Differentiation of active oxygen species for butane oxidation on vanadyl pyrophosphate

Daxiang Wang and Mark A. Barteau*

Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware, 19716

Received 14 August 2002; accepted 18 July 2003

The contributions of lattice oxygen and adsorbed oxygen to the oxidation of butane by VPO catalysts were quantitatively determined by measurement of the reaction kinetics with a novel oscillating microbalance reactor. At 674 K, with the gas composition of butane/oxygen/Ar/He = 1.75/2.1/1.6/balance (vol%), and a gas hourly space velocity (GHSV) of 30 000 h^{-1}, oxidation of butane by lattice oxygen accounts for only about 5% of the butane oxidation rate, with the remainder carried out by adsorbed oxygen, most likely O^-. Thus under steady state reaction conditions, the traditional Mars-van Krevelen mechanism is a minor contributor to the rate.

KEY WORDS: VPO catalyst; butane oxidation; maleic anhydride; oxygen activation.

1. Introduction

Selective oxidation of alkanes by heterogeneous catalytic reaction has been one of the most active areas in the field of catalysis. Understanding of the role of oxygen, the most commonly used oxidizing agent in these reactions, has long been of special interest [1]. In the selective oxidation of butane to maleic anhydride (MA) on vanadyl pyrophosphate (VPO) catalysts, many results have been reported on the respective roles of lattice and gas-phase oxygen in the formation of partial and complete oxidation products.

Kruchinin *et al*. [2], Pepera *et al*. [3] and Misono *et al*. [4] concluded that the lattice oxygen ions located in the top few surface layers are responsible for the oxidation of butane to MA, CO and CO_2. Taufig-Yap [5,6], Gleaves [7] and Bej [8] also obtained experimental evidence to support this conclusion. Recently, Abon *et al*. [9,10] claimed on the basis of isotopic labeling results that only lattice oxygen is active for the formation of MA and other products. The circulating fluidized-bed riser reactor technology for MA production described in the literature [11–18] is based upon the fact that, under anaerobic conditions, the lattice oxygen of VPO can selectively oxidize butane to maleic anhydride [11–18].

This problem becomes more complex when oxygen is co-fed with butane under steady state reaction conditions employed in industrial fixed-bed reactor processes. In addition to the conventional Mars-Van Krevelen mechanism, where lattice oxygen is the active agent for butane oxidation, gas-phase oxygen, surface lattice oxygen and/or activated chemisorbed oxygen have all been proposed as important oxidants in the formation of MA or in the formation of unselective products, CO and CO_2 [19–24]. For example, Trifiro *et al*. [19,20] proposed that adsorbed oxygen is responsible for selective oxidation and that it is involved in the oxygen insertion steps required for the formation of MA. Ebner and coworkers [20–22] concluded that adsorbed oxygen is selective only in the MA formation step. They proposed that two types of oxygen are involved in butane oxidation: surface lattice oxygen that is responsible for ring closure, and activated chemisorbed oxygen, O*, that is involved in the further step of MA formation. Rodemerck *et al*. [23] reported that adsorbed oxygen is active but not selective, i.e., it can only produce CO_2. In contrast to all of these studies, Zazhigalov *et al*. [24] concluded that MA formation over $(VO)_2P_2O_7$ is mainly due to gas-phase oxygen.

The controversy in the literature about the roles of lattice and chemisorbed oxygen calls for further clarification of the puzzle. Previously [25,26], we have used a novel microbalance reactor to carry out kinetic analyses of butane oxidation by VPO catalysts and of the oxidation of partially reduced VPO with oxygen. This technique provides us with the snapshot of the catalytic performance under transient reaction conditions. Such experimental studies can provide quantitative results that help to differentiate the contributions of different oxygen species under steady state conditions.

2. Experimental

The VPO catalyst sample with a nominal phosphorus to vanadium atomic ratio of 1.0 was prepared by an

* To whom correspondence should be addressed.
E-mail: barteau@che.udel.edu

1011-372X/03/0900–0007/0

organic method outlined in [25–27]. Briefly, a mixture of 5 g of vanadium pentoxide (Aldrich), 125 mL 2-butanol (Aldrich) and 4.5 mL phosphoric acid (Fisher) was refluxed at 363–373 K for 16 h. The resulting suspension was washed with diethyl ether until the filtrate became clear. The sample was then dried at room temperature overnight, and then at 393 K in air for 20 h. After activation at 698 K in a gas mixture containing oxygen/butane/He = 21/1.75/balance (vol%) for 24 h, the sample mainly contained the vanadyl pyrophosphate phase, as evidenced by XRD [26]. The catalyst was previously demonstrated to be stable after 12 h under these activation conditions [25–27].

