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Heats of Adsorption of Oxygen, Ethylene, and Butadiene on Al_2O_3-Supported Silver

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Heats of adsorption of oxygen on small, clean dispersed Ag crystallites have been measured directly. On the largest (27 nm) Al_2O_3-supported particles, the integral Q_{ad} values of 34–41 kcal mol^{-1} at 443 K were very consistent with those reported for Ag single crystals, and Q_{ad} increased to 50 kcal mol^{-1} on the smallest (3.7 nm) particles. The heats of adsorption measured at 300 K were slightly lower but showed the same trend with crystallite size. The heat of adsorption of ethylene on pure Al_2O_3 was 10.1 kcal mol^{-1} at 300 K, which, when combined with the sizable adsorption on the support, precluded any measurement on Ag; however, at 443 K a value of 10 kcal mol^{-1} could be estimated for C_2H_4 adsorption on clean Ag because adsorption on the support was significantly reduced. On an oxygen-covered Ag surface, Q_{ad} values for C_2H_4 were 5.2 and 64 kcal mol^{-1} at 300 and 443 K, respectively. Similar measurements for butadiene gave heats of adsorption of 10.9 and 13.1 kcal mol^{-1} on pure Al_2O_3 at 300 and 443 K, respectively, and on clean Ag at 443 K, the Q_{ad} value was 9 kcal mol^{-1}. On oxygen-covered Ag, Q_{ad} for butadiene was 21 kcal mol^{-1} at 300 K but, as with C_2H_4, it increased markedly to 65 kcal mol^{-1} at 443 K. The nearly identical values at 443 K for C_2H_4 and C_4H_6 on both clean and O-covered Ag imply a similar mode of bonding on each surface. The high values on the latter surface indicate a strong interaction with surface oxygen atoms, presumably involving only a single C=C bond.

INTRODUCTION

Silver plays a unique role as a partial oxidation catalyst, and it is used commercially to produce ethylene oxide from ethylene and molecular oxygen. However, the high selectivity to the epoxide in this reaction is not obtained when heavier olefins are used. This has been attributed to the presence of the more reactive allylic hydrogen atoms in the latter molecules; regardless, the adsorption bond strength of the olefin, as well as the oxygen, could also be important. Although a number of heat of adsorption values have been reported for O_2 on Ag, a value for ethylene on Ag was not available until recently, when it was determined for a Ag(110) surface (*1*), and no Q_{ad} values have been reported for other olefins. Only one study of O_2 heats of adsorption on supported Ag crystallites (on SiO_2) has been reported, and it was complicated by the presence of carbonaceous impurities (*2*). The measurement of Q_{ad} on clean, Al_2O_3-supported Ag crystallites is of interest not only because commercial catalysts are typically dispersed on Al_2O_3 but also because there is a possibility that Q_{ad} values may be dependent on crystallite size. Some evidence for both a difference in O_2 chemisorption and lower ethylene oxide turnover frequencies on very small Ag crystallites has already been reported (*3, 4*).

This study was undertaken to measure O_2 heats of adsorption over a range of crystallite size, to compare these values with those in the literature for bulk silver, and to determine if any change occurs on Ag crystallites as their size decreases below 10 nm. In addition, we wanted to obtain Q_{ad} values for C_2H_4 and C_4H_6 on both clean and oxygen-covered Ag particles, especially be-

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cause a comparison of the latter two values could provide information about the bonding state of butadiene.

EXPERIMENTAL

Two alumina supports were used to disperse the silver. The η-Al_2O_3 (from Exxon Research and Engineering Co., 220 m^2g^{-1}) was ground and the -100 mesh cut was heated at 823 K in flowing air for 2 h prior to impregnation by an incipient wetness method (0.50 ml g^{-1}). To reduce olefin adsorption on the support, a sintered alumina was prepared by calcining a sample of this η-Al_2O_3 at 1273 K in flowing air for 8 days. This support, designated Al_2O_3(S), had a surface area of 70 m^2 g^{-1} and required 0.84 ml g^{-1} for impregnation. The solution used was $AgNO_3$ (Aldrich Co., 99.999%) dissolved in doubly distilled, deionized water. After impregnation, the samples were dried in air at 383 K, bottled, and stored in a desiccator.

