Methanol: a “smart” chemical probe molecule

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Received 8 May 2000; accepted 15 June 2001

A novel chemisorption method was employed for the dissociative adsorption of methanol to surface methoxy intermediates in order to quantitatively determine the number of surface active sites on one-component metal oxide catalysts (MgO, CaO, SrO, BaO, Y_2O_3, La_2O_3, CeO_2, TiO_2, ZrO_2, HfO_2, V_2O_5, Nb_2O_5, Ta_2O_5, Cr_2O_3, MoO_3, WO_3, Mn_2O_3, Fe_2O_3, Co_3O_4, Rh_2O_3, NiO, PdO, PtO, CuO, Ag_2O, Au_2O_3, ZnO, Al_2O_3, Ga_2O_3, In_2O_3, SiO_2, GeO_2, SnO_2, P_2O_5, Sb_2O_3, Bi_2O_3, SeO_2 and TeO_2). The number of surface active sites for methanol dissociative adsorption corresponds to $\sim 3\ \mu\text{mol/m}^2$ on average for many of the metal oxide catalysts. Furthermore, the methanol oxidation product distribution at low conversions reflects the nature of the surface active sites on metal oxides since redox sites yield H_2CO, acidic sites yield CH_3OCH_3 and basic sites yield CO_2. The distribution of the different types of surface active sites was found to vary widely for the different metal oxide catalysts. In addition, the commonality of the surface methoxy intermediate during dissociative chemisorption of methanol and methanol oxidation on oxide catalysts also allows for the quantitative determination of the turnover frequency (TOF) values. The TOF values for the various metal oxide catalysts were found to vary over seven orders of magnitude (10^{-3} to $10^4\ s^{-1}$). An inverse relationship (for metal oxide catalysts displaying high (>85%) selectivity to either redox or acidic products) was found between the methanol oxidation TOF values and the decomposition temperatures of the surface $M–OCH_3$ intermediates reflecting that the decomposition of the surface $M–OCH_3$ species is the rate-determining step during methanol oxidation over the metal oxide catalysts.

KEY WORDS: active site titration by methanol; active site titration on oxides; methanol as probe molecule

1. Introduction

The ability to quantitatively determine the number of surface active sites on metal oxide catalysts remains a great challenge for the establishment of fundamental catalytic relationships for metal oxide catalysts. Knowledge of the active site surface density allows for direct comparison of intrinsic activities across different catalysts as expressed by their turnover frequencies (TOF = molecules converted per second per active surface metal oxide site) [1]. Several approaches have previously been proposed to quantify the number of surface active sites on metal oxide catalysts. Many authors [2–11] proposed O_2 chemisorption as a general method. The bulk (or supported) metal oxide catalyst is reduced only at the surface by H_2 and then reoxidized to determine the number of surface active metal oxide sites by the amount of oxygen consumed. However, this approach is very insensitive to over-reduction beyond the surface layer and is rather indirect [5,12–14]. An alternative method, based on a surface reaction between NO and NH_3, was proposed by Murakami and coworkers to quantify the surface V=O species on bulk V_2O_5 and supported vanadium oxide catalysts [15,16]. The technique involves the reaction between NO and NH_3 on a surface V=O site to produce N_2. However, recent studies demonstrated that the reaction mechanism of NO and NH_3 on vanadia/titania catalysts is more complicated and involves both Brønsted acid sites V–OH and V=O redox sites in adsorption and activation of ammonia [17,18].

Despite the extensive efforts to develop a reliable method to quantify the number of surface active sites on metal oxide catalysts, these studies possessed several limitations: (1) the number of surface active sites is determined with a different probe molecule than the actual reactant, (2) the oxide catalyst is pretreated with H_2 and the reduction stoichiometry of the catalyst is usually not known, (3) the chemisorption and reduction temperatures are usually far removed from the actual reaction conditions, and (4) both surface and bulk sites may be involved in the measurements.

The studies of Farneth *et al.* [19–21] on bulk MoO_3 and Sleight *et al.* [22] on bulk $Fe_2(MoO_4)_3$ were the first to suggest that quantitative methanol chemisorption may be a viable method for determining the surface active density of bulk metal oxides. The group performed methanol chemisorption at room temperature and temperature-programmed desorption (TPD) studies under high vacuum in order to elucidate the methanol oxidation mechanism, nature of surface intermediates, the number of surface active sites and peak desorption temperatures of the products formed. In addition to methanol, the investigations were extended to other probe molecules like ethanol, 2-propanol and *tert*-butyl alcohol to quantify the number of active sites on metal oxide surface and their dependence on the characteristics of the specific alcohol molecule. The surface active site densities were very similar when methanol, ethanol and 2-propanol were chemisorbed on the MoO_3 surface but ~3 times higher than the surface active site density obtained from the chemisorption of *tert*-butyl alcohol. The authors also demonstrated that the methanol adsorption stoichiometry to surface methoxy species and water must be incorporated into any quantitative chemisorption measurements that are obtained gravimetrically since moisture desorbs during methanol dissociative adsorption.

Subsequent studies were also carried on TiO_2 [23] using several probe molecules such as methanol, ethanol, 1-propanol and 2-propanol to quantify the number of active sites and to study the structure–reactivity relationships of TiO_2 (anatase) powders. The surface active site densities were very similar and independent of the probe molecules used for chemisorption.

However, these pioneering studies performed methanol adsorption at room temperature and previous studies demonstrated that methanol chemisorption on MoO_3 at room temperature results in both molecular and dissociatively adsorbed methanol [24]. The first mechanism can be considered as a physical adsorption process since the methanol molecules adsorb intact on the surface. Dissociative adsorption is a chemisorption process that involves the formation of a surface methoxy intermediate and a surface hydroxyl on an active site. Infrared studies by Groff demonstrated that at 100 °C, undissociated methanol molecules are volatile while the surface methoxy groups remain intact on the MoO_3 surface [24]. More recently similar conclusions were obtained by infrared analysis of methanol adsorbed onto supported molybdenum and vanadium oxide catalyst [25].

The objective of the present study is to improve the methanol chemisorption approach to quantify the number of surface active sites for pure metal oxide catalysts by optimizing the experimental conditions for dissociative adsorption of methanol. The primary reason for choosing methanol as the probe molecule to quantitatively determine the number of surface active sites on pure metal oxides is due to the commonality of the surface methoxy intermediate formed during dissociative chemisorption of methanol and methanol oxidation on oxide catalysts. This overcomes a major limitation of the previously proposed techniques to quantify the number of surface active sites on metal oxides. The secondary reason for choosing methanol as the probe molecule is because of its high reactivity towards metal oxides (unlike CO, H_2 and O_2).

Furthermore, knowledge of the number of surface active sites enables the calculation of the catalytic turnover frequency during methanol oxidation. The TOF is the true catalytic parameter for oxidation reactions since it is normalized per surface active site. These calculations will, for the first time, allow for direct comparison of the intrinsic methanol oxidation activities over a wide range of pure metal oxide catalysts, and will hopefully provide new insight into the fundamental catalytic properties of pure metal oxides.

The methanol chemisorption method can be also extended to obtain the decomposition temperatures of the surface methoxy species on various pure metal oxide catalysts by temperature-programmed desorption (TPD) experiments. The decomposition temperature of the surface methoxy species is a very important catalytic parameter since kinetic isotopic studies have shown that this surface reaction step is the rate-limiting step during methanol oxidation [26].

