

KINETICS, CATALYSIS, AND REACTION ENGINEERING

Kinetics of MnO₂-Catalyzed Acetic Acid Oxidation in Supercritical Water

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Acetic acid was oxidized in supercritical water over a bulk MnO₂ catalyst. CO₂, the complete oxidation product, was produced almost quantitatively. The rate of acetic acid disappearance exhibited saturation kinetics with respect to acetic acid, a maximum with respect to the oxygen concentration, and an independence from the water concentration. We identified a global rate law that was both qualitatively and quantitatively consistent with these experimental results. Using this catalytic rate law and literature rate laws for noncatalytic oxidation of acetic acid in supercritical water, we found that the use of MnO₂ as an oxidation catalyst can reduce the reactor volume required for treatment of aqueous solutions of acetic acid by more than 2 orders of magnitude.

Introduction

Water has unique properties above its critical point ($T_c = 374\text{ }^\circ\text{C}$, $P_c = 218\text{ atm}$) that make it an excellent reaction medium for oxidative destruction of hazardous organic waste under supercritical conditions.^{1,2} Supercritical water is completely miscible with organic compounds as well as with oxygen, so oxidation reactions can take place rapidly in a single homogeneous fluid phase with no interphase mass-transfer limitations. Conventional supercritical water oxidation (SCWO) technology relies on homogeneous (likely free radical) oxidation reactions at temperatures up to 650 °C. This temperature is well above that needed to ensure supercritical conditions, but such high temperatures are required to ensure complete destruction of the organic materials. An adverse consequence of such high-temperature operation, however, is that many salts (e.g., NaCl), if formed during SCWO treatment, will precipitate, adhere to solid surfaces, and perhaps hinder the proper operation of the process. At lower temperatures and consequently higher water densities, the salts are much more soluble and would largely remain in solution. Additionally, high-temperature operation implies higher energy costs. These considerations have motivated the exploration of heterogeneously catalyzed SCWO³ as a potential means of reducing the process temperature and thereby both solving the salt management problem and reducing the processing cost.⁴

Acetic acid is frequently used as a model compound in aqueous-phase oxidation studies. Its significance stems primarily from its appearance as a ubiquitous intermediate during the oxidation of more complex organic compounds. Acetic acid appears to be particularly resistant to oxidative degradation at lower, subcritical temperatures, a feature that has earned it the label "refractory intermediate." The "refractory" portion

of this label probably does not apply at supercritical conditions,⁵ however. Nevertheless, the conventional, noncatalytic SCWO of acetic acid has been investigated by many different groups.^{6–11} Therefore, an examination of the heterogeneously catalyzed SCWO of acetic acid is relevant.

In his theses, Frisch^{12,13} provided some experimental results for the catalytic oxidation of acetic acid in SCW over MnO₂/CeO₂ and over TiO₂. Chang et al.¹⁴ oxidized acetic acid using different oxidants at 400–460 °C in a batch reactor. Although not explicitly a catalytic oxidation study, this work revealed that KMnO₄ was the most effective of the oxidants examined. Its efficacy was attributed to the formation of MnO₂ and to this material's enhancement of the oxidation rate as a catalyst. Lee¹⁵ considered the possibility of catalytic effects from stainless steel batch reactor walls. He found that such effects did exist and that a power-law rate expression could correlate the observed kinetics. Krajnc and Levec^{11,16} examined the oxidation of acetic acid in SCW over two different supported, mixed transition metal oxide catalysts. Their results showed that the activation energy decreased from 182 kJ/mol without a catalyst to 110 kJ/mol with a copper oxide/zinc oxide/cobalt oxide catalyst and that catalytic oxidation favors the production of CO₂. These investigators also recommended a power-law rate equation that was 0.69 order in acetic acid and 0.47 order in oxygen for reactor modeling for catalytic SCWO of acetic acid.

The studies noted above are the only ones done to date on the catalytic SCWO of acetic acid. This previous work has identified some catalytically active transition metal oxides and showed that power-law kinetics have typically applied. The extent of available kinetics information for catalytic SCWO of acetic acid is, however, still extremely limited. This article provides such information for the oxidation of acetic acid over bulk MnO₂ in supercritical water.