Oxygen chemisorption and H_2 titration measurements were performed in a stainless steel adsorption system equipped with an Edwards Diffstak MK2 diffusion pump capable of a vacuum down to 10^{-8} torr. Sample temperatures were regulated by a furnace and temperature programmer/controller (Theall Engineering), and isotherm pressure readings were obtained with a Texas Instruments pressure gage. Further details have been given elsewhere (*5–7*). Chemisorption measurements of ethylene and butadiene were made in a separate stainless steel adsorption system equipped with a Balzers TSU-171 turbomolecular pump, which provided an ultimate vacuum near 5×10^{-9} torr, and isotherm pressures were obtained using an MKS Baratron Model 310 capacitance manometer. Details have been given previously (*8*).

The calorimetry system utilized a modified P–E DSC-2C differential scanning calorimeter operated isothermally. All gas flows were regulated by mass flow controllers (Tylan, Model FC260), and the Ar and He carrier gases (MG Scientific, 99.999%) could be mixed to give stable baseline behavior when an adsorbate was introduced (*9*). The exit stream of the calorimeter was analyzed with a mass spectrometer (UTI Model 100c) attached to a Balzers TSU-171 turbomolecular pump. This verified the absence of leaks into the system and guaranteed that the purge times used were sufficient to remove all unwanted gas-phase molecules from the DSC sample and reference cavities.

Adsorption measurements were conducted on samples (ca. 1 g) which had been given seveal cycles of a standard pretreatment to obtain stable O_2 uptakes. This pretreatment involved an initial calcination step in 10% O_2 at 773 K, reduction in flowing H_2 at 673 K, then evacuation at 673 K for 10 min before cooling in vacuum. Details are listed elsewhere (*6*). Asorption was then conducted at either 443 or 300 K between 10 and 200 torr. Olefin adsorption always followed the O_2 adsorption and H_2 titration experiments and it was sometimes conducted on an oxygen-covered Ag surface following an O_2 isotherm. The only difference in procedure was the longer evacuation time of 1 h following the first isotherm to ensure complete removal of weakly adsorbed olefin species. Olefin adsorption at 443 K was chosen because this is an optimum temperature for monolayer oxygen coverage (*4–7*).

From this larger, well-characterized, stable sample, small (50–100 mg) quantities were placed in the DSC for calorimetric measurements. The identical pretreatment was utilized except that reduction was in 20% H_2/80% Ar and a purge time of 1 or 3 h following reduction was used instead of a 20-min evacuation period. Some oxygen exotherms were obtained at 9 torr (Series I), and the base Ar carrier gas was flowed at 79 cm^3 min^{-1} while the make-up stream was switched from 1 cm^3 min^{-1} Ar to 1 cm^3 min^{-1} O_2. In the other case, the exotherms were obtained at 65 torr O_2 (Series II); then the base Ar flow rate was 32 cm^3 min^{-1} and the makeup stream was switched from a mixture of 2.9 cm^3 min^{-1} Ar and 0.1 cm^3 min^{-1}

He to 3 cm^3 min^{-1} O_2. This minimized baseline perturbations. In similar fashion, ethylene measurements were made at 19 torr using 78 cm^3 min^{-1} Ar and 2 cm^3 min^{-1} C_2H_4, while butadiene exotherms were obtained under 38 torr using 36 cm^3 min^{-1} Ar and 2 cm^3 min^{-1} C_4H_6. A purge time of 1 h at 80 cm^3 min^{-1} Ar was used between the first and second olefin exotherm measurements. The gases used were H_2 (from an Elhygen Mark V H_2 generator, 10 ppb impurities) and H_2 (99.999%),O_2 (99.999%), C_2H_4 (99.5%), and 1,3-C_4H_6 (99%)–all from MG Scientific Gases. All gases except the olefins were passed through drying tubes (Supleco Inc.) and the Ar and He also passed through Oxytraps (Alltech Assoc.). Additional details are provided elsewhere (*9, 10*).

RESULTS

Silver analyses by atomic absorption (AA) measurements gave weight loadings of 11.8% Ag/η-Al_2O_3 and 18.8% Ag/Al_2O_3(S) for the initial catalysts as taken from the desiccator. Weight losses during pretreatment were found to be 10.3 and 14.1%, respectively, thus giving weight loadings of 13.2% Ag/η-Al_2O_3 and 21.9% Ag/Al_2O_3(S) on a dry basis. AA analyses on these samples following O_2 chemisorption measurements gave 12.8 and 21.3%, which are good agreement, especially since a small amount of water could have readsorbed while the latter samples were weighed. Both uptakes and energy changes were normalized to the dry basis.