In addition, methanol oxidation reactions on oxide surfaces are very sensitive to the nature of active catalytic sites [27]. The methanol oxidation product distribution at low conversions reflects the nature of the surface active sites since redox sites oxidatively-dehydrogenate methanol to yield formaldehyde, basic sites yield CO_2 and Lewis and Brønsted acid sites lead to dehydration of the oxidized carbon species to yield dimethyl ether. Thus, methanol is a "smart" chemical probe molecule that can provide fundamental information about the number of surface active sites, the nature of surface active sites, the decomposition temperature of surface methoxy intermediates and the quantitative TOF values for methanol oxidation for pure metal oxide catalysts. This approach has generated new insights into the catalytic properties of pure metal oxide catalysts.

2. Experimental

2.1. Catalyst synthesis

The bulk metal oxide catalysts employed in the present investigation were either purchased as high purity commercial chemicals or prepared by decomposition of their corresponding hydroxides or metal salts, as shown in table 1. The pretreatment conditions of the precursors were obtained from the *Handbook of Chemistry and Physics* [28].

2.2. BET surface area

The BET surface area of each sample was determined by nitrogen adsorption–desorption isotherms on a Quantasorb surface area analyzer (Quantachrome Corporation, model OS-9) using a 3 : 7 ratio of a N_2/He mixture. Typically, 0.2–0.3 g of sample was used for the measurement and the sample was outgassed at 250 °C prior to N_2 adsorption.

2.3. Methanol chemisorption

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) coupled with a PC for temperature and weight monitoring. A detailed flow diagram can be found in a prior publication [29]. The system allowed for a controlled flow of high purity gases: air for pretreatment, a mixture of methanol in helium for adsorption experiments and helium for temperature-programmed desorption experiments.

The following experimental procedure was employed. After being weighed and loaded into the TGA, the samples were heated *in situ* to 350 °C for 1 h in flowing air (9.5 ml/min; ultra high purity; Air Gas) and helium (80 ml/min; ultrahigh purity; Air Gas) in order to remove adsorbed moisture and possible carbonaceous residues. The pretreated catalysts were then cooled to 100 °C in flowing helium. Methanol was quantitatively adsorbed from a flowing CH_3OH/He stream (2000 ppm CH_3OH) onto the catalyst

Table 1
Bulk metal oxide catalysts.

Catalyst	Source
MgO	$MgCO_3$, calcined at 350 °C for 3 h, Aldrich
CaO	$CaCO_3$, calcined at 350 °C for 3 h, Aldrich
SrO	Alfa Aesar, 99.5%
BaO	$Ba(ClO_4)_2 \cdot 3H_2O$, calcined at 400 °C for 3 h, Aldrich
Y_2O_3	Alfa Aesar, 99.999%
La_2O_3	Alfa Aesar, 99.999%
TiO_2	Degussa P-25
ZrO_2	Degussa
HfO_2	Alfa Aesar, 99.9%
CeO_2	Engelhard
V_2O_5	NH_4VO_3, calcined at 450 °C for 3 h, Alfa Aesar
Nb_2O_5	Niobium Products Company
Ta_2O_5	H.C. Starck Company
Cr_2O_3	$Cr(OH)_3$, calcined at 450 °C for 1 h
MoO_3	$(NH_4)Mo_7O_{24} \cdot 4H_2O$ at 300 °C for 5 h, Alfa Aesar
WO_3	H_2WO_4, calcined at 400°C for 48 h, Aldrich
Mn_2O_3	$Mn(OOCCH_3)_2$, calcined at 250 °C, overnight, Alfa Aesar
Fe_2O_3	Alfa Aesar, 99+%
Co_3O_4	Aldrich
Rh_2O_3	$Rh(NO_3)_3$, calcined at 300 °C for 4 h, Johnson Mathey
NiO	$Ni(OH)_2$, calcined at 230 °C, overnight, Alfa Aesar
PdO	$Pd(NO_3)_2$, calcined at 300 °C for 4 h, Johnson Mathey
PtO	$Pt(NH_3)_4Cl_2$, calcined at 400 °C for 4 h, Johnson Mathey
CuO	$Cu(NO_3)_2 \cdot 3H_2O$, calcined at 200 °C for 48 h, Alfa Aesar
Ag_2O	Alfa Aesar, 99%
ZnO	Aldrich, 99.97%
Al_2O_3	Engelhard
Ga_2O_3	Alfa Aesar, 99.999%
In_2O_3	Alfa Aesar, 99.997%
SiO_2	Cabosil EH-5
SnO_2	Aldrich, 99%
P_2O_5	Alfa Aesar, 99.998%
Sb_2O_3	Aldrich, 99.99%
Bi_2O_3	$Bi_2(C_2O_4)_3$ at 300 °C for 3 h, Aldrich
TeO_2	H_6TeO_6, calcined at 400 °C, overnight, Alfa Aesar

at 100 °C for 1 h to obtain the weight gain. The decomposition temperature of the surface methoxy intermediates was obtained by ramping up the temperature after methanol adsorption at a constant rate of 10 °C/min and monitoring the derivative of the weight loss.

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 2000 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. Some of the pure metal oxide catalysts (CuO, Sb_2O_3, PtO, PdO, Rh_2O_3 and Ag_2O) required lower adsorption temperatures because of catalyst reduction at 100 °C.

2.4. Methanol oxidation reaction

Methanol oxidation was used to examine the catalytic reactivity and product selectivity of the metal oxide samples. The reaction was carried out in an isothermal fixed-bed differential reactor, which was held vertically and made out of pyrex glass with 6.2 mm outer diameter. About 40 mg catalyst was tested for methanol oxidation at various temperatures at atmospheric pressure. The reactant gas mixture of $CH_3OH/O_2/He$, molar ratio $\sim 6/13/81$, was used with a total flow rate of 100 ml/min. The gas feed was controlled by mass flow controllers (Brooks model 5850). Analysis of the reactor effluent was performed using an on-line gas chromatograph (HP 5890 series II) equipped with FID and TCD detectors. A carboxene-1000 packed column and a CP-sil 5CB capillary column were used in parallel for TCD and FID, respectively. The catalytic activities were obtained by integrating the peak areas of the products and calculated according to mole products per hour per m^2 of catalyst used. The selectivities are expressed in mole percent for each product and defined as the ratio between the yield of this product and that of the total methanol reacted.

2.5. Temperature-programmed reduction (TPR)

TPR was carried out with an AMI-100 system (Zeton Altamira Instruments). The catalyst sample ($\sim$50 mg) was loaded in a U-type quartz tube and pretreated at 500 °C in flowing dry air for 1 h to remove adsorbed moisture and any surface residues. After cooling down in flowing Ar to 150 °C, the Ar gas was switched to a 10% H_2/Ar gas mixture. The temperature was then ramped from 150 to 700 °C with a constant heating rate in 10% H_2/Ar with a flow rate of 30 ml/min. An on-line TCD detector was used to record the H_2 consumption.

3. Results

3.1. BET surface area measurements

The surface areas of the pure metal oxide catalysts are presented in table 2. The results reveal that the highest surface areas are of metal oxides that are typically used as supports for supported metal oxide catalysts (Al_2O_3, TiO_2, ZrO_2, SiO_2, CeO_2 and Nb_2O_5). Purchased commercial catalysts were generally of low surface area with the exception of Fe_2O_3(21 m^2/g), Ga_2O_3(18 m^2/g), Y_2O_3(27 m^2/g), and P_2O_5(15 m^2/g), which showed a comparatively high surface area.

3.2. Methanol chemisorption

The selective oxidation of methanol involves the dissociative chemisorption of methanol to form reactive surface

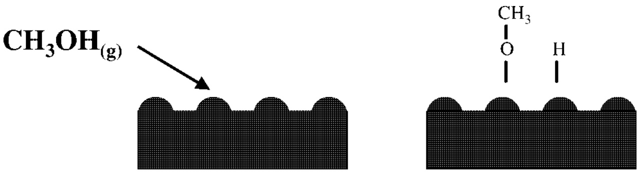
Table 2
BET surface areas.