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Table 1. Summary of Acetic Acid Oxidation over MnO₂ in SCW

reaction temp (°C)	reaction pressure (atm)	W/F_{A0} (kgcat s/mol)	HOAc conc (mM)	water conc (M)	oxygen conc (mM)	HOAc conv (%)	CO yield (%)	CO ₂ yield (%)	carbon balance (%)
380	250	2.8	3.1	26	16	37	0.0	45	108
380	250	3.3	3.2	26	16	45	0.2	49	104
380	250	4.0	3.2	25	16	51	0.1	54	103
380	250	5.3	3.1	25	16	69	0.0	60	92
381	250	7.2	3.2	25	16	66	0.0	60	94
381	250	2.8	3.0	25	24	65	0.5	66	102
381	250	3.2	3.1	24	23	74	0.0	74	100
380	250	3.9	3.3	26	24	83	0.1	80	97
380	250	5.3	3.2	26	25	89	0.0	90	101
380	250	7.6	3.2	26	24	96	0.2	95	99
380	250	2.7	3.2	25	45	49	0.0	50	101
380	250	3.3	3.2	26	45	62	0.0	57	95
380	250	4.0	3.2	26	45	69	0.0	63	93
380	250	5.3	3.2	26	45	74	0.0	70	97
380	250	7.6	3.2	25	44	78	0.0	76	98
380	250	2.8	3.2	26	68	43	0.0	51	108
380	250	3.3	3.2	26	68	53	0.0	79	125
380	250	4.0	3.2	25	67	60	0.0	65	105
380	250	5.3	3.1	25	67	68	0.0	69	100
381	250	7.9	3.1	25	68	62	0.0	70	109
381	250	8.4	1.1	25	25	67	0.0	62	96
382	250	8.5	1.1	24	23	73	0.0	70	97
380	250	10.5	1.2	26	24	68	0.0	73	105
380	250	14.1	1.2	26	24	98	0.0	88	90
380	250	19.7	1.2	26	24	92	0.0	91	99
380	250	1.5	5.7	25	24	35	0.0	32	97
380	250	1.8	5.7	25	24	52	0.0	50	98
380	250	2.2	5.8	25	24	66	0.1	63	97
381	250	2.9	5.7	25	24	72	0.0	72	100
380	250	4.1	5.8	25	24	87	0.0	83	96
381	250	1.0	8.3	25	24	17	0.0	27	110
381	250	1.2	8.4	25	24	32	0.1	40	108
381	250	1.5	8.4	25	23	45	0.1	47	102
381	250	2.0	8.3	25	24	60	0.1	62	102
381	250	2.8	8.3	25	23	76	0.1	70	94
381	219	5.1	2.2	9.2	31	36	0.4	31	95
380	219	2.0	3.1	9.3	24	32	0.3	26	94
381	219	1.4	3.2	9.2	24	31	0.5	24	93
380	219	1.2	3.2	9.5	25	23	0.0	22	99
379	219	1.0	3.4	9.9	25	24	0.0	20	96
380	273	3.1	3.1	28	25	79	0.2	85	107
380	273	3.8	3.1	28	25	89	0.0	96	107
380	273	4.5	3.2	28	24	95	0.0	94	99
380	273	6.0	3.2	28	24	96	0.0	99	103
380	273	8.6	3.2	28	24	96	0.0	100	104
380	300	3.3	3.2	30	24	85	0.3	84	100
380	300	4.0	3.2	30	24	91	0.0	98	107
380	300	4.9	3.1	30	24	95	0.0	100	105
380	300	6.3	3.2	30	24	97	0.0	98	101
380	300	9.6	3.1	30	24	95	0.0	102	107
439	250	3.3	0.8	6.5	6.7	28	0.3	15	87
439	250	3.6	0.8	6.5	6.7	28	0.5	20	92
440	250	4.1	0.8	6.5	6.7	35	0.7	23	89
440	250	5.2	0.8	6.5	6.6	39	0.9	30	92
440	250	7.5	0.8	6.5	6.6	50	0.9	42	93
420	250	2.2	1.2	7.5	8.3	25	0.0	17	92
420	250	2.7	1.1	7.5	8.5	42	0.1	52	110
420	250	3.4	1.1	7.5	8.5	23	0.3	28	106
421	250	4.2	1.2	7.5	8.3	34	0.1	34	100
421	250	6.2	1.2	7.4	8.4	30	0.3	42	112
399	250	6.1	1.5	9.7	11	38	0.2	37	100
399	250	4.2	1.5	9.7	11	27	0.2	26	100
399	250	3.3	1.5	9.8	11	27	0.0	34	107
399	250	2.7	1.5	9.8	11	21	0.0	26	105
398	250	2.2	1.6	10	11	22	0.0	23	101