O_2 Adsorption and Titration

Periodic chemisorption measurements were conducted on these catalysts to verify that no loss in Ag surface area occurred. These samples were very well behaved, as shown in Fig. 1 and the summary of adsorption results in Table 1, and the titration ratios are very close to 2, as expected (*5–7*). On the pure η-Al_2O_3, no irreversible oxygen chemisorption occurred at 300 K and a negligible amount (0.4 μmol/g cat) was observed at 443 K (*10*). To more closely duplicate the adsorption process in the DSC, which gave exotherms with some tailing after a step change to a given O_2 partial pressure (for examples, see Fig. 5), time-dependent O_2 uptakes such as those in Fig. 2 were measured at pressures close to those used in the DSC (*10, 11*). These uptakes were used to calculate ΔH_{ad} values in kcal mol^{-1} after a specified exposure time in the DSC, and they were found to be constant over a 15-min period (*10*); consequently, 3 min was chosen as an appropriate period to characterize the adsorption process.

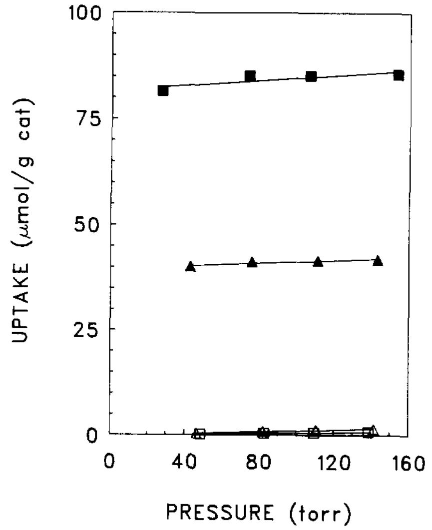

FIG. 1. O_2 adsorption and H_2 titration isotherms on 11.8% Ag/η-Al_2O_3 at 300 K. Total H_2, ■; reversible H_2, □; total O_2, ▲; reversible O_2, △.

Olefin Chemisorption

Substantial amounts of olefin adsorption on the alumina, some of it irreversible, complicated these experiments and made them very difficult to conduct quantitatively. For example, both total C_2H_4 uptake and irreversible adsorption at 443 K on the η-Al_2O_3 itself were greater than those on 11.8% Ag/η-Al_2O_3. This was the reason for sintering the η-Al_2O_3–to decrease the adsorption capacity of the support relative to the Ag. Ethylene adsorption on the sintered Al_2O_3(S) sample at 300 and 443 K was re-

TABLE 1

Oxygen Adsorption, H_2 Titration, and Isothermal Energy Changes for Ag Catalysts

Sample	T(K)	Gas uptake (μmol/g cat)					Dispersion (O_{ad/Ag_t})	$E^{b,c,d}$ (mcal/g cat)	Q_{ad} (kcal/mol O_2)
		O_2[a]	H_2 titr.[a]	H_2/O_2	O_2[b]	O_2 after 3 min[b]			
11.8% Ag/η-Al_2O_3 (I)	300	34.5 ± 1.2	77 ± 7	2.0	38.5	30.0	0.18	1146 ± 68	38 ± 2
	443	99 ± 14	195 ± 13	2.0	110	76.1	0.18	3264 ± 561	43 ± 7
11.8% Ag/η-Al_2O_3 (II)	300	33.2	67.3	2.0	37.0	30.0	0.18	1263 ± 17	42 ± 1
	443	100	204	2.0	112	76.1	0.18	3418 ± 105	45 ± 1
18.8% Ag/Al_2O_s(S) (I)	300	16.9 ± 3.0	33	2.1	20	—	0.050	—	—
	443	44.0 ± 6.3	98 ± 11	2.2	51	37.4	0.050	1274 ± 71	34 ± 2
18.8% Ag/Al_2O_3(S) (II)	300	18.7	39.0	2.1	21.8	17.6	0.050	564 ± 43	32 ± 2
	443	43.6	88.0	2.0	50.8	37.4	0.050	1534 ± 28	41 ± 1
1.5% Ag/η-Al_2O_3 (II)	300	9.7 ± 0.2	19.8 ± 0.2	2.0	10.8	9.2	0.37	387 ± 51	42 ± 6
	443	26.0 ± 0.9	43.4 ± 1.3	1.7	29.0	21.3	0.37	1063 ± 194	50 ± 9

[a] Average value ± standard deviation from final isotherm, based on initial sample weight.