Catalyst	Surface area (m^2/g)
MgO	23
CaO	20
SrO	6
BaO	2
Y_2O_3	17
La_2O_3	5
TiO_2	50
ZrO_2	39
HfO_2	2
CeO_2	33
V_2O_5	4
Nb_2O_5	55
Ta_2O_5	4
Cr_2O_3	21
MoO_3	3
WO_3	15
Mn_2O_3	9
Fe_2O_3	21
Co_3O_4	3
Rh_2O_3	11
NiO	43
PdO	17
PtO	2
CuO	1
Ag_2O	1
ZnO	9
Al_2O_3	180
Ga_2O_3	18
In_2O_3	3
SiO_2	300
SnO_2	8
P_2O_5	15
Sb_2O_3	0.7
Bi_2O_3	4
TeO_2	1

Table 3
Number of surface active sites at 100 °C.

Catalyst	N_s ($\mu mol/m^2$)
MgO	22.5
CaO	5.4
SrO	4.3
BaO	3.8
Y_2O_3	4.9
La_2O_3	34.1
TiO_2	3.7
ZrO_2	1.1
HfO_2	2.6
CeO_2	4.2
V_2O_5	0.7
Nb_2O_5	2.6
Ta_2O_5	4.6
Cr_2O_3	12.4
MoO_3	0.8
WO_3	2.3
Mn_2O_3	1.6
Fe_2O_3	3.7
Co_3O_4	2.8
Rh_2O_3	8.1[a] (3.5)
NiO	6.5
PdO	9.9[a] (4.3)
PtO	7.2[a] (3.1)
CuO	8.4[a] (3.6)
Ag_2O	12.0[a] (5.2)
ZnO	0.3
Al_2O_3	5.6
SiO_2	0.2
Ga_2O_3	4.1
In_2O_3	2.7
SnO_2	1.6
P_2O_5	3.6
Sb_2O_3	11.3[a] (4.9)
Bi_2O_3	2.1
TeO_2	4.1

[a] Methanol adsorption at 50 °C. Parentheses indicate values corrected for adsorption at 100 °C.



$$CH_3OH + 2S \xrightarrow{2000\ ppm,\ 100°C} CH_3O\text{---}S + H\text{---}S$$

Figure 1. Dissociative adsorption of methanol on oxide surface.

intermediates as shown in figure 1. A surface hydroxyl group is also produced upon dissociative adsorption, which desorbs by forming H_2O. Therefore, the knowledge of the amount of surface methoxy species formed during methanol chemisorption is the key for the determination of the number of surface active sites available for selective methanol oxidation. A series of pure metal oxides were examined with methanol chemisorption and the results are presented in table 3. The surface methoxy concentration is expressed as the number of accessible surface active sites per unit surface area (N_s). The number of surface methoxy species was calculated from the weight gain of the catalysts after adsorption of methanol at 100 °C, subtracting the contribution of the water molecules that are formed and desorbed during the methanol chemisorption process.

The adsorption of methanol mostly corresponds to ~3–4 CH_3O_{ads} $\mu mol/m^2$ on average. The higher N_s value for CuO, Sb_2O_3, Rh_2O_3, PdO, PtO and Ag_2O is due to the lower adsorption temperature required for these samples, 50 °C. CuO required a lower adsorption temperature because it was reduced at the typical adsorption temperature of 100 °C while Sb_2O_3 exhibited a very low surface area. Methanol chemisorption on precious metal group oxides, PtO, PdO, Rh_2O_3 and Ag_2O, was also performed at 50 °C because of the extremely reactive nature of these metal oxide surfaces at the typical adsorption temperature. A correction factor of 0.43 is obtained for metal oxides which required a lower adsorption temperature by comparing the surface active site density for Fe_2O_3 at 100 and 50 °C since methanol chemisorption at 50 °C results in both molecular and dissociatively adsorbed methanol. The corrected values of N_s for CuO, Sb_2O_3, PtO, PdO, Rh_2O_3 and Ag_2O are also presented in table 3. MgO and La_2O_3 are basic in nature and react with methanol to form carbonates and, thus, exhibit high N_s values. Pure Cr_2O_3 exhibited a somewhat higher than expected value of N_s. In table 3 it should be noted that N_s values could have a large error for low surface area materials (<3 m^2/g).

The transition metal oxide catalysts MoO_3, V_2O_5 and ZnO exhibit much lower values of N_s as compared to the average value of $\sim$3–4 μmol/m^2 suggesting that methanol does not utilize the entire exposed surface area for adsorption on these oxide catalysts. Low value of N_s for SiO_2 reflects the somewhat unreactive nature of this oxide surface. GeO_2 was also investigated, but did not adsorb methanol reflecting the extremely low surface area of the sample.

In addition to quantifying the number of surface active sites, methanol chemisorption can be extended to perform temperature-programmed desorption (TPD) studies in order to determine the decomposition temperature of the surface methoxy species. The maximum peaks in the decomposition temperatures (T_p) are obtained by plotting the derivative of the weight loss *vs*. temperature in the desorption region. The decomposition temperatures of the surface methoxy species on the various metal oxide catalysts are presented in table 4. Only those bulk metal oxide catalysts which exhibited close to 100% selectivity towards redox or acidic products are presented in table 4. The decomposition temperatures of high selectivity redox catalysts vary over a range of 240 °C with Ag_2O exhibiting the lowest surface methoxy decomposition temperature (125 °C) and TeO_2 exhibiting the highest surface methoxy decomposition temperature (366 °C). The oxides of precious metals (PdO and Ag_2O) exhibit relatively low methoxy decomposition temperatures. Among the transition metal oxides, Mn_2O_3 exhibited low decomposition temperatures. Al_2O_3 (180 °C) and Ga_2O_3 (171 °C) exhibited low decomposition temperatures and TiO_2 (380 °C) exhibited high decomposition temperature among catalysts exhibiting high selectivity to acidic products. The majority of the bulk metal oxides possess surface decomposition temperatures that fall in the range of 220–320 °C.

3.3. Methanol oxidation selectivity and turnover frequency (TOF)

Surface methoxy groups are the intermediate species in the production of partially oxygenated reaction products (formaldehyde, methyl formate, dimethoxymethane, dimethyl ether, etc.) during oxidation of methanol [26,27]. The catalytic selectivity data, obtained by on line GC analysis, are presented in figure 2. The figure shows the product distribution (redox, acidic and basic) for selective methanol oxidation over various metal oxides under differential conversions ($<10\%$). The primary redox reaction products are formaldehyde and methyl formate with dimethoxymethane produced in minimal quantities. Dimethyl ether is the acidic product and CO_2 is the basic product. CaO, La_2O_3, HfO_2, CeO_2, PdO, CuO, Ag_2O, Au_2O_3, SnO_2, Sb_2O_3 and TeO_2 exhibit 100% selectivity to redox products. Nb_2O_5, Ta_2O_5, WO_3, Al_2O_3, Ga_2O_3, and P_2O_5 exhibit 100% selectivity to dimethyl ether. Y_2O_3 and In_2O_3 are 100% selective to CO_2. MgO, SrO, BaO, ZrO_2, Cr_2O_3, Mn_2O_3, Co_3O_4, Rh_2O_3, NiO, PtO, ZnO and Bi_2O_3 yielded both redox and basic products. Among them MgO, SrO, BaO, ZrO_2, Mn_2O_3, Co_3O_4 and NiO were more selective to redox products, while Cr_2O_3, Rh_2O_3, PtO and ZnO were more selective to CO_2. TiO_2 and SiO_2 were selective to both dimethyl ether and CO_2, with TiO_2 being highly selective to dimethyl ether and SiO_2 being highly selective to CO_2. SiO_2 selectivity reflects its unreactive nature, since high temperatures are needed to achieve differential conversions, which leads to decomposition of the surface methoxy intermediate and over oxidation of the intermediate products. The transition metal oxide catalysts MoO_3 and V_2O_5 primarily yielded formaldehyde along with a minimal production of dimethyl ether. Fe_2O_3 exhibited almost equal selectivity to redox and acidic products. Ru_2O_3 and SeO_2 were also investigated and were found to completely volatilize before showing any measurable catalytic conversion of methanol. The temperatures at which these samples began to volatalize are also presented in figure 2. GeO_2 was also investigated, but it did not show

Table 4
Surface methoxy decomposition temperature (T_p).