Experimental Section

Acetic acid was oxidized in supercritical water in a nominally isothermal, isobaric packed-bed reactor operating at steady state. Oxygen was always present in stoichiometric excess. Table 1 lists all of the experimental conditions. Most experiments were conducted at 380 °C and 250 atm, but with different acetic acid and

oxygen concentrations and different values of the W/F_{A0} (catalyst mass/acetic acid molar flow rate into the reactor) ratio. Experiments were also completed at 219, 273, and 300 atm to determine the effect of the water density on the oxidation rate and at 400, 420, and 440 °C to determine the effect of temperature on the oxidation rate. We intentionally selected reaction condi-

tions that led to less than 100% conversion so that we would have experimental data suitable for determination of the reaction kinetics.

The reactor system and experimental procedures have been described previously for catalytic SCWO of phenol over MnO_2 ,¹⁷ so we provide only an overview here. The reactor assembly and feed stream preheating lines reside in a temperature-controlled fluidized sand bath. Deionized and degassed water was used to prepare the reactor feed solutions, which were fed to the reactor via separate high-pressure metering pumps and through a length of preheater tubing. An aqueous H_2O_2 solution served as the oxygen source. The H_2O_2 decomposed ($2\text{H}_2\text{O}_2 = \text{O}_2 + 2\text{H}_2\text{O}$) completely during preheating. The two separate aqueous feed streams, one containing acetic acid and the other containing oxygen, were thus delivered to a Hastelloy C-276 mixing tee at the desired reaction temperature and pressure. The mixed stream entered a 12-cm long and $1/4$ -in. (6.4-mm) o.d. stainless steel tube reactor packed with 60/230 mesh MnO_2 (>99%, Aldrich) particles. The density of the catalyst bed was 2.4 g/cm^3 , and the fresh catalyst had a BET surface area of $6.6 \text{ m}^2/\text{g}$. A porous Hastelloy disk (5 μm pore size) at the reactor exit allowed the fluid to pass through but kept the MnO_2 particles inside the reactor. After the fluid mixture had exited the reactor, it was quickly cooled, depressurized, and separated into gas and liquid phases. The volumetric flow rates of the gas and liquid streams were measured. The gas phase was analyzed on-line by a gas chromatograph with a thermal conductivity detector. The liquid phase from the reactor effluent was periodically sampled and analyzed by high-performance liquid chromatography. Acetic acid was quantified using a Supelco C610H column with an aqueous 0.1% H_3PO_4 solution serving as the mobile phase and UV detection at 210 nm.

Molar yields were calculated as the molar flow rate of a compound in the reactor effluent divided by its stoichiometric coefficient and the molar flow rate of acetic acid into the reactor. The stoichiometric coefficients for acetic acid, CO, and CO_2 are 1, 2, and 2, respectively. Normalizing the molar yields with the stoichiometric coefficient provides an upper bound of 100% for the yield of any individual product and for the sum of the yields of all carbon-containing products.

Results

Table 1 provides a complete list of the experimental conditions and results. We report here the acetic acid conversion, the molar yields of CO and CO_2 , and the carbon balance. These three compounds are the only ones detected in the reactor effluent. In 61 of the 65 individual experiments the carbon balance was between 90 and 110%, which indicates an essentially quantitative accounting for all of the carbon fed to the reactor. Moreover, the carbon balance exceeded 100% about as frequently as it was below 100%, which suggests the presence of random rather than systematic errors. CO_2 was always the most abundant gaseous product, as the CO molar yield was always low (<1%).