[b] Based on dry sample weight.

[c] The second (reversible) adsorption run gave $\Delta E \cong 0$; values are averages with standard deviations.

[d] Series I, P_{O_2} = 9 torr; Series II, P_{O_2} = 65 torr.

versible within experimental uncertainty and not affected by the exposure to O_2 that occurs during an oxygen isotherm measurement (*10*). One set of these isotherms is shown in Fig. 3a. Comparable isotherms on the 18.8% Ag/Al_2O_3(S) sample are provided in Fig. 3b, and they show that C_2H_4 adsorption is greater on this catalyst than on pure alumina at each temperature and completely reversible at 300 K, but that a small amount of irreversible adsorption occurs at 443 K. However, C_2H_4 adsorption on an oxygen-covered Ag surface is significantly higher and a large fraction is irreversibly adsorbed at each temperature, as shown in Fig. 3c. Mass spectrometric analyses were taken continuously during these runs in the calorimeter, and no evidence of ethylene oxide or CO_2 formation was observed at any time (*10*). The uptakes on the pure Al_2O_3(S) and the 18.8% Ag/Al_2O_3(S) sample, abstracted at the pressure at which the calorimetric measurements were made, are listed in Table 2. Comparable values for the 11.8% Ag/η-Al_2O_3 sample are listed elsewhere (*10*).

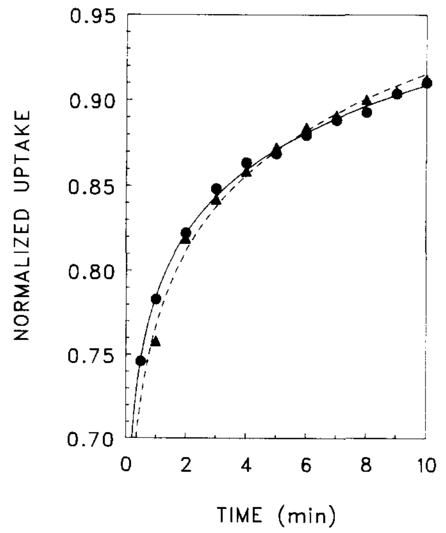

FIG. 2. Rate of oxygen adsorption on 1.7% Ag/Al_2O at 300 K (normalized to saturation uptake in Table 1). P = 63 torr: ●, solid line; P = 9 torr: ▲, dashed line.

The adsorption of 1,3-butadiene on Al_2O_3(S) and 18.8% Ag/Al_2O_3(S) equilibrated rapidly at either 300 or 443 K. Uptakes of C_4H_6 on pure Al_2O_3(S) were much higher than those for C_2H_4 at either 300 or 443 K, and it was nearly all reversible at 300 K, whereas a substantial amount was

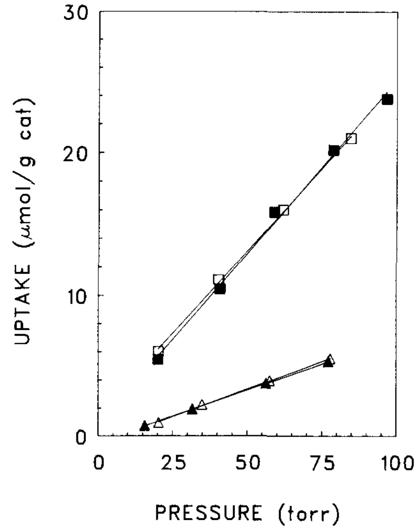

FIG. 3a. Adsorption isotherms for ethylene on Al_2O_3(S). T = 300 K: total C_2H_4, ■; reversible C_2H_4, □. T = 443 K: total C_2H_4, ▲; reversible C_2H_4, △.

