involved are one and the same on both series of catalysts.

Thus LTOC can be used as a probe to characterize $\text{V}_2\text{O}_5/\text{SnO}_2$ and $\text{MoO}_3/\text{SnO}_2$ catalysts.

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