Selective Oxidation of n-Butanol over Supported V_2O_5-K_2SO_4 Catalyst: Experiments and Models

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Although the oxidation of hydrocarbons and alcohols has been the subject of numerous invetigations, relatively little attention has been given to the kinetics of selective oxidation of analogous reactions on the same catalyst with the aim of proposing a common theory for all such similar reactions. This ultimately requires obtaining precise experimental data followed by model discrimination and parameter estimation. Such an approach has recently been applied to the rate of oxidation data for the production of benzaldehyde from toluene and formaldehyde from methanol over silica supported V_2O_5-K_2SO_4 catalyst which not only was useful in correlating the studies independently but provided a link between them (Sharma and Srivastava, 1981).

The present work is an extension of the above approach to a similar reaction system of commercial interest, the oxidation of butanol to butyraldehyde over silica supported V_2O_5-K_2SO_4 catalysts. Most of the earlier work in the oxidation of butanol to butyraldehyde was concerned with the use of metal oxides like ZnO (Rivkin et al., 1936). The use of some metal salts have also been reported (Sudo and Morita, 1970). A careful examination of the literature reveals that there is no prior detailed kinetic study available for this reaction.

EXPERIMENTAL

Experimental apparatus, procedures and catalysts were the same as in references (Sharma, Rai and Srivastava, 1980; Sharma and Srivastava, 1980; Sharma and Srivastava, 1981). All experiments described below were performed exclusively with 20% V_2O_5, 15% K_2SO_4, and balance as silica (V-20-K-15) since the activity for the formation of butyraldehyde from butanol was highest with this composition.

Preliminary experiments were also carried out with mixed feed to study inhibition to obtain enough information to be able to discriminate between possible kinetic schemes and models. The results indicated that oxygen pressure influenced the rate of reaction; however, adsorption of water and butyraldehyde had no appreciable effect on the reaction rate under the conditions studied (Figure 1).

RESULTS

A large number of experiments were carried out to study the kinetics of this system. The various compositions of feed at different space-times for each isothermal set of runs are given in Table 1. Data were collected at 240, 260, and 280°C. The average reactor temperature was controlled to within ±0.5°C of the desired value. The feed rates for butanol were between 0.2 to 0.3 mol·h^{-1}. Conversions were usually kept below 5% as based on the alcohol present in the feed. The measured reaction rate data are summarized in Appendix A. Because of large amounts of inert (nitrogen) present in the feed stream the pressures have been calculated up to five significant figures, though the pressures without including nitrogen were only known to three places.

DISCUSSION OF RESULTS

The experimental data (Appendix A) were analyzed with the use of currently available techniques for model discrimination and parameter estimation (Froment, 1975). Different models based on Langmuir-Hinshelwood, modified Hinshelwood, and two-stage redox mechanism, were formulated. The deviation of models and details on model discrimination and parameter estimation procedures have been described previously (Athappan and Srivastava, 1980; Sharma and Srivastava, 1981). Reference will be made to the various models and notations as indicated in the preceding paper (Sharma and Srivastava, 1981). The reaction under study is:

$$\underset{(A)}{C_4H_9OH} + \underset{(B)}{1/2\,O_2} \rightarrow \underset{(R)}{C_3H_7CHO} + \underset{(W)}{H_2O}:\underset{(N)}{\text{Nitrogen}}$$

The converged values of the parameters of the rate models derived from Langmuir-Hinshelwood and modified Hinshelwood with all positive constants which had to be retained statistically after isothermal regressions are presented in Table 2A. The discrimination was basd upon the requirement that the kinetic and adsorption constants had to be positive. The models with the large approximate 95% confidence intervals for the various parameters have also been omitted because they were meaningless. The data were not satisfactorily correlated by model SSA-M, based on modified Hinshelwood mechanism. Although this model has close values of RSS and confidence limits with the remaining models of this table, the choice was based upon the requirement of the proper trend of the constants with the temperature. Based on the sequential experimentation procedures, model SA-2 has been rejected since partial pressure of oxygen has also been shown to influence the rate of reaction.