This VPO sample was tested for its catalytic performance for the selective oxidation of butane to maleic anhydride and its redox properties were examined using a microbalance reactor. The setup and the features of this instrument have been detailed previously [25–30]. In each experiment, a sample of 100 mg of activated VPO catalyst was loaded in the microbalance reactor. While heating the reactor from 313 to 674 K in a gas mixture of butane/oxygen/Ar/He (1.75/2.1/1.6/balance, vol%) at GHSV = 30 000 h^{-1}, the effluent gas was analyzed with an online quadrupole mass spectrometer (UTI100C). Mass fragments with $m/q = 43$, 40 and 32 were used to monitor the concentration of butane, argon and oxygen respectively. With argon as the internal standard, butane and oxygen conversions were calculated.

After the catalyst was stabilized at 674 K for 2 h in butane/oxygen/Ar/He (1.75/2.1/1.6/balance, vol%), the reactor was purged with N_2/He to clean the line of residual reactants. Oxidation in oxygen (2.1 vol%)/He or reduction in butane (1.75 vol%) was then started at 674 K by switching to the respective gas mixtures while maintaining a total flowrate of 50 mL min^{-1}. The mass changes of the catalyst were recorded to measure the oxidation/reduction rate.

In a separate experiment, steady state butane oxidation was carried out in a fixed-bed tubular reactor. The reactor was formed from a 25 cm long, 6 mm o.d. quartz tube that was flared to 13 mm in the center over a distance of 2 cm. The VPO catalyst (0.1 mL) was loaded in the center portion as a sandwich between quartz chips. The reaction temperature was controlled within ±1 K of the temperature set point. Reactant mixtures were prepared in a gas manifold by mixing helium (grade 5), oxygen (Matheson purity) and butane (4.3 vol% in helium). Compositions of the reactant and product gases were analyzed with an on-line GC. Analysis of butane and MA was carried out on a 30 m, 0.32 mm o.d. HP-05 capillary column using a flame ionization detector. CO and CO_2 were detected with a thermal conductivity detector (TCD) after separation with 13X molecular sieve and Hayesep Q columns respectively. All columns were operated isothermally at 423 K.

3. Results

Figure 1 shows the mass spectrometer (MS) signals for butane and oxygen for steady state reaction at 674 K under the conditions described above. By comparing these signals to those obtained by flowing the reactant stream over the catalyst at 313 K (where no reaction occurs), one can determine the fractional conversion of the reactants. The measured conversions of butane and oxygen are 7 and 27%, respectively, for the experiment in figure 1. A similar blank experiment in which the microbalance reactor was filled with quartz chips (figure 2) showed that the MS signals were unchanged upon increasing the temperature from 313 to 674 K. Thus, no gas-phase combustion of butane with co-fed oxygen occurs at 674 K. The conversions determined from figure 1 therefore represent those of the catalytic oxidation of butane carried out with VPO. Considering the feed composition (2.1 vol O_2) and flow rate (50 mL min^{-1}), the consumption rate of oxygen is about 6.8 $\mu g\%\ s^{-1}$ for a 100 mg catalyst sample at 674 K under the steady state reaction conditions of figure 1.

Figure 3 illustrates the mass change of the VPO catalyst upon oxidation in 2.1 vol% O_2 in He. The catalyst, at the beginning of this experiment, had been run under the steady state reaction conditions noted above for two hours and then purged with an inert gas mixture containing N_2/He. The initial oxidation rate was measured as the slope of the curve at the beginning of the oxidation. This rate is 0.37 $\mu g(100\ mg_{cat})^{-1}s^{-1}$. Similarly, the initial reduction rate of the same catalyst in butane (1.75 vol%)/He was measured from the mass change upon reduction, shown in figure 4. This reduction rate is 0.34 $\mu g(100\ mg_{cat})^{-1}s^{-1}$.