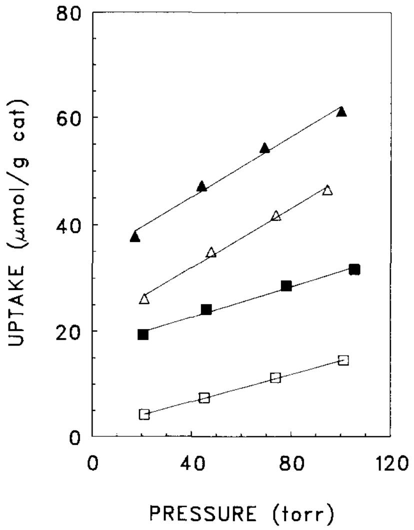

FIG. 3c. Adsorption isotherms for ethylene on oxygen-covered 18.8% Ag/Al_2O_3(S). T = 300 K: total C_2H_4, ▲; reversible C_2H_4,△. T = 443; total C_2H_4, ■; reversible C_2H_4, □.

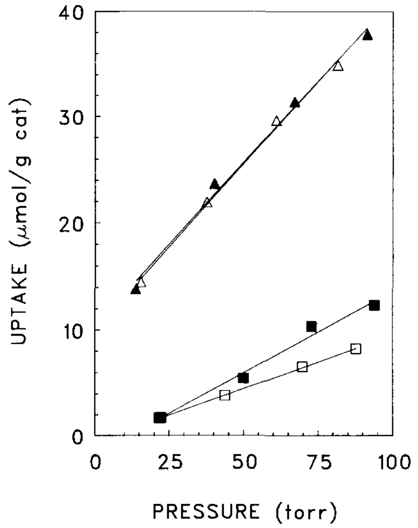

FIG. 3b. Adsorption isotherms for ethylene on 18.8% Ag/Al_2O_3(S). T = 300 K: total C_2H_4, ▲; reversible C_2H_4, △. T = 443 K: total C_2H_4, ■; reversible C_2H_4, □.

irreversibly adsorbed at 443 K, as shown in Fig. 4a. However, at either temperature both the total and the irreversible uptakes increased on the 18.8% Ag/Al_2O_3(S) sample, as indicated in Fig. 4b. Adsorption of C_4H_6 on an O-covered Ag surface significantly increased the amount of irreversibly adsorbed C_4H_6 at either temperature, as shown in Fig. 4c. Again, time-dependent uptakes were also measured (*10*), and both sets of butadiene uptakes are listed in Table 3.

Calorimetric Measurements

The samples placed in the calorimeter had already been pretreated several times in the adsorption system; hence all energy changes were normalized to the dry weight. Because the O_2 chemisorption on Ag was irreversible with only a negligible amount of reversible adsorption on the support, the exotherms were relatively straightforward to obtain with either support, as indicated by the example in Fig. 5. However, a slower uptake process follows the rapid initial adsorption, which is well known in the literature, and this complicates these measurements. To minimize this difficulty and to focus on the initial adsorption, these exotherms were integrated over the first 3-min period, during which time most of the uptake occurred (see Fig. 2), and the results

TABLE 2

Ethylene Adsorption on Al_2O_3 and Al_2O_3-Supported Ag at 300 and 443 K Before and After O_2 Chemisorption

Sample	T(K)	Gas uptake[a] (μmol/g catalyst)		ΔE (mcal/g catalyst)		Q_{ad} (kcal/mol)
		Rev.[b]	Irrev.	Total	Rev.	
Al_2O_3(S)						
Clean	300	6.4	0	63[e]	67[e]	10.1 ± 0.3
	443	1.2	0	—	—	—
O_2-exposed	300	8.1[c]	0[c]	—	—	—
	443	0.6[d]	0.8[d]	—	—	—
18.8% Ag/Al_2O_3(S)[f]						
Clean	300	16.3	0	—	—	Not determined
	443	2	4	250 ± 45	210	10
O-covered	300	43[d]	55.9[d]	502 ± 144	213 ± 5	5.2 ± 2.6
	300	30.3[c]	16.1[c]	—		
	443	3.5[d]	19.1[d]	2234 ± 5	1014 ± 223	64 ± 11

[a] Based on weight of dried catalyst.
[b] At 19 torr.
[c] O_2 preadsorbed at 300 K.
[d] O_2 preadsorbed at 443 K.
[e] With glass beads in reference cavity.
[f] Corrected for adsorption on the support.

are listed in Table 1. Oxygen adsorption is known to be time-dependent under these conditions (*6, 10, 11*), but extending the integration time to include more of the tail had no influence on Q_{ad} values when the appropriate time-dependent O_2 uptake was used (*10*); therefore, the shorter time period was routinely used. This also reduced any errors attributable to small baseline shifts in the region with the long tail.

