Quantitative Determination of the Number of Active Surface Sites and the Turnover Frequencies for Methanol Oxidation over Metal Oxide Catalysts

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Methanol chemisorption was successfully developed to quantify the number of surface active sites (N_s) and the methanol oxidation turnover frequencies (TOF) of metal oxide catalysts (supported molybdenum oxides, bulk metal molybdates and bulk metal oxides). This is the first example in the catalysis literature where the N_s and TOF values of different types of metal oxide catalysts have been *quantitatively* compared for an oxidation reaction. Comparable values of N_s and TOF were obtained for the corresponding molybdate catalysts (e.g., MoO_3/Al_2O_3 and $Al_2(MoO_4)_3$), which reflect the influence of the cation ligands in these catalysts (e.g., Al). Further comparison with the pure metal oxides (e.g., MoO_3 and Al_2O_3), suggests that the bulk metal molybdate catalysts are enriched in surface Mo and may actually possess a surface molybdenum oxide overlayer. These new insights account for the special properties of bulk metal molybdates during catalytic oxidation reactions.

1. INTRODUCTION

Several approaches have previously been proposed to quantify the number of surface active sites on metal oxide catalysts (oxygen chemisorption after pre-reduction in H_2, reaction of NO and NH_3, etc. [1-3]). However, these methods suffer because (1) the number of surface active sites is determined with a different probe molecule than the actual reactant, (2) the oxide catalysts are treated with H_2 and the reduction stoichiometry of the catalyst is usually not known, and (3) the chemisorption and reduction temperatures are far removed from the actual reaction temperatures. The present study reports on a novel chemisorption method that employs the dissociative adsorption of methanol to surface methoxy intermediates in order to quantitatively determine the number of surface active sites on metal oxide catalysts. The commonality of the surface methoxy intermediate during dissociative chemisorption of methanol and methanol oxidation on oxide catalysts overcomes the limitations of the previously proposed techniques to quantify the number of surface active sites on metal oxide catalysts and their turnover frequencies during oxidation reactions [4]. In addition, the methanol oxidation product distribution at low conversions reflects the nature of the surface active sites since redox sites yield H_2CO, acidic sites yield CH_3OCH_3

and basic sites yield CO_2 [5]. Thus, methanol is a "smart" probe molecule that can provide fundamental information about the number of surface active sites, the TOF values and distribution of different types of surface sites of metal oxide catalysts.

2. EXPERIMENTAL

2.1. Catalyst Synthesis

Three different types of metal oxide catalysts were employed in the present investigation: supported molybdenum oxide catalysts (e.g. MoO_3/Al_2O_3), bulk metal molybdate catalysts (e.g., $Al_2(MoO_4)_3$) and bulk metal oxide catalysts (e.g., MoO_3 and Al_2O_3). The supported molybdenum oxide catalysts were prepared via incipient wetness impregnation of the oxide supports by aqueous solutions of ammonium heptamolybdate [6]. The bulk molybdates were formed by coprecipitation of aqueous solutions of the metal salts (e.g., ammonium heptamolybdate and the corresponding metal nitrate). The bulk metal oxide catalysts were purchased as high purity commercial chemicals.

1.2. Catalyst Characterization

The various metal oxide catalysts were extensively characterized to obtain their physical and chemical properties: BET surface area, X-ray Photoelectron Spectroscopy (XPS), X-ray diffraction (XRD), Raman spectroscopy, and X-ray Absorption Near Edge Spectroscopy (XANES). Experimental details about the various characterization instruments can be found in prior publications [6,7]. This combination of characterization techniques provided detailed information about the bulk structure/composition and surface structure/composition of the various metal oxide catalysts.