Figure 1 compares the acetic acid conversions obtained from catalytic SCWO over MnO_2 at 380°C and 273 atm with those anticipated from conventional noncatalytic SCWO in the same reactor and under the same conditions if the MnO_2 were completely inert. The catalytic conversion is a function of W/F_{AO} , whereas the noncatalytic conversion is a function of the residence

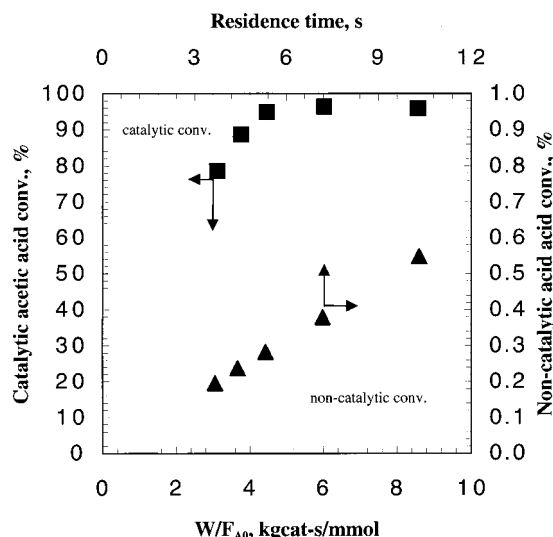


Figure 1. Acetic acid conversion from SCWO with and without MnO_2 catalyst ($T = 380^\circ\text{C}$, $P = 273 \text{ atm}$, $[\text{HOAc}]_0 = 3.2 \text{ mmol/L}$, $[\text{O}_2]_0 = 24 \text{ mmol/L}$).

time. The values for the noncatalytic SCWO of acetic acid were calculated from a rate equation in the literature,⁹ and the residence time was taken to be the reactor void volume divided by the volumetric flow rate through the reactor under reaction conditions. Figure 1 shows that the acetic acid conversion would be less than 1% if the MnO_2 were simply an inert material. The experimental conversions reached 97%, however, which clearly demonstrates the ability of MnO_2 to accelerate the acetic acid disappearance rate during SCWO.

Kinetics Analysis

Previous kinetics studies for catalytic SCWO have used power-law, Langmuir–Hinshelwood, and Mars–van Krevelen rate laws to correlate the results. The former two rate-law forms have been employed previously^{11,15} for catalytic SCWO of acetic acid, but for oxidation over materials other than MnO_2 . In this section, we use the experimental results to determine an appropriate functional form for the rate law for acetic acid oxidation over MnO_2 , and then we determine numerical values for the rate law parameters. Before proceeding, we note that the rate of acetic acid disappearance is essentially the same as the rate of CO_2 formation [or total organic carbon (TOC) disappearance]. This correspondence exists in this particular case because the CO yields were always very low, no organic byproducts were detected, and the carbon balance was always around 100%. Additionally, we note that neither intraparticle nor interphase mass transfer limited the rate of the oxidation reaction in our experiments. We used the analytical criteria¹⁸ of Weisz and Prater and of Mears to verify the absence of potential mass-transfer limitations.

Knowledge of the reaction rate response to changes in the concentrations of the components in the feed stream allows one to draw inferences regarding the functional form of the global rate law. Therefore, we carried out experiments at 380°C and 250 atm wherein the concentration of one component was varied and the concentrations of the other two were fixed at roughly constant values. These experiments allowed us to determine the effects of the concentrations of acetic acid, oxygen, and water, individually, on the reaction rate.