Table 2B gives the nonlinear estimates of the parameters of the two-step redox models with all positive constants. Model VK-4 satisfactorily explains the kinetic data. The variation in the constants of the remaining models, model VK-2 and model VK-5, showed an improper trend with temperature, and were therefore rejected.

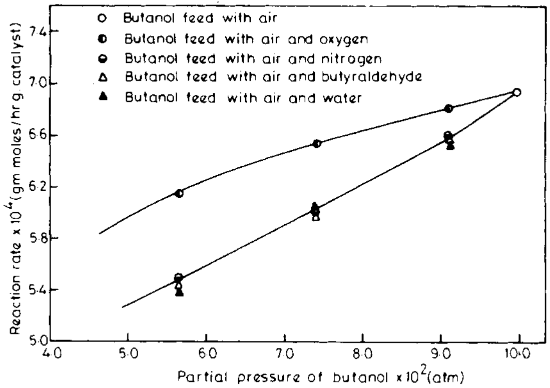

Figure 1. Partial rate data at 280°C, *W/F* = 40 g·h/mol.

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TABLE 1. SUMMARY OF EXPERIMENTS

No. of Series	Feed Composition, mol %			Space-Time g·h/mol^{-1}
	Butanol	Oxygen	Nitrogen	
5	0.056	0.198	0.746	40–80
5	0.074	0.194	0.732	40–80
5	0.090	0.190	0.720	40–80
Total Number of Experiments, 45				

Although modified Hinshelwood and two-stage redox mechanisms resulted in an identical rate expression, the significance of the parameters of the two models is different. Hinshelwood mechanism suggests that only adsorbed oxygen molecules or atoms are removed by reacting with the reductant molecules, which remain exclusively in the gas phase. According to this assumption, the specific rate of adsorption of oxygn k_B should be independent of the organic compound oxidized when the same catalyst is used. Since the same catalyst was used in the present work and for both toluene and methanol oxidations (Sharma and Srivastava, 1981), a check is available (Table 3). In contrast, the k_B values differed by an order of magnitude. The k_B value of butanol were extrapolated to the temperatures of toluene and methanol work.

On the other hand, the redox mechanism proposes the removal of actual lattice oxygen atoms by direct interaction with the reductant, which must hence be chemisorbed. In fact, the removal of lattice oxygen from V_2O_5 during the oxidation of butanol was observed by conducting a separate set of experiments when only butanol was allowed to pass over the catalyst; the color of the catalyst became black (characteristic of lower oxides of vanadium).

These may therefore be taken as supporting the view that the two-stage redox model is a useful one for this type of reaction; same rate expression (model VK-4) explained the kinetic behavior of methanol and toluene oxidation. This interpretation therefore provides a link between butanol, toluene and methanol oxidation on silica supported V_2O_5-K_2SO_4 catalyst.

TABLE 2A. ISOTHERMAL REGRESSION

Langmuir-Hinshelwood

Model	Temp. °C	k (gmol·h^{-1}·g^{-1}·atm^{-1})	K_B (atm^{-1})	K_R (atm^{-1})	Avg. Abs. % Error	R.S.S.
SA-2	240	(0.0063± 0.0001)		(149.7420 ± 24.4650)	0.237	0.3298× 10^{-8}
	260	(0.0083 ± 0.0002)		(148.5770 ± 24.8710)	0.908	0.8585 × 10^{-8}
	280	(0.0097 ± 0.0006)		(122.3300 ± 36.2351)	0.035	0.4457 × 10^{-7}
SB-2	240	(0.0018 ± 0.0004)		(181.5460 ± 184.4611)	0.036	0.3821 × 10^{-6}
	260	(0.0023 ± 0.0008)		(348.5270 ± 3.5155)	0.022	0.1130 × 10^{-5}
	280	(0.0026 ± 0.0012)		(381.5740 ± 11.88450)	0.013	0.1882 × 10^{-5}
SSAOD-4	240	(0.0119 ± 0.0005)	(41.6332 ± 12.7803)		0.011	0.1539 × 10^{-6}
	260	(0.0121 ± 0.0008)	(48.9660 ± 22.4930)		0.003	0.2649 × 10^{-7}
	280	(0.0187 ± 0.0282)	(5.7934 ± 174.8015)		0.005	0.1468 × 10^{-5}