2.3. Methanol Chemisorption and Oxidation

The experimental conditions required to quantify the number of surface active sites via methanol chemisorption were determined over a wide range of temperature and methanol partial pressure in a Cahn TGA microbalance (Model TG-131). Methanol adsorption was performed in a flowing helium stream. Adsorption temperatures below 100 °C resulted in the coadsorption of surface methoxy intermediates and physically adsorbed molecular methanol, and adsorption at temperatures significantly higher than 100 °C resulted in the decomposition of the surface methoxy intermediates. Thus, 100 °C was chosen as the adsorption temperature for methanol since it was above the desorption temperature of physically adsorbed molecular methanol, at the temperature where methanol readily dissociatively adsorbed as surface methoxy intermediates and below the decomposition temperature of the surface methoxy intermediates. The methanol partial pressure also influenced the amount of physically adsorbed molecular methanol that condensed on the catalyst pores, and 2,000 ppm of methanol in helium was found to essentially eliminate the condensation of molecular methanol in the pores of the oxide catalysts at 100 °C. The methanol oxidation steady state kinetics were obtained in a fixed-bed catalytic reactor under differential conditions and the product formation was determined with an on-line gas chromatograph [7].

3. SUPPORTED MOLYBDENUM OXIDE CATALYSTS

Model supported molybdenum oxide catalysts (e.g., MoO_3 supported on ZrO_2, TiO_2, Al_2O_3, Nb_2O_5, etc.) were initially investigated for methanol chemisorption since such catalysts (1) possess 100% dispersion of the active molybdenum oxide component, (2) the number of surface active sites are independently known from other characterization experiments (e.g., Raman spectroscopy) and (3) their surface structures are known from *in situ* characterization studies (e.g., Raman and X-ray Absorption Near Edge (XANES) spectroscopy) [6]. The surface Mo coverages employed in the present investigation corresponded to about monolayer surface Mo coverage in order to minimize adsorption of methanol on exposed oxide support sites (~7 umol of Mo/m^2). The surface Mo_s densities and the methoxy chemisorption stoichiometries (CH_3O_{ads}/Mo_s) are presented in Table 1. The methoxy chemisorption stoichiometry was found to be about 1 CH_3O_{ads} per 3-4 Mo_s for the chosen adsorption conditions and reflects the presence of lateral

Table 1
Methanol chemisorption stoichiometry and methanol oxidation turnover frequencies for supported molybdenum oxide catalysts

Catalyst	Surface Mo (umol/m^2)	N_s (CH_3O_{ads}) (umol/m^2)	CH_3O_{ads}/Mo_s	TOF (sec^{-1})
3% MoO_3/ZrO_2	5.31	1.25	0.24	0.47
6% MoO_3/Nb_2O_5	7.64	2.10	0.28	0.14
6% MoO_3/TiO_2	7.64	3.07	0.40	0.18
2% MoO_3/MnO	7.50	1.14	0.15	0.44
3% MoO_3/Cr_2O_3	7.42	2.87	0.39	0.08
18% MoO_3/Al_2O_3	6.97	2.78	0.40	0.04
4% MoO_3/NiO	7.32	1.47	0.20	0.04

interactions in the surface methoxy overlayer. Methanol oxidation over these supported MoO_3 catalysts primarily yielded redox products with H_2CO as the primary product. The methanol oxidation turnover frequencies were calculated by determining the production rate of redox products at 280 ^0C and normalizing the rate to the number of surface sites available for adsorption of CH_3O_{ads} (N_s), and the resulting TOF values are also presented in Table 1. The methanol oxidation TOF was found to vary over an order of magnitude for the supported MoO_3 catalysts. The TOF variation was not found to correlate with the coordination of the surface molybdenum oxide species, which was independently determined with *in situ* Raman and XANES [6]. However, the TOF variation was found to correlate with the characteristics of the bridging M-O-Support bond rather than the terminal Mo=O bond. In summary, the methanol chemisorption studies with the model supported molybdenum oxide catalysts confirm that methanol chemisorption can be employed to quantitatively determine the number of active surface sites of metal oxide catalysts, which also allows for the quantitative determination of the TOF values for oxidation reactions such as methanol oxidation.