Because the oxygen and butane concentrations used in the oxidation and reduction gases are the same as those used in the steady state reaction, the reduction and oxidation rates thus measured should reflect the rate of

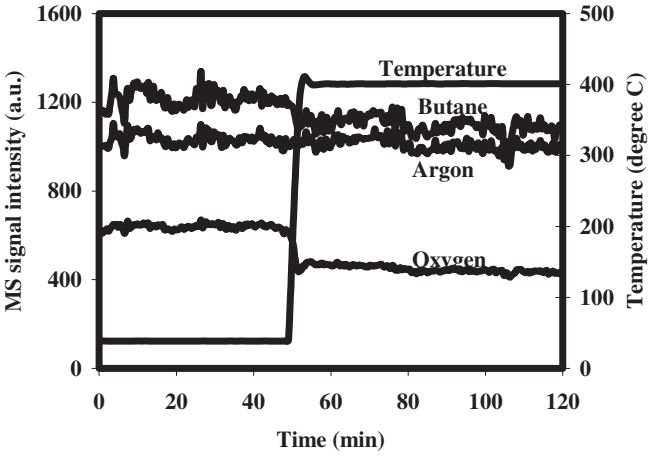

Figure 1. Oxidation of butane with a VPO catalyst. Conditions: 100 mg VPO catalyst, total gas flowrate = 50 mL min^{-1}, gas composition: butane/oxygen/Ar/He = 1.75/2.1/1.6/bal. (vol%), temperature as indicated.

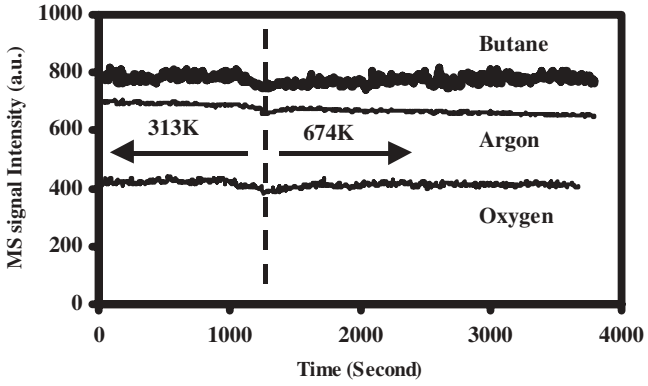

Figure 2. Oxidation of butane over quartz chips. Conditions: reactor filled with quartz chips. Total gas flowrate = 50 mL min^{-1}, gas composition: butane/oxygen/Ar/He = 1.75/2.1/1.6/bal. (vol%), temperature as indicated.

lattice oxygen removal and replacement under steady state reaction conditions. The experimental results above, as well as those reported previously in our detailed studies of VPO oxidation and reduction kinetics [25,26], showed that the oxidation and reduction rates of the equilibrated VPO catalyst (equilibrated in this case in butane/oxygen/Ar/He = 1.75/2.1/1.6/balance, vol%) are very close to each other, in spite of the different rate-determining processes involved. This similarity explains the steady mass of the catalyst under such steady state reaction conditions, i.e. there is no net depletion or accumulation of lattice oxygen at steady state—the rates of oxygen removal and replacement are in balance. The slightly higher initial oxidation rate compared to reduction rate may reflect a small contribution of chemisorbed oxygen to the mass of the oxidized catalyst [26]; before the oxidation, the catalyst was purged free of adsorbed oxygen, and when oxidation started, the addition of a small amount of reversibly adsorbed oxygen may have also contributed to the recorded mass change.

Comparison of the redox rate of the lattice oxygen with the reaction rate of oxygen indicates that the oxygen consumption rate under steady state reaction conditions ($6.8\,\mu g(100\,mg_{cat})^{-1}s^{-1}$) is more than an order of magnitude higher than either the instantaneous oxidation or reduction rates of the catalyst (0.37 and $0.34\,\mu g(100\,mg_{cat})^{-1}\ s^{-1}$ respectively), that represent the rate of consumption or replacement of the lattice oxygen. This implies that, under steady state reaction conditions, the oxidation of butane does not take place solely through redox reactions involving the lattice oxygen of the VPO catalyst. There exists a separate pathway for the oxidation of butane. Furthermore, gas-phase oxidation can be ruled out from our experiments with a quartz-filled reactor (figure 2). Therefore, the only possible alternative pathway left must be the oxidation of butane by a reactive adsorbed form of oxygen.