Modified Hinshelwood

Model	Temp. °C	k (gmol·h^{-1}·g^{-1}·atm^{-1})	gmol·h^{-1}·g^{-1}·atm^{-1})	Avg. Abs. % Error	R.S.S.
SSA-M	240	(0.0059 ± 0.0004)	(0.0022 ± 0.0006)	0.056	0.3841 × 10^{-6}
	260	(0.0060 ± 0.0002)	(0.0032 ± 0.0001)	0.019	0.1358 × 10^{-8}
	280	(0.0156 ± 0.0004)	(0.0034 ± 0.0002)	0.016	0.2874 × 10^{-8}

SA-2 $r = \dfrac{kp_A}{(1 + K_Rp_R)}$

SSAOD-4 $r = \dfrac{kK_Bp_ap_B}{(1 + \sqrt{K_Bp_B})^2}$

SB-2 $r = \dfrac{kp_B}{(1 + K_Rp_R)}$

SSA-M $r = \dfrac{kk_Bp_Ap_B}{(k_Bp_B + \alpha kp_A)}$

TABLE 2B. TWO-STAGE REDOX MODELS

Model	Temp. (°C)	k_1 (gmol·h^{-1}·g.$^{-1}$·atm)	k_2 (gmol·h^{-1}·g.$^{-1}$·atm^{-n})	Avg. Abs. % Error	R.S.S.
VK-2	240	(0.0077 ± 0.0001)	(0.0008 ± 0.0001)	0.054	0.1972 × 10^{-8}
	260	(0.0111 ± 0.0002)	(0.0006 ± 0.0001)	0.018	0.1420 × 10^{-8}
	280	(0.0169 ± 0.0004)	(0.0005 ± 0.0001)	0.035	0.2557 × 10^{-8}
VK-4	240	(0.0059 ± 0.0004)	(0.0022 ± 0.0006)	0.056	0.3841 × 10^{-8}
	260	(0.0080 ± 0.0002)	(0.0032 ± 0.0001)	0.019	0.1358 × 10^{-8}
	280	(0.0156 ± 0.0004)	(0.0034 ± 0.0002)	0.016	0.2874 × 10^{-8}
VK-5	240	(0.0008 ± 0.0018)	0.0144 ± 0.0021)	0.050	0.9418 × 10^{-6}
	260	(0.0024 ± 0.0012)	(0.0009 ± 0.0021)	0.015	0.1410 × 10^{-5}
	280	(0.1615 ± 0.0052)	(0.0010 ± 0.0001)	0.016	0.1381 × 10^{-7}

$$\text{VK-2}\ r = \frac{k_1p_a}{\left(1 + \dfrac{\alpha k_1p_a}{k_2}\right)}$$

$$\text{VK-4}\ r = \frac{k_1p_A}{\left(1 + \dfrac{\alpha k_1p_a}{k_2p_B}\right)}$$

$$\text{VK-5}\ r = \frac{k_1{P_A}^{0.5}}{\left(1 + \dfrac{\alpha k_1{p_A}^{0.5}}{k_2{p_B}^{0.5}}\right)}$$