Catalyst	Decomposition temperature (°C)
	(a) *Redox catalysts*
CaO	355
ZrO_2	326
HfO_2	278
CeO_2	300
V_2O_5	228
MoO_3	270
Mn_2O_3	165
NiO	240
PdO	138
CuO	225
Ag_2O	125
SnO_2	250
Sb_2O_3	375
TeO_2	366
	(b) *Acidic catalysts*
TiO_2	380
Nb_2O_5	308
Ta_2O_5	269
WO_3	260
Al_2O_3	180
Ga_2O_3	171
P_2O_5	250
	(c) *Average temperatures for catalysts exhibiting multiple products*
SrO	362
BaO	400
Cr_2O_3	216
Fe_2O_3	280
Co_3O_4	180
Rh_2O_3	170
PtO	60
ZnO	232
SiO_2	560
Bi_2O_3	260

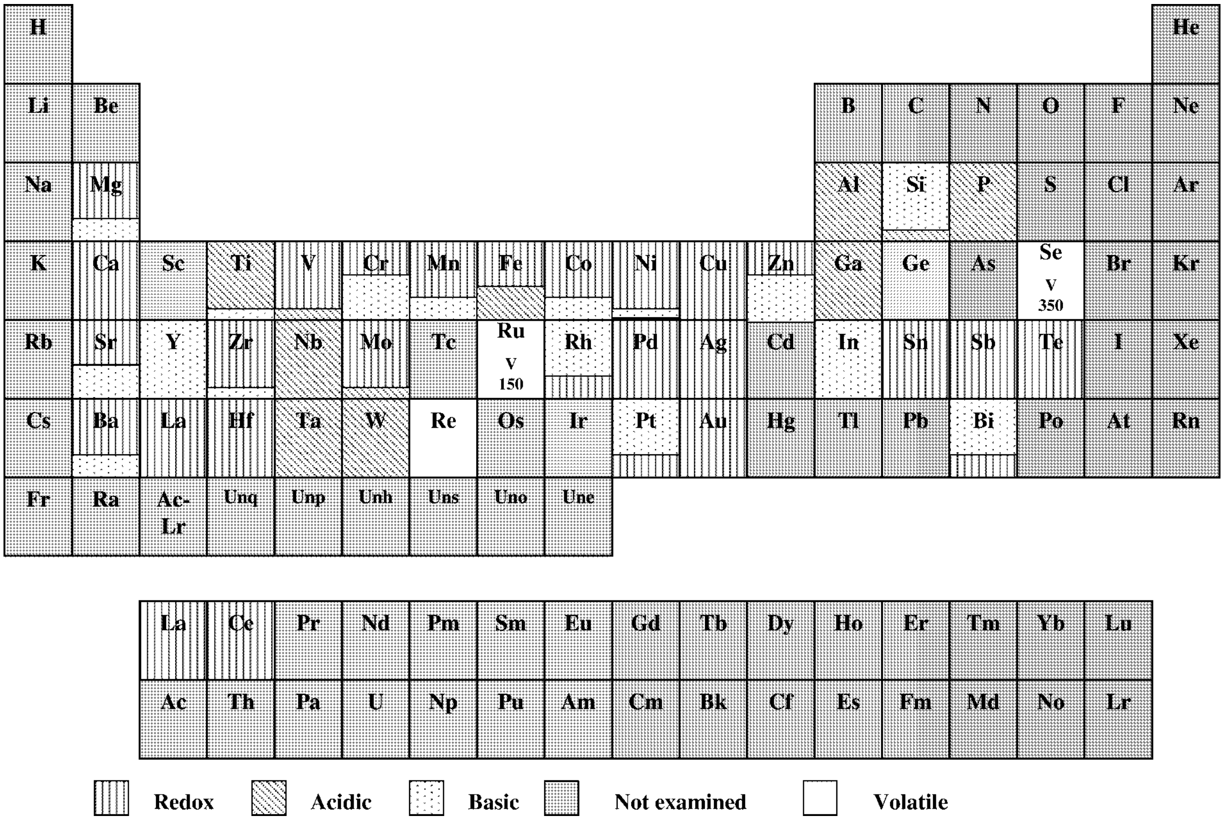


Figure 2. Methanol oxidation selectivity over pure metal oxide catalysts.

any conversion in the temperature range investigated (100–500 °C) due to the extremely low surface area of this sample.

The commonality of the surface methoxy intermediate during dissociative chemisorption of methanol and methanol oxidation on metal oxide catalysts allowed for the quantitative determination of the turnover frequency (TOF) values by normalizing the activities at 300 °C to the number of surface active sites. The well known activation energy of this reaction of ∼20 kcal/mol [27,30] was used to calculate the activity values at a common temperature of 300 °C.

As recently reviewed by Tatibouët [27], methanol oxidation can lead to the formation of various products as methanol reactions on oxide surfaces are very sensitive to the nature of surface active sites. Methanol oxidation reactions can be divided into two principal pathways: (1) reactions of oxidation that need oxygen and (2) reactions of dehydration that do not need oxygen. Except for dimethyl ether the formation for all products needs at least one oxidation step. The selectivity to dimethyl ether is attributed to the dehydration ability of the catalyst which in turn is related to its acidic character. Thus the term "methanol oxidation" refers to the network of oxidation/dehydration reactions as described in the review by Tatibouët [27] and the apparent activation energy is always close to 20 kcal/mol for methanol oxidation, whatever the catalyst.

The turnover frequencies are shown in table 5. The TOF_{redox}, TOF_{acidic} and TOF_{basic} were calculated by multiplying the overall TOF with the selectivity to redox, acidic and basic products, respectively. For comparative purposes, data from table 5 is plotted on a log scale and presented in figure 3. The results reveal that the methanol oxidation TOF values vary over seven orders of magnitude from 10^{-3} to 10^{4} s^{-1}. PtO exhibits the highest turnover frequency (3.3×10^{4} s^{-1}) and SiO_2 (1.2×10^{-3} s^{-1}) exhibits the lowest turnover frequency. The very low activity of SiO_2 has been previously reported in the literature [30,31]. The precious metal oxides, PtO (3.3×10^{4} s^{-1}), PdO (1.5×10^{2} s^{-1}), Rh_2O_3 (5.8×10^{1} s^{-1}) and Ag_2O (3.6×10^{2} s^{-1}) possess the highest turnover frequencies. Several transition metal oxide catalysts, Cr_2O_3 (8.3×10^{1} s^{-1}), Co_3O_4 (7.7×10^{1} s^{-1}) and Mn_2O_3 (3.9×10^{1} s^{-1}) also exhibit comparatively high turnover frequencies.

3.4. Temperature-programmed reduction

The TPR technique was used to probe the reducibility or oxygen availability of different metal oxide catalysts. Diluted hydrogen was used to reduce the catalysts. Similar to methanol chemisorption, hydrogen reduction of a metal oxide proceeds through dissociative adsorption of H_2, which reacts with lattice oxygen to form surface hydroxyl species. Subsequently, H_2O leaves the surface by eliminating the surface hydroxyl species. The TPR onset (threshold) temperature of the pure metal oxide catalysts, which reflects the reducibility of the sample, are shown in table 6. The initial reduction temperatures (T_{onset}) vary over 504 °C with PdO

Table 5
Methanol oxidation turnover frequencies (TOFs) at 300 °C.

