

## RESEARCH NOTE

## Reactant-Probe Method for Estimating Active Site Number in Catalysts

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The number of surface sites on catalysts can be measured by well-established chemisorption techniques employing small molecules or by a reactant-probe method utilizing the actual reacting species in a catalytic reaction. The latter approach gives the advantage of directly titrating the actual reactive sites on the surface and has been demonstrated in a number of systems. An example is given for the case of manganese oxide supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub>, which are good catalysts for the decomposition of ozone. Reasonable correspondence is found between oxygen chemisorption and temperature-programmed desorption of adsorbed ozone species, but the latter is better able to account for dual sites found on the ZrO<sub>2</sub> support. © 2001 Elsevier Science

Estimation of the number of active sites on a catalyst surface is a central problem in catalysis, as it permits the calculation of turnover rates and the comparison of catalytic activity of different catalysts for the same reaction (1). In this work we describe and compare two methods for counting active sites on supported manganese oxide, a chemisorption technique and a reactant-probe method.

In the case of metals, the number of surface atoms is obtained by chemisorption of gases like H<sub>2</sub>, NO, or CO (2, 3), or is estimated from the size of metal clusters determined by physical techniques like transmission electron spectroscopy. When metal loading is very low (4) or in the case of bimetallic alloys (5), the percentage metal exposed can also be obtained by measuring the specific rate of two structure-insensitive reactions. In the case of nonmetals a plethora of techniques have also been developed to estimate the number of surface sites. Many rely on chemisorption of small probe molecules, as exemplified by O<sub>2</sub> (6) or NH<sub>3</sub> (7) on oxides, O<sub>2</sub> (8, 9) or NO (10) on sulfides, and CO or O<sub>2</sub> on carbides (11).

The probe molecules used in standard chemisorption measurements are typically unrelated to the reaction to be catalyzed on the active surface. They are generally employed for convenience and are nondiscriminating in the

sense that they ideally measure all surface atoms. Furthermore, the conditions of adsorption are usually far from those of reaction. An alternative to the use of these molecules is the employment as a probe of the actual reactant that will be tested in the catalytic reaction. This is what is referred to as the *reactant-probe method* in this paper. There are a number of examples of this in the literature. Nitrogen has been used for the ammonia synthesis reaction on iron (12), methanol for methanol oxidation on supported oxides (13), and ethylamine for hydrodenitrogenation on sulfides and carbides (14). In this work we explore the use of ozone for supported manganese oxides used in ozone decomposition. There have been detailed studies on the mechanism of the decomposition in this system (15) using *in situ* laser Raman spectroscopy (16, 17). In this study we develop techniques to measure surface Mn sites based on high-temperature oxygen chemisorption and the reactant-probe method.

## HIGH-TEMPERATURE CHEMISORPTION

The standard chemisorption technique employed here to measure the number of surface manganese oxide sites on these supported catalysts is based on oxygen adsorption. The methodology has been described earlier by our laboratory for supported molybdenum oxide catalysts (18). The procedure involved carrying out oxygen chemisorption on the catalyst sample after pre-reduction at an elevated temperature. This elevated temperature, designated as  $T_{red}$ , occurs just prior to bulk catalyst reduction, and is determined using a temperature-programmed reduction (TPR) technique.

The preparation, characterization, and ozone decomposition reactivity of the supported manganese oxide catalysts used here are reported elsewhere (19, 20). Briefly, the catalysts (3 wt% loading) were prepared by incipient wetness impregnation of aqueous solutions of manganese acetate (Mn(CH<sub>3</sub>COO)<sub>2</sub> · 4H<sub>2</sub>O, Aldrich > 99.99%) on Al<sub>2</sub>O<sub>3</sub> (Degussa, Aluminum oxide C), ZrO<sub>2</sub> (Degussa, VP ZrO<sub>2</sub>),

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TiO<sub>2</sub> (Degussa, Titanoxid P25), and SiO<sub>2</sub> (Cabosil, L-90). The resulting samples were dried at 393 K for 6 h and calcined at 773 K for 6 h, both in air. The catalysts did not show any X-ray diffraction patterns for bulk manganese oxide phases, and probably consisted of manganese oxide oligomeric species deposited on the support. Surface area and dispersion values are reported in Table 1.

The system used to measure oxygen chemisorption was a standard flow adsorption system using a computer interfaced mass spectrometer (Dycor/Ametek Model MA100) (18). The TPR experimental procedure typically involved pretreatment of the sample at 773 K for 2 hours in O<sub>2</sub> flow (Air Products > 99.6%) to remove accumulated moisture and other impurities. The reduction temperature of the bulk catalyst was determined by reducing the sample in H<sub>2</sub> flow (Air Products > 99.6%) from room temperature to 1073 K at a heating rate of 10 K/min. The mass spectrometer signal ( $m/e = 18$ ) corresponding to H<sub>2</sub>O<sup>+</sup> was monitored during the reduction process. The onset of bulk reduction ( $T_{\text{red}}$ ) was the temperature at which the intensity of this signal increased dramatically.