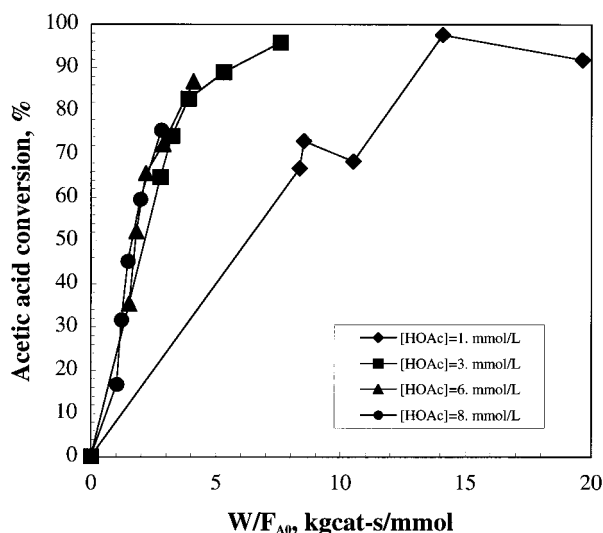


Figure 2. Effect of acetic acid feed concentration on acetic acid conversion during catalytic SCWO ($T = 380\text{ }^{\circ}\text{C}$, $P = 250\text{ atm}$, $[\text{O}_2]_0 = 24\text{ mmol/L}$).

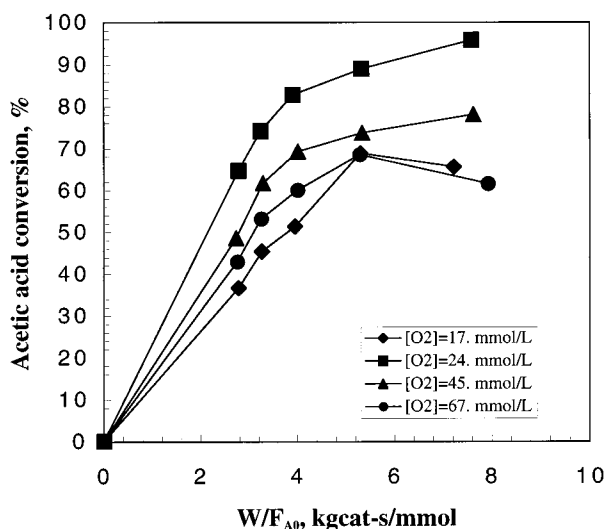


Figure 3. Effect of oxygen feed concentration on acetic acid conversion during catalytic SCWO ($T = 380\text{ }^{\circ}\text{C}$, $P = 250\text{ atm}$, $[\text{HOAc}]_0 = 3.2\text{ mmol/L}$).

Figures 2–4 display the results for the effects of the acetic acid, oxygen, and water feed concentrations. The results are displayed as plots of conversion (X) vs W/F_{A0} because the derivative at any point on these curves is equal to the reaction rate according to eq 1.

$$\text{rate} = - \frac{dX}{d(W/F_{A0})} \quad (1)$$

Figure 2 shows that increasing the acetic acid concentration in the reactor feed from 1 to 3 mmol/L increases the conversion at a given value of W/F_{A0} and, hence, increases the oxidation rate. Additional increases in the acetic acid concentration, however, have no additional effect on the reaction rate. Therefore, the functional form of any proposed global rate law must be able to accommodate the saturation kinetics apparent for acetic acid.

Figure 3 shows that increasing the oxygen concentration in the reactor feed from 17 to 24 mmol/L increases the conversion at a given value of W/F_{A0} and, hence, increases the oxidation rate for acetic acid. Increasing

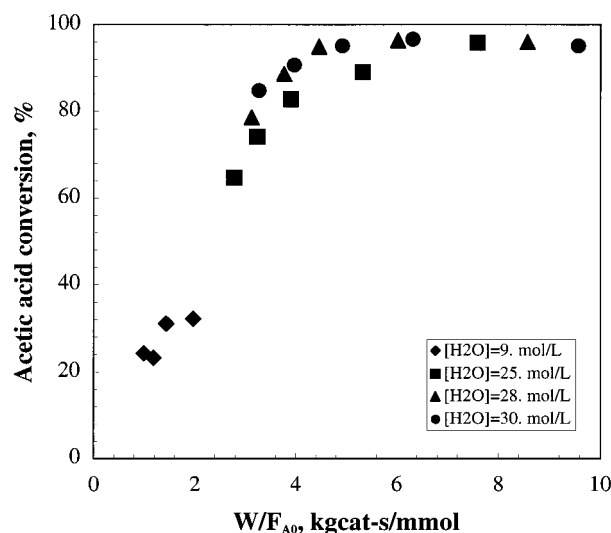


Figure 4. Effect of water feed concentration on acetic acid conversion during catalytic SCWO ($T = 380\text{ }^{\circ}\text{C}$, $[\text{HOAc}]_0 = 3.2\text{ mmol/L}$, $[\text{O}_2]_0 = 25\text{ mmol/L}$).

the oxygen concentration further to 45 mmol/L causes the reaction rate to decrease. An additional increase in oxygen concentration to 67 mmol/L causes an additional decrease in the rate. Therefore, the functional form of any global rate law proposed for acetic acid oxidation over MnO_2 must be able to accommodate the fact that the rate first increases, reaches a maximum, and then decreases as the oxygen concentration increases.