Catalyst	TOF_{redox} (s^{-1})	TOF_{acidic} (s^{-1})	TOF_{basic} (s^{-1})
MgO	0.02	0	0.01
CaO	0.087	0	0
SrO	0.008	0	0.006
BaO	0.004	0	0.002
Y_2O_3	0	0	0.007
La_2O_3	0.003	0	0
TiO_2	0	0.003	0.0003
ZrO_2	0.11	0	0.018
HfO_2	0.93	0	0
CeO_2	0.14	0	0
V_2O_5	2.2	0.26	0
Nb_2O_5	0	0.02	0
Ta_2O_5	0	0.09	0
Cr_2O_3	30	0	53
MoO_3	0.42	0.07	0
WO_3	0	0.26	0
Mn_2O_3	31	0	8
Fe_2O_3	1.2	0.7	0
Co_3O_4	51	0	26
Rh_2O_3	20	0	38
NiO	4.3	0	0.46
PdO	151	0	0
PtO	9143	0	23511
CuO	5.7	0	0
Ag_2O	359	0	0
ZnO	2	0	2.4
Al_2O_3	0	1	0
Ga_2O_3	0	1.15	0
In_2O_3	0	0	0.54
SiO_2	0	0.0002	0.001
SnO_2	1.9	0	0
P_2O_5	0	0.35	0
Sb_2O_3	0.01	0	0
Bi_2O_3	1.4	0	4.5
TeO_2	0.02	0	0

Table 6
Temperature-programmed reduction (TPR) onset temperatures of bulk metal oxides.

Catalyst	T_{onset} (°C)
MgO	N.R.[a]
CaO	300
SrO	326
BaO	330
Y_2O_3	325
La_2O_3	468
TiO_2	N.R.[a]
ZrO_2	N.R.[a]
HfO_2	N.R.[a]
CeO_2	594
V_2O_5	550
Nb_2O_5	N.R.[a]
Ta_2O_5	340
Cr_2O_3	219
MoO_3	575
WO_3	544
Mn_2O_3	184
Fe_2O_3	200
Co_3O_4	288
Rh_2O_3	100
NiO	278
PdO	90
PtO	345
CuO	268
Ag_2O	200
ZnO	N.R.[a]
Al_2O_3	N.R.[a]
Ga_2O_3	320
In_2O_3	350
SiO_2	N.R.[a]
SnO_2	500
P_2O_5	N.R.[a]
Sb_2O_3	563
Bi_2O_3	400
TeO_2	355

[a] N.R.: no reduction detected between 150 and 700 °C.

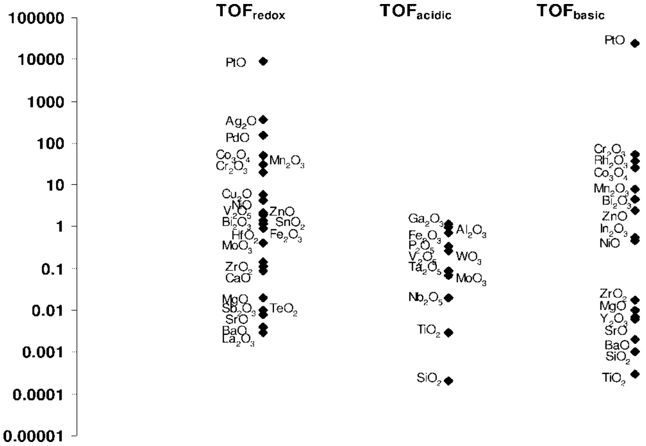


Figure 3. Semi-log plot of methanol oxidation turnover frequencies (TOFs).

showing the lowest onset temperature and CeO_2 showing the highest onset temperature. Most of the bulk metal oxides exhibited multiple peaks in their TPR profiles due to their multiple oxidation states when extensively reduced. Note, however, that only the onset reduction temperatures are reported in table 6. In addition to the bulk metal oxides presented in table 6, other samples (HfO_2, MgO, ZnO, TiO_2, Al_2O_3, SiO_2, ZrO_2, P_2O_5 and Nb_2O_5) were also investigated but no detectable H_2 consumption was observed for these oxides in the temperature range of 150–700 °C. Some of these samples (TiO_2, Al_2O_3, ZrO_2 and Nb_2O_5) probably experienced slight surface reduction because their color changed after a TPR run and the color quickly disappeared when the sample was exposed to ambient conditions.

3.5. Correlations

The extensive information obtained from methanol chemisorption (number of surface active sites (N_s) and the decomposition temperature of surface methoxy intermediates), methanol oxidation (reactivity and product distribution) and the combination of both of these techniques (TOF values) is correlated with other catalytic parameters to elucidate fundamental insights about these catalytic bulk metal oxides. Special emphasis is placed on correlating the TOF_{redox} values because of the commercial importance of such catalysts for the selective oxidation of methanol.

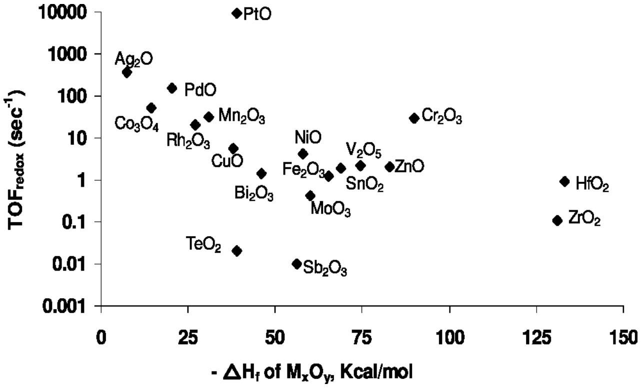


Figure 4. Semi-log plot of TOF_{redox} *vs.* heat of formation of bulk metal oxide catalysts.

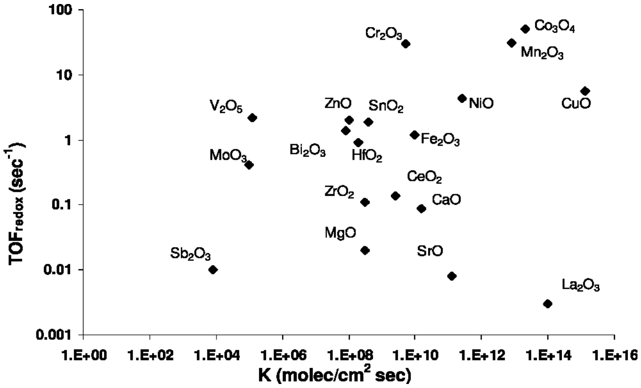


Figure 5. Log–log plot of TOF_{redox} *vs.* isotopic dioxygen exchange rate constant.

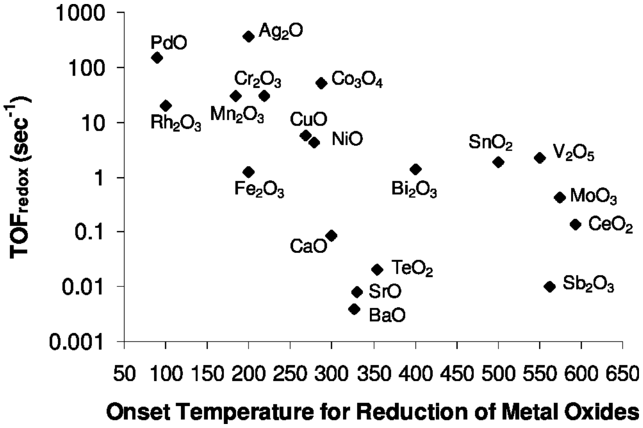


Figure 6. Semi-log plot of TOF_{redox} *vs.* onset temperature for reduction of metal oxides.

