BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (10), 3061—3062 (1978)

Kinetic Evidence for the Participation of a Diatomic Oxygen Species in Vapor-Phase Oxidation of Butadiene over Silver Catalyst

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(Received February 15, 1978)

Synopsis. The participation of an adsorbed diatomic oxygen species in the oxidation of butadiene with O_2 or N_2O to maleic anhydride over silver catalyst was confirmed by the following finding: reaction order with respect to O_2 or N_2O is 0.83 or 1.95, respectively, whereas that to butadiene is negative.

Formation of O_2^- over reduced silver metal has been confirmed by means of ESR.[1–4] There are some observations showing that the diatomic oxygen species is active for epoxide formation.[4–7] However, no concrete evidence has been reported for the formation of the electronegative oxygen species during the course of oxidation of hydrocarbons over reduced silver metal. Our studies on the oxidation of furan over promoted anatase-titania catalyst revealed incorporation of oxygen atoms into maleic anhydride *via* the formation of O_2^-.[8] In this work, the formation of maleic anhydride in vapor-phase oxidation of butadiene with oxygen or nitrous oxide N_2O over silver catalyst has been kinetically investigated in order to confirm the formation of O_2^- during the oxidation.

Experimental

Vapor-phase catalytic oxidation of butadiene was carried out at 560—680 K using a conventional flow type fixed-bed reactor under atmospheric pressure. The shape of reactor and method of reaction were the same as those reported, and H_2O and CO_2 contained in air were removed in the same way as described.[8] Research grade butadiene (purity >99.9%) was used. Nitrogen, H_2, He and N_2O were supplied from commercial cylinders. Gas chromatographic analysis indicated a trace (≈0.4 vol%) of O_2 in the N_2O. The silver catalyst was prepared by reacting $AgNO_3$ with NaOH in an aqueous medium followed by the reduction of the silver oxide formed with 36% formalin at pH=11±0.5.[9] The surface area was <1.0 m^2 g^{-1}. The catalyst was reduced with H_2 (100 NTPml min^{-1}) at 583 K for 1.0 h prior to the experiment. The gaseous effluent from the reactor was analyzed by gas chromatography.[8] Since maleic anhydride was confirmed to be the only acid formed, the anhydride was absorbed in water, followed by boiling of the solution in order to remove dissolved CO_2 and by titration with an aqueous solution of NaOH. Carbon monoxide was not analyzed. X-Ray diffraction study was carried out using nickel-filtered Cu $K\alpha$ radiation (30 kV, 20 mA).

Results

Table 1 shows the effect of reaction temperature on the oxidation of butadiene over silver catalyst. The reaction initiated at ≈560 K. However, butadiene was preferentially converted into CO_2 with low yields of 2,5-dihydrofuran (2,5-DHF), furan (F) and maleic anhydride (MA). The selectivity to 2,5-dihydrofuran was negligible above 602 K but that to furan decreased gradually in contrast to that to maleic anhydride.

TABLE 1. EFFECT OF THE REACTION TEMPERATURE ON THE OXIDATION OF BUTADIENE OVER SILVER CATALYST[a)]

Reaction temp (K)	Conversion of C_4'' (%)	Yield of CO_2 (%)	Selectivity (%)		
			2,5-DHF	F	MA
561	1.4	0.2	8.3	8.3	5.1
578	5.4	2.2	15.2	4.0	5.3
591	21.0	17.1	1.0	1.2	6.6
602	34.2	31.1	0.0	0.9	6.7
612	39.0	34.0	0.0	1.0	7.8
630	40.7	35.5	0.0	0.7	7.6

a) Feed concentration: C_4'' 3.82 vol%, O_2 10.0 vol%, Contact time *W*/*F*: 0.202 g-cat·h g-mol^{-1}.

The steady state of silver catalyst during the course of oxidation at 583 K, *W*/*F*=0.249 g-cat·h g-mol^{-1} and the feed concentration of butadiene 3.85 vol% and O_2 10.0 vol% was quenched by introduction of helium (200 NTPml min^{-1}) for 5 min to eliminate the reactant gas followed by rapid decrease in temperature. X-Ray diffraction revealed that the catalyst consists of silver metal (2θ=38.15, 44.34, and 64.45°) and a small amount of Ag_2O (2θ=26.71°) and Ag_2O_2 (2θ=34.20 and 37.26°). This structure was kept even when the feed concentration of O_2 was increased to 14.0 vol% and the temperature to 635 K. Oxidation of butadiene with Ag_2O at 551 K by means of pulse technique gave only CO_2 and a small amount of acrylaldehyde.