Figure 4 shows that the acetic acid conversion at a given value of W/F_{A0} (and, hence, of the acetic acid disappearance rate) did not appreciably change as the water concentration was increased from 25 to 30 mol/L (by changing the system pressure). The effect of lower water concentrations cannot be determined conclusively because the data in Figure 4 do not allow a direct comparison of conversions at the low and high water densities at similar W/F_{A0} values. Nevertheless, it appears that the water concentration does not have a strong effect on the catalytic oxidation rate.

To summarize, inspection of Figures 2–4 reveals that the rate of acetic acid oxidation in supercritical water over MnO_2 exhibits saturation kinetics with respect to acetic acid, exhibits a maximum with respect to the oxygen concentration, and is largely independent of the water density. A power-law rate equation with fixed reaction orders is not capable of capturing these qualitative behaviors for acetic acid and oxygen. A rate law (but certainly not the only one) with the necessary functional form is

$$\text{rate} = - \frac{k_1[\text{HOAc}][\text{O}_2]}{(1 + k_2[\text{HOAc}](1 + k_3[\text{O}_2]))^2} \quad (2)$$

The parameters k_1 , k_2 , and k_3 should be viewed simply as empirical parameters. Until a chemical mechanism is identified that leads to the rate law in eq 2, the rate-law parameters will possess no chemical significance. Because eq 2 is consistent with the qualitative trends observed experimentally, namely, saturation kinetics for acetic acid and a maximum in rate with increasing oxygen concentration, we next performed a quantitative analysis to determine how well this rate law described the experimental data.

Substituting the proposed rate law into eq 1, writing the acetic acid concentration as a function of conversion,

Table 2. Parameters for Global Rate Law in Equation 2

parameter	values
k_{10} [L ² /(mol gcat s)]	$10^{4.2}$
E_1 (kJ/mol)	70
k_{20} (L/mol)	$10^{8.9}$
E_2 (kJ/mol)	75
k_{30} (L/mol)	$10^{6.1}$
E_3 (kJ/mol)	56

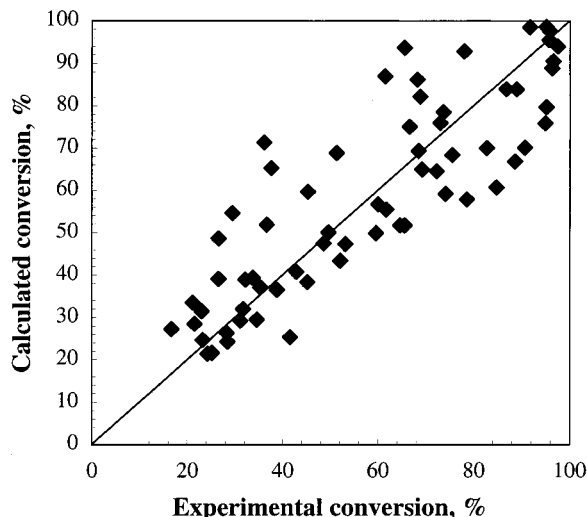


Figure 5. Comparison of conversion obtained experimentally and calculated from eq 3.

taking the oxygen concentration to be conversion-invariant because it is present in excess, and then solving the resulting differential equation leads to

$$W/F_{A0} = \frac{(1 + k_3[O_2]_0)^2 \{k_2[HOAc]_0 X - \ln(1 - X)\}}{k_1[HOAc]_0[O_2]_0} \quad (3)$$

This equation cannot be solved explicitly for the acetic acid conversion, so we used W/F_{A0} as the fitting variable in an unweighted nonlinear regression analysis to find optimal numerical values for k_1 , k_2 , and k_3 . We assumed that all three parameters exhibited an Arrhenius-like temperature dependence [$k_i = k_{i0} \exp(-E_i/RT)$]. Table 2 lists the values of the six different parameters in the rate law. Figure 5 displays the parity plot for acetic acid conversion. It is clear that this rate law provides a reasonably good description of the experimental data.