4. BULK METAL MOLYBDATE CATALYSTS

A series of bulk metal molybdate catalysts ($NiMoO_4$, $Al_2(MoO_4)_3$, $Fe_2(MoO_4)_3$, etc.) were synthesized and structurally characterized by XRD and Raman spectroscopy to confirm their crystalline structures as well as the absence of excess crystalline MoO_3 (see Table 2). Unlike the model supported metal oxide catalysts where the number of Mo_s were independently known (see section **3**), the number of Mo_s for the bulk metal molybdate catalysts is not known. Thus, methanol chemisorption was employed to determine the number of CH_3O_{ads} sites, N_s, which are presented in Table 2. Comparison of the number of CH_3O_{ads}, N_s, for the bulk and supported molybdate catalysts gives very similar adsorption

Table 2
Methanol chemisorption stoichiometries and methanol oxidation turnover frequencies for bulk metal molybdate catalysts

Catalyst	N_s (CH_3O_{ads}) (umol/m^2)	TOF (sec^{-1})	Selectivity to partial oxidation products
$Zr(MoO_4)_2$	1.0	24.8	65.2
$TiMoO_5$	1.5	0.7	100.0
$MnMoO_4$	3.1	6.6	99.8
$Cr_2(MoO_4)_3$	12.6	3.1	91.0
$Al_2(MoO_4)_3$	5.0	1.8	26.1
$NiMoO_4$	2.8	0.9	100.0
$CoMoO_4$	4.1	0.9	88.2
$CuMoO_4$	23.9	1.1	100.0
$Fe_2(MoO_4)_3$	7.6	0.8	61.0

surface densities for most of the catalysts, ~ 3 umol CH_3O_{ads}/m^2, which reflects the very similar adsorption stoichiometries for these different types of metal oxide catalyst systems. Two of the bulk metal molybdate catalysts, however, exhibited somewhat higher values, which may be due to special structural or compositional properties of these specific catalysts. Nevertheless, it appears that *comparable* surface densities of CH_3O_{ads} are obtained for most bulk and supported molybdate catalysts.

Methanol oxidation over the bulk metal molybdate catalysts primarily yielded redox products with H_2CO as the primary product (see Table 2). The methanol oxidation TOF values were calculated by determining the production rate of redox products at 380 °C and normalizing the rate to the number of surface sites available for adsorption of CH_3O_{ads} (N_s), and the resulting TOF values are also presented in Table 2. Comparison of the TOF values with the known bulk structures of these bulk metal molybdates reveals that there is no correlation between the bulk Mo cation coordination and the TOF for methanol oxidation. The lower surface areas of the bulk metal molybdate catalysts, 5-10 m^2/g, compared to the supported molybdenum oxide catalysts, 20-200 m^2/g, required that the bulk metal molybdate catalysts be studied at a higher reaction temperature of 380 °C. In order to compare the TOF

values of both the bulk metal molybdate and supported molybdenum oxide catalysts at comparable temperatures, the TOF values for the supported molybdenum oxide catalysts were extrapolated from 250 to 380 °C from the well known activation energy of this reaction of ~20 Kcal/mol [8]. Comparison of the methanol oxidation TOF values for the corresponding bulk and supported molybdate catalysts at 380 °C reveals that they are very *comparable*, usually within a factor of ~2-3 and sometimes even identical. Thus, the very similar number of surface active sites (Ns) and methanol oxidation TOF values for bulk metal molybdate and supported molybdenum oxide catalysts reveals the significant influence of ligands in oxidation catalysis (bridging Mo-O-M, where M is either an oxide support or a bulk metal oxide cation). This is the first example in the catalysis literature where the TOFs of bulk mixed metal oxide and supported metal oxide catalysts have been quantitatively compared. The new findings demonstrate that the same factors control the oxidation catalysis of bulk and supported metal oxide catalysts.