In our previous report [26] in which we examined the kinetics of VPO catalyst oxidation, we proposed the following mechanism for the oxidation of partially reduced VPO catalyst with gas-phase oxygen:

$$O_2 + 2[^*] \overset{K_1}{\longleftrightarrow} 2O^* \quad (1)$$

$$O^* \overset{slow}{\longrightarrow} [O] \quad (2)$$

In this mechanism, oxidation of VPO catalyst involves two sequential steps: first the dissociative

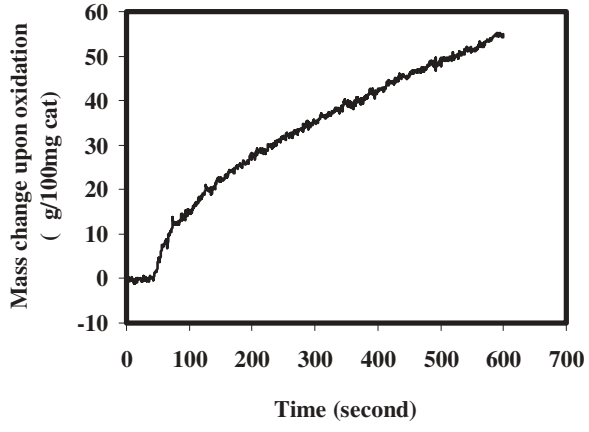

Figure 3. Isothermal oxidation of equilibrated VPO catalyst in 2.1 (vol%) O_2/He. Conditions: 100 mg VPO catalyst, total gas flowrate = 50 mL min^{-1}, temperature = 674 K.

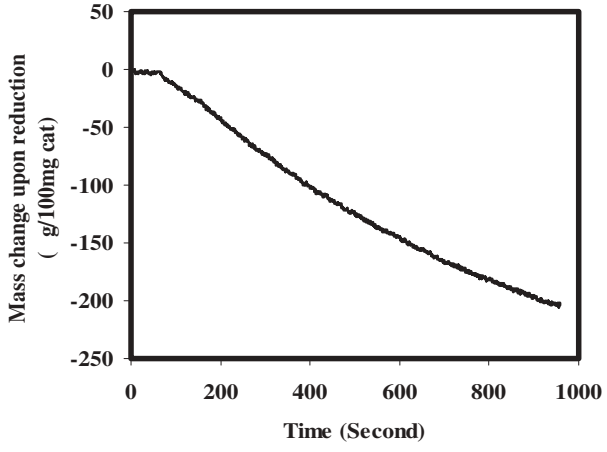

Figure 4. Isothermal reduction of equilibrated VPO catalyst in 1.75(vol.)% butane/He. Conditions: 100 mg VPO catalyst, total gas flowrate = 50 mL min^{-1}, temperature = 674 K.

adsorption of oxygen, and then the conversion of adsorbed oxygen into lattice oxygen through electron transfer from surface cations, i.e., V^{4+}, to the oxygen adspecies. In this scheme, an asterisk denotes a reduced surface site, species with an asterisk denote surface species and [O] represents lattice oxygen. K_1 is the equilibrium constant for the dissociative adsorption of oxygen.

In this sequence, the catalyst oxidation rate can be expressed as [26]:

$$r_{ox} = k_2 \; K_1^{1/2} \; P_{O_2}^{1/2} \theta \tag{3}$$

where r_{ox} is the oxidation rate, which can be measured as the catalyst mass change rate upon oxidation, dm/dt in $\mu g(100\,mg_{cat})^{-1}(s)^{-1}$, k_2 is the rate constant for reaction (2), K_1 is the equilibrium constant for reaction (1), P_{O_2} is the oxygen partial pressure (in torr) and θ is the concentration of reduced surface sites on the VPO catalyst. According to previous results [27], the reduced surface sites on the VPO catalysts are V^{4+}, which act as adsorption sites and provide oxygen vacancies to convert adsorbed oxygen to lattice oxygen. Filling of oxygen vacancies near V^{4+} oxidizes the vanadium to V^{5+} and decreases the number of adsorption sites.

It has been well established that, when oxygen is adsorbed on transition metal oxides, O_2^-, O^- and/or O^{2-} are energetically favorable species [1]. Therefore, the adspecies denoted as O^* in reactions (4) and (5) are most likely to be O^-, which is a dissociated intermediate to lattice O^{2-}.

As was mentioned above, the catalyst stabilized under steady reaction conditions was first purged with an inert gas mixture containing N_2/He. The purpose of this purging was to clear the line of any residual reactants, butane or oxygen, to avoid interference with the oxidation-rate measurement. After calibration of the apparent mass change because of the gas density change when switching gases [30], the net catalyst mass loss was below the instrumental detection limits ($>5\,\mu g$) when purged with inert gas. Therefore, reversible adsorption of oxygen did not occur to a large extent, that is, the surface coverage of O^* species must be very small under the current oxidation conditions at temperatures up to 674 K.