Having identified a rate law that is consistent with the experimental results, we next attempted to identify a reaction mechanism that is consistent with the rate law. The Mars–van Krevelen mechanism¹⁹ and its associated kinetics, although widely used for modeling oxidation reactions over transition metal oxides, are not adequate here. This rate-law form anticipates saturation kinetics for both acetic acid and oxygen. Mars–van Krevelen kinetics are incapable of modeling the observed maximum in rate obtained by varying the oxygen concentration. Therefore, the Mars–van Krevelen rate law cannot be used to describe the present kinetics data for acetic acid disappearance during catalytic SCWO over MnO_2 .

The Langmuir–Hinshelwood and Eley–Rideal rate laws are also commonly used to correlate heterogeneous catalytic kinetics. Our examination of different rate laws drawn from these mechanisms failed to provide a rate equation with the functional form of eq 2. It does not

appear to be possible to satisfy simultaneously the dual requirements of saturation kinetics for acetic acid and a maximum in rate with increasing oxygen concentration. For example, a dual-site Langmuir–Hinshelwood mechanism (chemically distinct adsorption sites exist for acetic acid and for oxygen) is required to obtain two separate terms in the denominator as in eq 2, but dual-site mechanisms predict saturation kinetics for both acetic acid and oxygen. A single-site mechanism (acetic acid and oxygen adsorb on the same type of site) can lead to a rate law consistent with a maximum in rate as the oxygen concentration increases and also consistent with saturation kinetics for acetic acid. Unfortunately, the rate law is not capable of displaying both of these features simultaneously under similar reaction conditions, as is required to be consistent with the experimental results.

Although we are not able to ascribe mechanistic meaning to the rate law in eq 2, we can nevertheless use it to address engineering issues relevant to catalytic SCWO technology. One such issue is reactor sizing. For example, it would be of interest to determine how the sizes (volumes) of a catalytic and noncatalytic reactor compare for treatment of a given aqueous solution of acetic acid. To illustrate, we will calculate the reactor volume required to achieve 99.99% conversion of the acetic acid in a stream flowing at 20 gal/min under ambient conditions. We will take the treatment conditions to be 380 °C and 250 atm and the acetic acid and oxygen concentrations in the feed (at reaction conditions) to be 3.0 and 30 mmol/L, respectively.

Using two published rate laws^{9,10} for conventional homogeneous SCWO of acetic acid, we calculated the plug-flow reactor volumes required for the noncatalytic treatment to be 20 and 16 m³. In contrast, according to the rate law in eq 2, the packed-bed reactor volume required for catalytic SCWO using MnO_2 is only 0.06 m³. According to the rate law of Krajnc and Levec,¹¹ the reactor volume required for their supported, mixed transition metal oxide catalyst is 0.05 m³. One must recognize, of course, that there is uncertainty in all of these reactor volume calculations because analytical rate laws never provide perfect fits of experimental rate data. This uncertainty (perhaps $\pm 50\%$ at most) is small, however, relative to the 300- to 400-fold difference in the catalytic and noncatalytic reactor volumes. Therefore, this comparison clearly shows that catalytic oxidation of acetic acid in SCW can be accomplished with orders-of-magnitude smaller reactor volumes and, hence, lower capital costs than noncatalytic SCWO.

Summary and Conclusions

Bulk MnO_2 is an active catalyst for the oxidation of acetic acid in supercritical water. Under the reaction conditions investigated, the oxidation rate displays saturation kinetics with respect to acetic acid and is independent of the water density. The rate exhibits a maximum as the oxygen concentration is increased. The experimental data can be adequately described, both qualitatively and quantitatively, by an empirical global rate law. No conventional mechanism for heterogeneous catalysis could be found that would lead to a rate law with the necessary functional form. Using MnO_2 as a catalyst for SCWO of acetic acid can reduce the reactor volume required for treatment by more than 2 orders of magnitude.

Acknowledgment

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