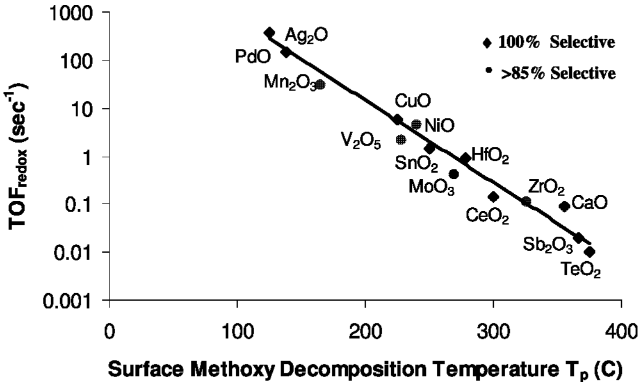


Figure 7. Semi-log plot of TOF_{redox} *vs.* surface methoxy decomposition temperature.

3.5.1. Turnover frequency correlations

Methanol oxidation turnover frequency is plotted against the enthalpies of formation of bulk metal oxides (M_xO_y) normalized per mole of oxygen atom in figure 4, and the TOF_{redox} does not appear to correlate with the bulk metal–oxygen bond strength. The TOF_{redox} is also plotted against the isotopic dioxygen exchange rate constant K (molecules/cm^2 s) for various metal oxide catalysts in figure 5 and no correlation appears to be obtained. Essentially the same results are obtained if TOF_{redox} is replaced by methanol oxidation activity (mol/cm^2 s). The isotopic oxygen exchange rate constants for the various metal oxide catalysts were obtained by Boreskov [32] at a common temperature of 300 °C and were normalized to the surface area of the sample. No relationship was found between the TOF_{redox} and the onset TPR temperature obtained from H_2 temperature-programmed reduction over the bulk metal oxide catalysts, as shown in figure 6. Obviously, only those bulk metal oxides that exhibited detectable H_2 consumption can be included in this figure.

Strong inverse relationship was found between the methanol oxidation TOF_{redox} values and the decomposition temperature of the surface methoxy intermediate obtained from methanol chemisorption/TPD experiments, as shown in figure 7. Only those bulk metal oxide catalysts, which exhibited close to 100% selectivity towards redox products, are shown in figure 7. A similar inverse relationship was found for TOF_{acidic} *vs.* surface methoxy decomposition temperature. The inverse relationships were obtained by curve fitting a linear best-fit solution. For the plot of TOF_{redox} *vs.* surface methoxy decomposition temperature the regression error was less than 2% and for the plot of TOF_{acidic} *vs.* surface methoxy decomposition temperature the regression error was less than 5%.

3.5.2. Methanol oxidation selectivity correlations

The methanol oxidation selectivity to redox products was plotted against TOF_{redox} and the isotopic dioxygen exchange rate constant (K), but no apparent correlations were obtained between these parameters, as shown in figures 8 and 9, respectively.

4. Discussion

It has previously been shown by *in situ* Raman spectroscopy that during the oxidation of methanol, the surfaces of Rh, Pd, and Pt metals remain oxidized as Rh_2O_3, PdO, and PtO, respectively [33–35]. A similar finding was reported for *in situ* Raman spectroscopy studies performed during the oxidation of methanol over polycrys-

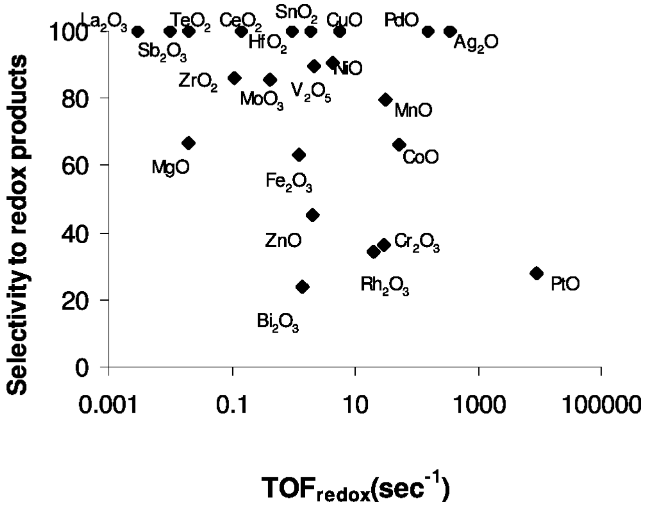


Figure 8. Semi-log plot of selectivity to redox products *vs.* $\mathrm{TOF_{redox}}$.

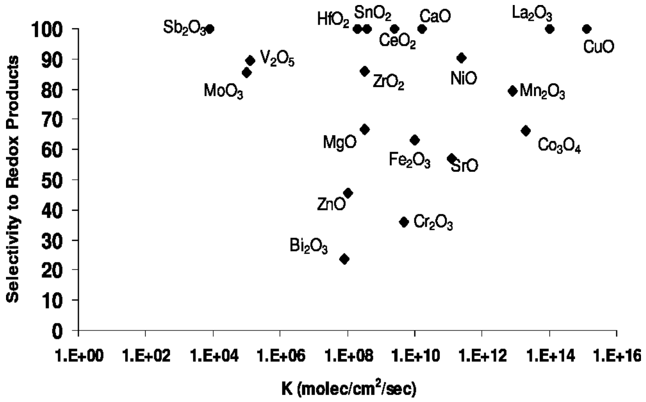


Figure 9. Semi-log plot of selectivity to redox products *vs.* isotopic dioxygen exchange rate constant.

talline Ag [36] and for X-ray absorption spectroscopy of methanol oxidation over Cu [37,38]. Analogous *in situ* Raman observations were also made with V_2O_5 and MoO_3 during methanol oxidation [39]. Based on these observations the results presented above have both qualitative and quantitative implications for the development of fundamental structure–reactivity relationships about methanol oxidation over bulk metal oxide catalysts. Quantitatively, methanol chemisorption provides the number of surface active sites for bulk metal oxide catalysts. During methanol oxidation not all the exposed surface sites present on the bulk metal oxide can simultaneously participate in the surface reaction due to steric interactions. The maximum number of surface sites on which methanol can chemisorb are defined as the active surface sites and they need to be quantified for determining the TOF values for methanol oxidation. Unlike the model supported metal oxide catalysts, where the total number of deposited metal atoms present in the two-dimensional metal oxide overlayer are taken as the number of surface active sites [14], the number of surface active sites for bulk metal oxide catalysts are not known in advance. Thus, the most significant advantage of redefining TOF according to the methanol chemisorption surface site densities is that TOF values may now be calculated and compared for different bulk metal oxide catalysts. Comparison of the number of active surface sites for bulk metal oxide catalysts gives very similar adsorption surface site densities for most of the catalysts, generally ~3–4 μmol $\mathrm{CH_3O_{ads}/m^2}$ on average as shown in table 3, which reflects the very similar adsorption stoichiometries for these different bulk metal oxide catalyst systems.

Qualitatively, methanol chemisorption also provides information about bulk metal oxide catalyst morphology. Isotropic metal oxides possess ~3–4 μmol/m^2 of surface active sites on average and methanol utilizes the entire exposed surface area for adsorption. Anisotropic metal oxides possess ~0.6 μmol/m^2 of active sites on average. The low N_s value reflects the platlet morphology of these anisotropic catalysts and the preferential adsorption of methanol on the edge sites [21]. Bulk MoO_3, V_2O_5, and ZnO exhibit anisotropic morphology, as shown by their relatively low N_s values in table 3. The remaining metal oxides exhibit isotropic morphology, with the exception of SiO_2 because of its low surface reactivity.