When butane is oxidized with the VPO catalyst under anaerobic conditions, the following reaction may occur:

$$\text{Butane} + \text{n[O]} \;\rightarrow\; [^*] + \text{MA} + \text{CO/CO}_2 \tag{4}$$

This is the foundation for the development of circulating fluidized-bed riser reactor technique for butane oxidation to maleic anhydride [12–18]. The kinetics for this reaction have been reported in [25]:

$$r_{rd} = k_4 \; P_{C_4H_{10}}^{0.4} [O]^4 \tag{5}$$

where r_{rd} is the rate of reaction (4) expressed as rate of catalyst mass loss, $-dm/dt$, in $\mu g(100\,mg_{cat})^{-1}\,(s)^{-1}$, k_4 is the apparent reaction rate constant, $P_{C_4H_{10}}$ is butane partial pressure (torr) and [O] is the lattice oxygen concentration.

Under steady state reaction conditions, the oxygen conversion rate, $r_{[O]}$, through the lattice oxygen route (i.e. through the catalytic cycle composed of reaction steps (1), (2) and (4),) must equal the rates of oxygen removal and replacement on the VPO catalyst, i.e.

$$r_{[O]} = r_{ox} = r_{rd} = 0.34\,\mu g(100\,mg_{cat}^{-1}\;s^{-1}). \tag{6}$$

According to the current experimental results, under aerobic conditions $r_{[O]}$ only accounts for about 5% of the total reaction rate ($6.8\,\mu g(100\,mg_{cat}^{-1}\;s^{-1})$). Therefore, about 95% of consumed oxygen was converted through the adsorbed form, bypassing the lattice oxygen formation step.

As is indicated in the oxidation mechanism in equations (1) and (2), the transformation of chemisorbed oxygen to lattice oxygen is much slower than the formation of the adsorbed oxygen. In that case, the lifetime of adsorbed oxygen may be long enough to react with butane or other intermediates (expressed more generally as reductant) to form MA, CO and CO_2, through reaction (7), even though the steady state coverage of O^* may be very small.

$$n\;O^* + \text{reductant(butane/intermediate)} \;\rightarrow\; \text{MA, CO, CO}_2 \tag{7}$$

The rate of reaction (7) can be expressed as:

$$r_{[O^*]} = k_6\;[O^*]^a\;[\text{reductant}]^b \tag{8}$$

where $r_{[O^*]}$ is the rate of reaction (7) in $\mu g(100\,mg_{cat}^{-1}\;s^{-1})$; k_6 is the reaction rate constant; $[O^*]$ and [reductant] are concentrations of adsorbed oxygen and butane (or organic reaction intermediates), respectively; a and b are reaction orders in $[O^*]$ and [reductant] respectively. The total oxygen conversion rate r_O, under aerobic conditions, can be expressed as

$$r_O = r_{[O]} + r_{[O^*]} \tag{9}$$

There is no reason from the results presented thus far to attribute *selective* oxidation to a particular oxygen species. In order to do so, it is necessary to evaluate the selectivity of the reaction under steady state conditions. Our experience is that such experiments are better carried out in the conventional tubular reactor described in the experimental section above, rather than in the microbalance. Results obtained in the tubular reactor showed that under steady state oxidation conditions in a gas mixture of butane/oxygen/Ar/He (1.75/2.1/1.6/balance, vol%), at 674 K, SV = 30 000 h^{-1}, the selectivity to maleic anhydride is about 64% at a butane conversion of 7%.

If one assumes that reaction (4) (reaction of butane with lattice oxygen) is 100% selective to MA formation, and considering the 5 and 95% contributions of reactions (4) and (7), respectively, to the overall butane oxidation rate, reaction (7) (butane plus adsorbed oxygen) must be at least 62% selective for MA. That is to say that chemisorbed oxygen is selective for maleic anhydride formation, and is more active than lattice oxygen under steady state reaction conditions.

4. Conclusions

Both lattice oxygen and adsorbed oxygen on VPO catalyst can selectively oxidize butane to maleic anhydride. Under aerobic conditions, the oxidation of butane by adsorbed oxygen species is much faster than by lattice oxygen.