Figure 1 shows the H<sub>2</sub>O ( $m/e = 18$ ) TPR traces for the various samples. In all cases the traces showed a sharp increase at a given temperature ( $T_{\text{red}}$ ) followed by additional features at higher temperature, which were sometimes accompanied by a shift in baseline. For MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (Fig. 1a)  $T_{\text{red}}$  was at 623 K, for MnO<sub>x</sub>/ZrO<sub>2</sub> catalyst (Fig. 1b)  $T_{\text{red}}$  was at 558 K, for MnO<sub>x</sub>/TiO<sub>2</sub> (Fig. 1c)  $T_{\text{red}}$  was at 523 K, and for MnO<sub>x</sub>/SiO<sub>2</sub>  $T_{\text{red}}$  was at 498 K. The H<sub>2</sub>O signals are an indication of bulk reduction of manganese oxide. This is in agreement with the limited results already reported in the literature; for example, in the case of MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, it was concluded that greater interaction with the support led to a larger bulk reduction temperature. Blank runs (not shown) indicated very little contribution from the supports.

The point at which bulk reduction begins,  $T_{\text{red}}$ , for our catalysts, follows the trend Al<sub>2</sub>O<sub>3</sub> > ZrO<sub>2</sub> > TiO<sub>2</sub> > SiO<sub>2</sub>. This trend agrees with the trend for the pH at the point of zero charge (PZC) for the various supports (21), where

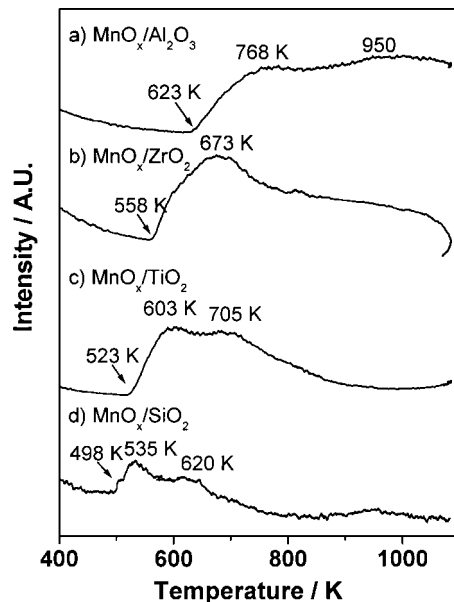


FIG. 1. TPR traces (H<sub>2</sub>O,  $m/e = 18$ ) for supported manganese oxide: (a) MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, (b) MnO<sub>x</sub>/ZrO<sub>2</sub>, (c) MnO<sub>x</sub>/TiO<sub>2</sub>, (d) MnO<sub>x</sub>/SiO<sub>2</sub>.

the strongest interaction is expected between the Al<sub>2</sub>O<sub>3</sub> and the acidic manganese acetate solution. Since the oxidation state of manganese is the lowest for MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (19), it can be deduced that greater interaction with the support leads to a lower oxidation state and larger bulk reduction temperature for the supported manganese oxides.

The temperature right before the onset of bulk reduction ( $T_{\text{red}}$ ) was the temperature at which the oxygen chemisorption experiments were performed. The procedure involved pretreatment of the sample at 773 K for 2 h in O<sub>2</sub> flow (air products > 99.6%) followed by the reduction of the sample in H<sub>2</sub> flow (air products > 99.6%) at  $T_{\text{red}}$  for 2 h. Following reduction, the oxygen uptake was measured using a standard pulse technique. The results are shown in Table 1.

## THE REACTANT-PROBE METHOD

As an alternative to the chemisorption method, the number of active sites was also estimated using a reactant-probe technique. The procedure was developed specifically to measure active sites for the ozone decomposition reaction for which the catalysts are very active (22). The technique involved measuring the temperature-programmed desorption (TPD) traces (for oxygen) taken from the catalysts after ozone adsorption (the reactant) at low temperature. Quantifying the amount of these adsorbed oxygen species gave a direct estimate of the number of active sites involved in the reaction. The two methods are compared to confirm the validity of the obtained site densities.

TABLE 1

Comparison of Active Site Density Estimates

Catalyst	$S_g$ (m <sup>2</sup> g <sup>-1</sup> )	$T_{\text{red}}$ (K)	Oxygen		
			chemisorption ( $\mu\text{mol g}^{-1}$ )	Ozone TPD ( $\mu\text{mol g}^{-1}$ )	Dispersion (%)
MnO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	92	623	44	40	12
MnO <sub>x</sub> /ZrO <sub>2</sub>	45	558	87	81 <sup>b</sup>	24 <sup>b</sup>
MnO <sub>x</sub> /TiO <sub>2</sub>	47	523	28	31	8.6
MnO <sub>x</sub> /SiO <sub>2</sub>	88	498	17 <sup>a</sup>	13	4.3

<sup>a</sup> Measured at 483 K.

<sup>b</sup> Values shown are for only one TPD desorption peak (see Fig. 2). The total number of sites is better given as 163  $\mu\text{mol g}^{-1}$ , counting both TPD peaks, giving a dispersion of 49%.