Methanol oxidation over bulk metal oxide catalysts yielded redox (formaldehyde, methyl formate and dimethoxymethane), acidic (dimethyl ether) and basic (CO_2) products and the selectivities to different products are illustrated for each metal oxide in figure 2. The product distribution under differential conversions reflects the nature of the surface active sites on oxide catalysts since secondary reactions are minimized and redox sites oxidatively dehydrogenate to yield formaldehyde, basic sites yield CO_2 and Lewis and Brønsted sites lead to dehydration of the oxidized carbon species to yield dimethyl ether [27].

The majority of the bulk metal oxide catalysts (MgO, CaO, SrO, BaO, La_2O_3, CeO_2, ZrO_2, HfO_2, V_2O_5, MoO_3, Mn_2O_3, Fe_2O_3, Co_3O_4, NiO, PdO, CuO, Ag_2O, Au_2O_3, SnO_2, Sb_2O_3 and TeO_2) primarily yield redox products. Some of the bulk metal oxides such as Nb_2O_5, Ta_2O_5, WO_3, Al_2O_3, Ga_2O_3, and P_2O_5 are known to possess significant Lewis acidity and, thus, yield only dimethyl ether. Similar results have been obtained in previous studies with Al_2O_3 [30,40,41] and Nb_2O_5 [42]. Y_2O_3 and In_2O_3 were highly selective to CO_2 reflecting that the surface active sites of these oxide catalysts are dominated by basic surface sites. SrO, BaO, Cr_2O_3, Rh_2O_3, PtO, ZnO, and Bi_2O_3 also exhibit high selectivity to CO_2 and agree well with previous studies on Bi_2O_3 [43,44], MgO [31] and ZnO [45,46]. Group IIA metal oxides (MgO, CaO, SrO and BaO), though known to be basic in nature, also yield redox products indicating the use of adsorbed oxygen as surface active sites for methanol oxidation on these metal oxide catalysts. No apparent trend is observed in the nature of the surface active sites as function of position in the periodic table (from left to right or top to bottom).

The methanol oxidation TOF ($\mathrm{TOF_{redox}}$, $\mathrm{TOF_{acidic}}$ and $\mathrm{TOF_{basic}}$) values were calculated by determining the production rates of redox, acidic and basic products at 300 °C and normalizing the rates to the total number of surface sites available for adsorption of CH_3O_{ads} (N_s) at 100 °C (see table 5). For those metal oxides that possessed more than one type of surface site (redox, acidic or basic), it was not possible to determine the corresponding fractions. However, this correction would only result in a minor change in TOF values since the catalytic activities varied by a factor of $\sim 10^7$. Comparison of the methanol oxidation TOF values at 300 °C reveals that they vary over seven orders of magnitude from 10^{-3} to 10^4 s^{-1}, as shown in figure 3.

Previous studies [47,48] have qualitatively compared the acid and base properties of bulk metal oxide catalysts by performing oxidation reactions on a wide variety of acid–base reactants (olefinic and aromatic hydrocarbons, alcohols, carboxylic acids and phenol) and comparing the relative activities of various bulk metal oxide catalysts for these reactions, but this is the first example in the catalysis literature where the TOF values of bulk metal oxide catalysts have been quantitatively compared. The present data are consistent with the studies of Ai [47] with the exception of SnO_2, which demonstrates 100% selectivity to redox products under differential conversions. Both studies concluded that Cr_2O_3, Co_3O_4, Mn_2O_3, Bi_2O_3, ZnO and NiO exhibit significant basic characteristics and Fe_2O_3, V_2O_5, WO_3 and MoO_3 exhibit significant acidic properties. Even though bulk V_2O_5 exhibits a low selectivity for acidic products (figure 2), its TOF_{acidic} value is equivalent to the TOF_{acidic} value of WO_3 which is 100% selective to acidic products, reflecting the much higher acidic activity of bulk V_2O_5 compared to bulk WO_3. The data in figure 3 also reveal that the magnitude of the TOF values of redox and basic products are comparable and much larger than the TOF values of acidic products (*i.e.*, $TOF_{redox} \approx TOF_{basic} \gg TOF_{acidic}$) when methanol oxidation is employed as the probe reaction. This suggests that the redox and basic sites are much more active than the acidic sites present on the surface of various metal oxides, even though they might contain comparable surface active site densities (N_s).

It is generally acknowledged that the catalytic oxidative dehydrogenation of methanol to oxidation products occurs *via* the Mars–van Krevelen mechanism [26,27,49–51]. According to the kinetic pathways reported in the literature, methanol first dissociatively chemisorbs as a surface methoxy intermediate and a surface hydroxyl on an active site. The surface methoxy intermediate subsequently decomposes into gas phase formaldehyde and another surface hydroxyl. To complete the catalytic cycle, the surface hydroxyls then recombine and desorb as water; this step also extracts an oxygen anion from the catalyst that is reoxidized by a "pool" of bulk or adsorbed oxygen atoms supplied by excess oxygen in gas phase.

Kinetic isotope studies have demonstrated that for methanol oxidation, the surface decomposition of the adsorbed methoxy intermediate is the rate-determining step [52]. In addition, Holstein and Michaels have empirically verified that the methanol oxidation reaction is first-order in methanol partial pressure and zero-order in O_2 partial pressure [26]. The overall rate of reaction is given as

$$\mathrm{TOF} = \frac{k_{\mathrm{rds}} K_{\mathrm{methanol}} P_{\mathrm{CH_3OH}}}{K_{\mathrm{H_2O}}^{1/2} P_{\mathrm{H_2O}}^{1/2}}, \tag{1}$$

where k_{rds} is the rate constant for the rate-determining surface decomposition step of the surface methoxy intermediate, which involves breaking a C–H bond, $K_{methanol}$ is the methanol equilibrium adsorption constant and K_{H_2O} is the water equilibrium adsorption constant. A simplification can be made for single-pass reactors at low methanol conversions (below 10%), without significant water in feed stream, in which the water dependence is pseudo zero-order. Under these conditions, the expression for the overall rate of reaction reduces to

$$\mathrm{TOF} = k_{\mathrm{overall}} P_{\mathrm{CH_3OH}}, \tag{2}$$

where $k_{overall} = k_{rds} K_{ads}$ and K_{ads} is the methanol adsorption equilibrium constant.

The valuable information obtained from the combination of the methanol chemisorption and the methanol oxidation techniques, N_s and TOF values, is further analyzed by correlating it with other catalytic parameters that may elucidate additional fundamental insights about these bulk metal oxides for redox reactions. The absence of any apparent relationship between the TOF_{redox} and the bulk metal–oxygen bond strength, as shown in figure 4, is not suprising since TOF_{redox} is a *surface* catalytic parameter, defined as the number of molecules converted per second per active surface metal oxide site [1], whereas the metal–oxygen bond strength is a *bulk* property. Thus, the random scatter of the data points reflects the inappropriateness of attempting to correlate a *surface* catalytic parameter with a *bulk* catalyst property.

To probe deeper into the fundamental catalytic properties of bulk metal oxides, an attempt was made to correlate methanol oxidation TOF_{redox} with the isotopic dioxygen exchange rate constant K (molecules/cm^2 s). The absence of a relationship between TOF_{redox} and isotopic dioxygen exchange rate constant (see figure 5) is consistent with the methanol oxidation reaction mechanism. The isotopic dioxygen exchange rate constant is a surface catalytic parameter and is defined as the total number of exchanging molecules per unit surface per unit time [32] and is a measure of the exchange between between gas phase oxygen and surface oxygen atoms of bulk metal oxide catalysts, whereas the TOF_{redox} is dependent on the rate-determining surface decomposition of the surface methoxy intermediate that involves breaking of a C–H bond. Hence, the TOF_{redox} and the isotopic dioxygen exchange rate constants represent different surface steps in the catalytic oxidation of methanol and should not be expected to correlate with each other.