References

[1] A. Bielanski and J. Haber, Catal. Rev.-Sci. Eng. 19 (1979) 1.
[2] Yu.A. Kruchinin, Yu.A. Mishcenko, P.R. Nechiporuk and A.I. Gol'bshtein, Kinet. Catal. 25 (1984) 328.
[3] M. Pepera, J.L. Callahan, M.J. Desmond, E.C. Milberger, P.R. Blum and N.J. Bremer, J. Am. Chem. Soc. 107 (1985) 4883.
[4] M. Misono, K. Miyamoto, K. Tsuji, T. Goto, N. Mizuno and T. Okuhara, in *New Developments in Selective Oxidation*, eds. G. Centi and T. Trifiro (Elsevier, Amsterdam, 1990) p. 605.
[5] Y.H. Taufiq-Yap, B.H. Sakakini and K.C. Waugh, Catal. Lett. 48 (1997) 105.
[6] B.H. Sakakini, Y.H. Taugiq-Yap and K.C. Waugh, J. Catal. 189 (2000) 253.
[7] Y. Schuurman and J.T. Gleaves, Catal. Today 33 (1997) 25.
[8] S.K. Bej and M.S. Rao, Ind. Eng. Chem. Res. 30 (1991) 1819.
[9] M. Abon, K.E. Bere and P. Delichere, Catal. Today 33 (1997) 15.
[10] J.-M. Herrmann, P. Vernoux, K.E. Bere and M. Abon, J. Catal. 167 (1997) 106.
[11] Chem. Eng. News (1999) 16.
[12] R.M. Contractor, H.S. Horowitz, G.M. Sisler and E. Bordes, Catal. Today 37 (1997) 51.
[13] G. Emig, K. Uihlein and C.-J. Hacker, in *New Developments in Selective Oxidation II*, eds. V. Cortes Corberan and S. Vic Bellon (Elsevier, Amsterdam, 1994) p. 243.
[14] R.M. Contractor, D.I. Garnett, H.S. Horowitz, H.E. Bergna, G.S. Patience, J.T. Schwartz and G.M. Sisler, in *New Developments in Selective Oxidation II*, eds. V. Cortes Corberan and S. Vic Bellon (Elsevier, Amsterdam, 1994) p. 233.
[15] R.M. Contractor, U.S. Patent 4,668,802 issued May, 26, 1987 to E. I. du Pont de Nemours and Company.
[16] R.M. Contractor, H.E. Bergna, H.S. Horowitz, C.M. Blackstone, B. Malone, C.C. Toradi, B. Griffiths, U. Chowdhry and A.W. Sleight, Catal. Today 1 (1987) 49.
[17] R.M. Contractor and A.W. Sleight, Catal. Today 1 (1988) 175.
[18] R.M. Contractor and A.W. Sleight, Catal. Today 1 (1987) 587.
[19] F. Trifiro, C. Banfi, G. Caputo, P. Forzatti and I. Pasquon, J. Catal. 30 (1973) 393.
[20] G. Centi, F. Trifiro, G. Busca, J.R. Ebner and J.T. Gleaves, *Proc. 9th Intern. Cong. Catal.* Vol. 4 (1988) 1538.
[21] J.T. Gleaves, J.R. Ebner and T.C. Kuechler, Catal. Rev.-Sci. Eng. 30 (1988) 49.
[22] G. Centi, F. Trifiro, J.R. Ebner and V.M. Franchetti, Chem. Rev. 88 (1988) 55.
[23] U. Rodemerk, B. Kubias, H.-W. Zanthoff and M. Baerns, Appl. Catal., A: Gen. 153 (1997) 203.
[24] V. A. Zazghigalov, Yu. P. Zaitsev, V. W. Belousov, N. Wyustnek and H. Wolf, React. Kinet. Catal. Lett. 24 (1984) 375.
[25] D. Wang and M.A. Barteau, J. Catal. 197 (2000) 17.
[26] D. Wang and M.A. Barteau, Appl. Catal., A 223 (2002) 205.
[27] D. Wang, H.H. Kung and M.A. Barteau, Appl. Catal., A 201 (2000) 203.
[28] J.E. Rekoske and M.A. Barteau, J. Phys. Chem., B 101 (1997) 1113.
[29] S.C. Fung, C.A. Querini, K. Liu, D.C. Rumschitzki and T.C. Ho, in *Catalyst Deactivation*, eds. B. Delmon, G.F. Froment (Elsevier, Amsterdam, 1994) p. 305.
[30] *TEOM™ Series 1500 Pulse Mass Analyzer* (Rupprecht & Patashnick Co., Inc., Albany, New York, 1994).