5. BULK METAL OXIDE CATALYSTS

A series of pure metal oxides (NiO, Al_2O_3, Fe_2O_3, etc.) was also examined with methanol chemisorption and methanol oxidation in order to better understand the role of the metal components in the bulk metal molybdates, and the results are presented in Table 3.

Table 3
Methanol oxidation turnover frequencies and selectivities over pure metal oxides

Catalyst	$N_s(CH_3O_{ads})$ (umol/m^2)	TOF (sec^{-1})	Selectivity		
			H_2CO	CO_2	Others
Cr_2O_3	12.4	79.6	15.5	79.7	4.8
NiO	4.37	53.1	27.3	67.6	5.1
CoO	2.23	526.8	23.2	69.1	2.2
CuO	7.03	55.6	32.6	64.0	0.9
Fe_2O_3	3.24	26.9	13.9	83.7	2.4
MoO_3	0.8	5.3	84.1	00.0	12.0

Again, the adsorption of methanol mostly corresponds to ~3 CH_3O_{ads} umol/m^2. The higher N_s for CuO is due to the lower adsorption temperature required for this sample, 50 °C, because it was reduced at the typical adsorption temperature required of 100 °C. Similar to bulk $Cr_2(MoO_4)_3$, pure Cr_2O_3 exhibited a somewhat high value of N_s. The low value of N_s for pure MoO_3 reflects the platelet morphology of this oxide and the preferential adsorption of methanol on the edge sites [4]. The TOF values for the pure metal oxides were found to be orders of magnitude greater than the corresponding bulk metal molybdates at 380 °C (see Table 2). Furthermore, the high selectivity towards CO_2 formation during methanol oxidation, at low conversions, for the pure metal oxides (e.g., Cr_2O_3, NiO, CoO, CuO and Fe_2O_3) revealed the presence of significant amounts of basic surface sites, which were not significant for the bulk metal molybdate catalysts. In contrast to these pure metal oxides, pure MoO_3 exhibits a low TOF and a high selectivity of H_2CO. These observations suggest

that bulk metal molybdate catalysts are enriched in surface Mo and may actually possess a surface molybdenum oxide overlayer (analogous to the supported molybdenum oxide catalysts). Such a scenario would account for the somewhat low TOF values and high H_2CO values of bulk metal molybdate catalysts during methanol oxidation. Indeed, XPS surface analysis of the bulk metal molybdates confirmed that the bulk metal molybdate catalysts were surface enriched with Mo. Thus, the catalytic properties of bulk metal molybdates are dominated by the surface Mo sites.

6. CONCLUSIONS

Methanol chemisorption was successfuly developed to quantify the number of surface actives sites in metal oxide catalysts (supported molybdenum oxides, bulk metal molybdates and bulk metal oxides). For the model supported molybdenum oxide catalysts, it was found that one CH_3O_{ads} surface intermediate occupies about 3-4 surface Mo sites due to lateral interactions in the surface methoxy overlayer. This fundamental information allowed for the quantitative determination of the TOF for the methanol oxidation reaction. The variation in TOF was not related to the Mo_s coordination or the terminal $Mo=O$ bond, but was related to the characteristics of the bridging Mo–O-Support bond. For the bulk metal molybdates, the surface densities of CH_3O_{ads} were mostly comparable to the supported molybdenum oxide catalysts, and the methanol oxidation TOF variation did not correlate with the bulk Mo cation coordination. Comparison of the methanol oxidation TOF values of the corresponding bulk and supported molybdate catalysts reveals that they are comparable. This suggests that the same factor controls the oxidation catalysis of bulk and supported metal oxide catalysts: the nature of the bridging Mo-O-M bond, where M is either an oxide support or a bulk metal oxide cation. Comparison of the bulk metal molybdates with the corresponding pure metal oxides, suggests that bulk metal molybdate catalysts are enriched in surface Mo and may actually possess a surface molybdenum oxide overlayer (analogous to the supported molybdenum oxide catalysts). These new insights account for the special properties of bulk metal molybdates during catalytic oxidation.

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