The rate of maleic anhydride formation was kinetically studied using a differential reactor:

$$r(\mathrm{MA}) = k_1[C_4'']^{-0.21}[O_2]^{0.83} \quad \text{at 573 K} \qquad \text{(A)}$$

overall activation energy=32.3 kcal g-mol^{-1}
C_4'': 3.3—7.8 vol%, O_2: 7.0—14.6 vol%

where

TABLE 2. OXIDATION OF BUTADIENE WITH N_2O OVER SILVER CATALYST[a)]

Reaction temp (K)	Conversion of C_4'' (%)	Selectivity (%)		
		2,5-DHF	F	MA
606	7.9	0.8	0.0	2.0
633	13.4	1.2	0.0	4.1
637	17.7	1.3	0.0	4.6
660	49.1	1.1	0.0	4.9
679	45.6	0.8	0.0	4.1

a) Feed concentration: C_4'' 3.94 vol%, N_2O 20.0 vol%. Contact time *W*/*F*: 0.200 g-cat·h g-mol^{-1}. Yield of CO_2 was not determined because the retention times of CO_2 and N_2O were the same.

$r(\text{MA})$: initial rate of maleic anhydride formation,
k_1: overall reaction rate constant,
[ ]: concentration of butadiene or O_2 in the feed.

Formation of 2,5-dihydrofuran and maleic anhydride was also observed in the oxidation with N_2O (Table 2). Conversion of butadiene reached 49.1% at 660 K, but the selectivity to these oxidation products was low. The rate of maleic anhydride formation:

$$r(\text{MA}) = k_2[\text{C}_4'']^{-0.20}[\text{N}_2\text{O}]^{1.95} \quad \text{at } 613 \text{ K} \qquad \text{(B)}$$

overall activation energy = 28.5 kcal g-mol^{-1}
C_4'': 3.9—8.6 vol %, N_2O: 20.0—30.0 vol %

Discussion

The maximum conversion of butadiene (Tables 1 and 2) was attributed to the almost total consumption of O_2 or N_2O in the feed. 2,5-Dihydrofuran was postulated to be the first intermediate for maleic anhydride formation from butadiene: anhydride is formed from 2,5-dihydrofuran through two reaction paths, one *via* furan and the other *via* a direct path from 2,5-dihydrofuran.10) Furan and maleic anhydride formation is in line with the above reaction mechanism. On the other hand, a negligible change was observed in the structure of silver catalyst with rise in oxygen concentration in the feed and with rise in temperature. No selective oxidation products in the reduction of Ag_2O with butadiene at 551 K suggests an important role of adsorbed oxygen species formed on metallic silver in the formation of 2,5-dihydrofuran, furan and maleic anhydride. Our previous studies on the formation of maleic anhydride from butadiene show that the activation energy for 2,5-dihydrofuran formation is the highest, the step thus being rate-determining.10) Hence, the negative reaction order with respect to butadiene (A) indicates a competitive adsorption of butadiene with gaseous oxygen on the surface. The reaction of adsorbed species resulted in maleic anhydride formation. Accordingly, the reaction order with respect to gaseous oxygen, 0.83, is a strong indication of the reaction between an adsorbed diatomic oxygen species and adsorbed butadiene. Similarly, the negative reaction order with respect to butadiene (B) shows that the anhydride is formed through the Langmuir-Hinshelwood mechanism in the oxidation with N_2O as in the case with gaseous oxygen. Furthermore, as judged from the formation of $O_2$11) and O_2^- 2) in the catalytic decomposition of N_2O over reduced silver metal, the reaction order of N_2O, 1.95 (B), is an evidence for the participation of an adsorbed diatomic oxygen species in the anhydride formation.

Olefinic hydrocarbons adsorbed on metal oxide generally have positive charge.12) Since the surface of silver catalyst during the oxidation of butadiene is partially oxidized as shown elsewhere in this paper, the adsorbed butadiene species seems to be positively charged. It has not been clarified what kind of charge the adsorbed diatomic oxygen species has. However, judging from the ESR observation of O_2^- 1–4) and the addition of O_2^- to positively charged adsorbed furan species over promoted anatase-titania catalysts through a nucleophilic mechanism,8) the diatomic oxygen species seems to be O_2^-. The reaction of adsorbed neutral oxygen molecule ($^3\Sigma_g^-$) with adsorbed butadiene seems to be less probable, since the former is electrophilic and less nucleophilic as judged from the electron affinity of 0.15 eV,13) but it can not be denied either. The present work indicates the presence of an adsorbed diatomic oxygen species and its participation in the selective oxidation of butadiene over reduced silver catalyst. Oxygen atoms are possibly incorporated into maleic anhydride *via* the formation of this oxygen species. The oxygen species which promotes the complete oxidation of butadiene and serves to abstract hydrogen in maleic anhydride formation has not been clarified.

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