Calorimetric measurements of C_2H_4 adsorption were complicated by the significant amount of reversible adsorption that occurred on both the Ag and the support, and the η-Al_2O_3 could not be used at all for this reason. The Ag/Al_2O_3(S) sample gave exotherms such as those in Fig. 6, which represents the most favorable conditions, and from integrating a series of these peaks the average values (± standard deviations) in Table 2 were obtained. During measurements with the 18.8% Ag/Al_2O_3(S) catalyst, an equal amount of pure Al_2O_3(S) was placed in the reference cavity to compensate for reversible adsorption on the support; however, the high loading of Ag appeared to alter the support surface to such an extent that such compensation did not seem to be appropriate in many cases. The energy changes for Al_2O_3(S) itself were then acquired using an equal weight of nonporous glass beads ($0.1 m^2/g$) in the reference cell because adsorption on this low surface area silica was minimal.

With butadiene the difficulties that existed with ethylene were compounded by both the very large reversible uptakes on the support, which were sometimes larger than those on the catalyst, and the measurable irreversible adsorption on the support. The coverage of surface sites on the Al_2O_3(S) by the Ag made accurate cancellation of adsorption on the support uncertain. To accommodate this situation, additional runs using the nonporous glass beads in the reference side were conducted, and energy changes due to butadiene adsorption on both the Ag/Al_2O_3(S) catalyst and the pure

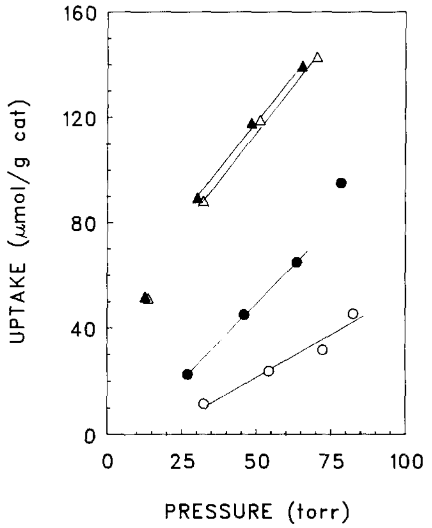

FIG. 4a. Adsorption isotherms for butadiene on Al_2O_3(S). $T = 300$ K: total C_4H_6, ▲; reversible C_4H_6, △. $T = 443$ K: total C_4H_6, ●; reversible C_4H_6, ○.

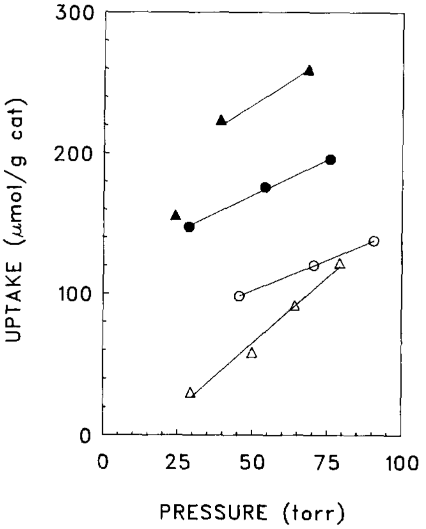

FIG. 4c. Adsorption isotherms for butadiene on oxygen-covered 18.8% Ag/Al_2O_3(S). $T = 300$ K: total C_4H_6, ●; reversible C_4H_6,○. $T = 443$ K: total C_4H_6, ▲; reversible C_4H_6, △.