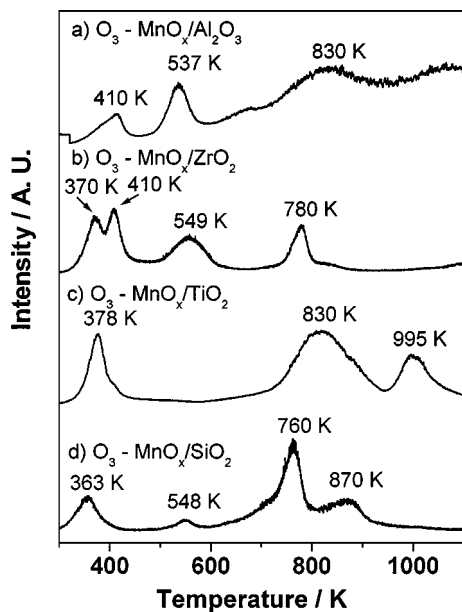
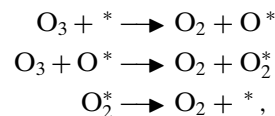


FIG. 2. Ozone TPD traces ( $O_2$ ,  $m/e = 32$ ) for supported manganese oxide: (a)  $MnO_x/Al_2O_3$ , (b)  $MnO_x/ZrO_2$ , (c)  $MnO_x/TiO_2$ , (d)  $MnO_x/SiO_2$ .

The oxygen TPD experiments were conducted in a flow apparatus equipped with a computer-interfaced mass spectrometer (Dycor/Ametek Model MA100) (18). The catalyst (0.9 g) was pretreated in oxygen (air products, Grade 2.6) flow for 2 h, cooled to 233 K using an isopropanol-liquid nitrogen gel mixture, and exposed for 2 h to a 2 mol%  $O_3/O_2$  mixture produced by a generator (OREC, V5-0). The temperature-programmed desorption was carried out in helium (air products, Grade 5.0) flow by heating the sample to 1273 K at  $0.17\text{ K s}^{-1}$  while monitoring the  $m/e$  signals 16 ( $O$ ), 32 ( $O_2$ ), and 48 ( $O_3$ ). Finally, the sample was cooled down to room temperature and pulses of oxygen from a calibrated volume ( $39\text{ }\mu\text{mol}$ ) were injected in order to quantitate the peaks corresponding to the adsorbed species. These measured values provided the site densities (sites/g catalyst).

The TPD results after ozone adsorption are shown in Fig. 2. The peaks correspond to molecular oxygen desorption as no ozone desorption was ever detected. Blank experiments (not shown) demonstrated that the high temperature peaks (above 700 K) were all due to the supports. The low (below 450 K) and intermediate (500–600 K) temperature peaks were due to adsorbed oxygen species derived from ozone. From *in situ* Raman measurements the low temperature peaks could be assigned to adsorbed peroxide intermediates ( $O_2^{2-}$ ) with vibrational frequency  $878\text{--}884\text{ cm}^{-1}$  (16, 19, 20). The  $MnO_x/ZrO_2$  sample alone had two types of peroxide groups (20), consistent with the TPD results. The intermediate temperature peaks could be assigned to adsorbed atomic oxygen species ( $O^{2-}$ ), with a slightly higher vibrational frequency (20).

Previous work (16, 17, 20) indicated that the ozone decomposition reaction proceeds by the sequence



where \* represents surface sites. The kinetics indicate that  $O_2^*$  is the most abundant surface species, and that the low temperature of adsorption used here (233 K) results in saturation and titration of the majority of sites.

Table 1 presents a comparison of the manganese active site values for the catalysts, obtained using the oxygen chemisorption and ozone TPD methods. There is general agreement between the methods. In the case of  $MnO_x/SiO_2$  the chemisorption technique was applied at 483 K not 498 K as indicated by  $T_{red}$  from the TPR measurement. This was because the Mn in this case was not as well dispersed as in the other samples and some bulk reduction and reoxidation were likely to occur if reduction was carried out at 498 K.

In the case of  $MnO_x/ZrO_2$  the chemisorption value was  $87\text{ }\mu\text{mol g}^{-1}$  while the correct TPD value was  $183\text{ }\mu\text{mol g}^{-1}$  when counting the two TPD peaks observed (Fig. 2). The oxygen chemisorption measurement in the case of the  $MnO_x/ZrO_2$  was likely probing only the manganese sites involved in the reaction. The TPD measurements (Fig. 2) indicate the presence of two distinct adsorbed species, suggesting the presence of a second site possibly due to a manganese support interaction (20). These could be Mn–O–Zr sites. It was therefore likely that the TPD method in this case was probing sites that were not counted by the oxygen chemisorption technique.

Because studies of the mechanism indicate that both sites are important in the ozone decomposition reaction (20), it is concluded that the reactant-probe method gives a better estimate of the total active sites involved in the ozone decomposition reaction because it measures the actual reacting species. Nevertheless, the chemisorption technique gives the right order of magnitude for the active sites and could be used as a preliminary estimate of their number.

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