APPENDIX A: SUMMARY OF RATE DATA

Run No.	Average Partial Pressure (atm) Oxygen	Butanol × 10	Butyraldehyde × 10	Water × 10	Nitrogen	Avg. Reaction Rate × 10^3 ($g \cdot mol \cdot h^{-1} \cdot g^{-1}$)
			Average Temperature = 240°C			
1	0.1979	0.5619	0.0039	0.0039	0.7457	0.350
2	0.1978	0.5611	0.0046	0.0046	0.7451	0.333
3	0.1977	0.5602	0.0056	0.0056	0.7450	0.333
4	0.1976	0.5591	0.0066	0.0066	0.7449	0.330
5	0.1975	0.5585	0.0073	0.0073	0.7448	0.325
6	0.1941	0.7341	0.0063	0.0061	0.7312	0.429
7	0.1940	0.7330	0.0074	0.0074	0.7312	0.415
8	0.1939	0.7315	0.0088	0.0088	0.7311	0.410
9	0.1938	0.7299	0.0103	0.0101	0.7311	0.406
10	0.1937	0.7284	0.0086	0.0088	0.7178	0.402
11	0.1903	0.8988	0.8979	0.0106	0.7178	0.487
12	0.1902	0.8979	0.0106	0.0106	0.7178	0.470
13	0.1901	0.8958	0.0127	0.0127	0.7177	0.466
14	0.1900	0.8939	.00145	0.0145	0.7176	0.457
15	0.1899	0.8919	0.0170	0.0170	0.7175	0.448
			Average Temperature = 260°C			
16	0.1978	0.5609	0.0049	0.0049	0.7451	0.437
17	0.1977	0.5596	0.0062	0.0061	0.7450	0.440
18	0.1976	0.5584	0.0073	0.0073	0.7450	0.433
19	0.1976	0.5573	0.0084	0.0084	0.7449	0.428
20	0.1975	0.5560	0.0097	0.0097	0.7449	0.431
21	0.1939	0.7320	0.0079	0.0079	0.7312	0.537
22	0.1938	0.7307	0.0096	0.0096	0.7311	0.530
23	0.1937	0.7288	0.0114	0.0114	0.7330	0.516
24	0.1936	0.7269	0.0133	0.0133	0.7309	0.514
25	0.1935	0.7250	0.0147	0.0147	0.3709	0.512
26	0.1902	0.8976	0.0109	0.0109	0.7178	0.600
27	0.1900	0.8948	0.0136	0.0136	0.7177	0.600
28	0.1899	0.8924	0.0158	0.0158	0.7176	0.583
29	0.1898	0.8901	0.0181	0.0181	0.7175	0.571
30	0.1896	0.8654	0.0208	0.0208	0.7174	0.575
			Average Temperature = 280°C			
31	0.1977	0.5596	0.0062	0.0062	0.7450	0.550
32	0.1976	0.5581	0.0076	0.0076	0.7449	0.540
33	0.1975	0.5567	0.0090	0.0090	0.7449	0.533
34	0.1974	0.5552	0.0104	0.0104	0.7449	0.528
35	0.1973	0.5538	0.0118	0.0118	0.7446	0.525
36	0.1939	0.7325	0.0088	0.0088	0.7311	0.609
37	0.1937	0.7292	0.0111	0.0111	0.7320	0.607
38	0.1936	0.7269	0.0133	0.0133	0.3710	0.604
39	0.1935	0.7246	0.0155	0.0154	0.7319	0.602
40	0.1933	0.7223	0.0177	0.0177	0.7308	0.601
41	0.1901	0.8963	0.0120	0.1020	0.7177	0.662
42	0.1899	0.8957	0.0154	0.0154	0.7174	0.680
43	0.1898	0.8895	0.0186	0.0186	0.7175	0.683
44	0.1896	0.8863	0.0217	0.0217	0.7174	0.685
45	0.1894	0.8635	0.0244	0.0244	0.7172	0.675

TABLE 3. k_B VALUES

	320°	345°C	370°C
Butanol	4.6×10^{-3}	5.6×10^{-3}	6.7×10^{-3}
Toluene	1.1×10^{-3}	8.9×10^{-3}	1.5×10^{-2}
Methanol	9.1×10^{-3}	5.7×10^{-2}	9.2×10^{-2}

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