Furthermore, previous studies [25] have shown that at methanol oxidation reaction temperatures of ~300 °C, the fractional surface coverage (θ_{OCH_3}) of adsorbed methoxy intermediates corresponds to about 0.1–0.2. This suggests that the surface of metal oxide catalyst is not starved of oxygen, and thus, is not dependent on the exchange with gas phase oxygen (kinetics are zero-order in the oxygen partial pressure). Note, however, that the dioxygen exchange rate constant values would be expected to be comparatively higher during methanol oxidation than those reported in the literature in the absence of a reducing component [32] because the number of oxygen vacancies should be greater in the presence of methanol.

H_2 temperature-programmed reduction (TPR) is a characterization technique extensively used for metal oxides and reflects the ease of reduction or oxygen removal from the catalyst [53]. The absence of any strong correlation (see figure 6) between the TOF_{redox} and the TPR onset temperatures for the bulk metal oxide catalysts is not too suprising since a different probe molecule, H_2, than the actual reactant, CH_3OH, is employed for H_2-TPR. In addition, the rate-determining step in H_2-TPR may be either dissociative adsorption of molecular H_2 or recombination of surface hydroxyls to form H_2O, and may vary with the specific metal oxide catalyst. Furthermore, the rate-determining step during methanol oxidation involves breaking the C–H bond of the surface methoxy intermediate rather than extracting an oxygen atom from the metal oxide catalyst.

The TOF_{redox} values were also plotted against the surface methoxy decomposition temperatures obtained from the TPD studies. This removed the major limitation of H_2-TPR since the same probe molecule as the actual reactant is used in both methanol oxidation and TPD studies of the decomposition of adsorbed surface methoxy intermediates. In addition, both the methanol oxidation and the TPD studies proceed via the same surface reaction mechanism (surface decomposition of adsorbed methoxy intermediates) and rate-determining step. An inverse correlation is obtained between the methanol oxidation TOF_{redox} values and the decomposition temperatures of the surface methoxy intermediates as shown in figure 7. This suggests that the adsorption or formation of the surface methoxy intermediates is not rate-determining and only the thermal stability of surface methoxy intermediates is kinetically significant. This is also consistent with the kinetic isotope studies that have demonstrated that surface decomposition of the adsorbed methoxy intermediate is the rate-determining step during methanol oxidation [52]. In addition, previous studies for methanol oxidation over supported vanadium oxide and molybdenum oxide catalysts [25] have demonstrated that the methanol adsorption equilibrium constant, K_{ads}, is relatively constant for significantly different surface methoxy decomposition constants (k_{rds}). Only those bulk metal oxide catalysts that exhibit high selectivities (>85%) towards redox products are shown in figure 7. Bulk metal oxides which exhibit bifunctional catalytic surfaces (*i.e.*, a combination of redox, acidic and basic) are not included since it is difficult to differentiate the overlap of surface methoxy decomposition temperatures towards different reaction products in the current thermal-gravimetric apparatus.

The data presented in figure 7 demonstrate that only the right-hand side of the classic volcano plot [54] is obtained when TOF_{redox} is plotted against the surface methoxy decomposition temperatures. A similar correlation has been found in support of only the right-hand side of the volcano plot by considering the thermal stability of surface formate and methoxide intermediates on group IB and group VIII metals as represented by the peak temperatures in TPD experiments [55]. According to Barteau, volcano plot behavior is likely to be exhibited within any family of metals, but might not hold for jumps across columns of the periodic table.

Analogous to the mechanism of methanol oxidation over metal oxides is the decomposition of formic acid over metals which has long been a common test reaction for examining the activity of metal catalysts. In fact, the variation of the activity of transition metals for this reaction forms the basis for perhaps the best-known example of a "Balandin volcano plot" illustrating Sabatier's principle of the optimum instability of catalytic intermediates [54]. The conventional interpretation of Balandin volcano plot suggests that there is a shift in the rate-determining step as one crosses the peak; the rate-determining step on the "left-hand" side is related to the formation of the surface intermediate and the rate-determining step on the "right-hand" side is the decomposition of that surface intermediate. While this interpretation is likely to be correct for surface reactions where adsorption of probe molecules on the catalyst surface is an activated process, it may not hold for surface reactions where adsorption is relatively easy and the decomposition of surface intermediate is the rate-determining step.

The methanol oxidation selectivity to redox products is also plotted against the TOF_{redox} and the isotopic dioxygen exchange rate constant, as shown in figures 8 and 9, respectively. According to literature models [56,57], the selectivity in Mars–van Krevelen oxidation reactions should be associated with oxygen mobility and the intrinsic activity of individual oxygen species. High oxygen mobility should result in abstraction of many hydrogen atoms from the hydrocarbon leading to breaking of C–C bonds and, consequently, to over-oxidation and low selectivity. The absence of any apparent correlations between selectivity and oxygen mobility for oxidative dehydrogenation of methanol in figures 8 and 9 suggests that the redox selectivity is primarily associated with the nature of the specific surface metal oxide active sites and is independent of the intrinsic activity and oxygen mobility of that sample. Bulk metal oxide catalysts that exhibit high selectivity to redox products are dominated by redox surface active sites on these samples. Furthermore, figure 9 demonstrates that bulk metal oxides exhibiting high oxygen mobility can also be highly selective to redox products.

In the field of partial oxidation catalysis, a variety of multi-component oxides, containing a combination of two or more kinds of metal oxides, are typically employed as practical catalysts. The fundamental information presented above employing methanol as a chemical probe molecule should assist in the design of improved mixed metal oxide catalysts for selective oxidation reactions [58].

5. Conclusions

Methanol chemisorption was successfully developed to quantify the number of surface active sites in bulk metal oxide catalysts and provide information about the bulk metal oxide catalyst morphology. Isotropic metal oxides were found to possess $\sim$3–4 μmol/m^2 of surface active sites on average and anisotropic metal oxides possessed $\sim$0.6 μmol/m^2 of surface active sites on average. Most of the bulk metal oxide catalysts exhibited isotropic morphology except for bulk MoO_3, V_2O_5 and ZnO, which exhibited anisotropic morphology. Furthermore, the methanol oxidation product distribution at low conversions reflected the nature of the surface active sites on metal oxides since redox sites primarily yield H_2CO, acidic sites yield CH_3OCH_3 and basic sites yield CO_2. The distribution of the different types of surface active sites was found to vary widely for the different metal oxide catalysts. The commonality of the surface methoxy intermediate during dissociative chemisorption of methanol and methanol oxidation on metal oxide catalysts as well as the knowledge of the number of surface active sites enabled the calculation of catalytic activity per surface active site (TOF) during methanol oxidation. These calculations, for the first time, allowed for direct comparison of the intrinsic TOFs over a wide range of bulk metal oxide catalysts. The TOF values for the various metal oxide catalysts were found to vary over seven orders of magnitude (10^{-3} to 10^4 s^{-1}). The variation in TOF was not related to metal–oxygen bond strength, isotopic dioxygen exchange rate constant or the H_2-TPR onset reduction temperature, but was inversely related to the decomposition temperature of the surface methoxy intermediate because the decomposition of the surface methoxy intermediates is the rate-determining step during these reactions. The fundamental information obtained by employing methanol as a "smart" chemical probe molecule will hopefully assist in the design of improved mixed metal oxide catalysts for selective oxidation reactions.

Acknowledgement

The authors are grateful to Laura Briand for her invaluable assistance in the study and the United States Department of Energy–Basic Energy Sciences for financial support (grant # DEFG02-93ER14350).

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