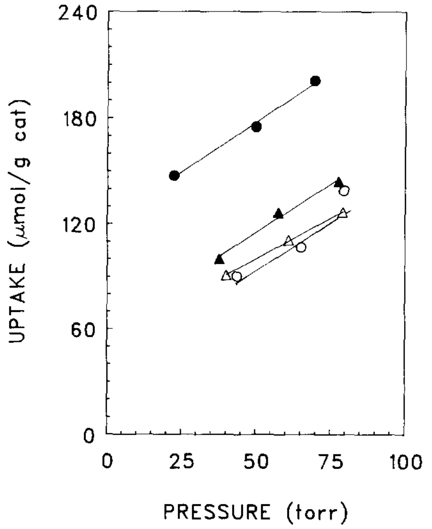

FIG. 4b. Adsorption isotherms for butadiene on 18.8% Ag/Al_2O_3(S). $T = 300$ K: total C_4H_6, ▲; reversible C_4H_6, △. $T = 443$ K: total C_4H_6, ●; reversible C_4H_6, ○.

support were measured. Such a set of exotherms is shown in Fig. 7, and the results are listed in Table 3. As mentioned earlier, mass spectrometric analyses were conducted continuously during exotherm measurements, and no oxidation products were detected at any time.

DISCUSSION

O_2 *Adsorption*

Oxygen chemisorption on unsupported silver has been extensively studied and numerous heat of adsorption (Q_{ad}) values have been reported varying from 12 to over 100 kcal mol^{-1} (*12–24*), as shown in Table 4. In some cases, integral Q_{ad} values could be estimated from the data given. This wide range of values can at least partially be attributed to surface contamination and the purity of the Ag samples, particularly in the older studies, and slow adsorption processes must also have affected these measurements. However, even among the more recent UHV studies, initial Q_{ad} values have ranged from 22 to 45 kcal mol^{-1}. Surprisingly, only one investigation has addressed dispersed Ag systems (*2*), and this study by Auroux and Gravelle reported extremely high Q_{ad} values, as shown in Table 4. However, they found that their catalysts contained significant amounts of carbonaceous

TABLE 3

Adsorption of 1,3-Butadiene on Al_2O_3 and Al_2O_3-Supported Ag

Sample	T(K)	C_4H_6 uptake (μmol/g catalyst)[a]				ΔE (mcal/g catalyst)		Q_{ad} (kcal/mol)	
		From isotherms		After 3 min.		Total	Rev.	Total	Irrev.
		Rev.	Irrev.	Rev.	Irrev.				
Al_2O_3(S)	300	90	3	114	2	1265 ± 48[b]	1101 ± 91[b]	10.9	82
	443	17	20	11	5	210 ± 19[b]	97 ± 77[b]	13.1	23
18.8% Ag/Al_2O_3(S)									
Clean	300	86	17	97	16	230 ± 35[c]	96 ± 6[c]	—	18[d]
						1348 ± 310[b]	712 ± 87[b]	—	35
	443	89	71	21	13	80 ± 15[c]	64 ± 7[c]	—	9[d]
O-covered	300	91	65	97	57	208 ± 89[c]	114 ± 38[c]	—	4[d]
						2392 ± 68[b]	1112 ± 24[b]	—	21
	443	47	170	17	32	623 ± 47[c]	0[c]	—	23[d]
						1929 ± 370[b]	0[b]	—	65

[a] At 38 torr, based on weight of dry catalyst.

[b] Energy change with glass beads as reference.

[c] Energy change with Al_2O_2(S) as reference.

[d] Estimated *minimum* value assuming no irreversible adsorption on the catalyst support.

impurities (formaldehyde was used in their preparation) and, although they tried to correct for this complication, it is very likely these high values are attributable to the oxidation of these impurities. The measurement of O_2 heats of adsorption on small, clean, supported Ag crystallites was the main purpose of this study. Of particular interest is the question of whether Q_{ad} values for O_2 are dependent on crystallite size be-

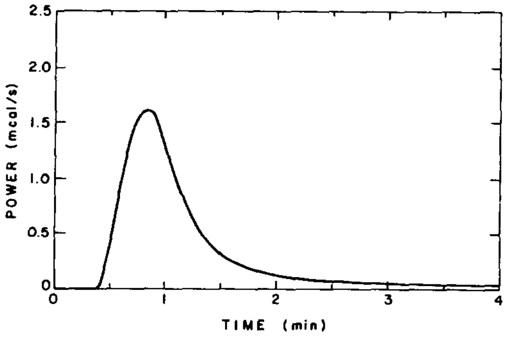

FIG. 5. Calorimeter exotherm for oxygen adsorption on 11.8% Ag/η-Al_2O_3. T = 300 K, P_{O_2} = 19 torr.

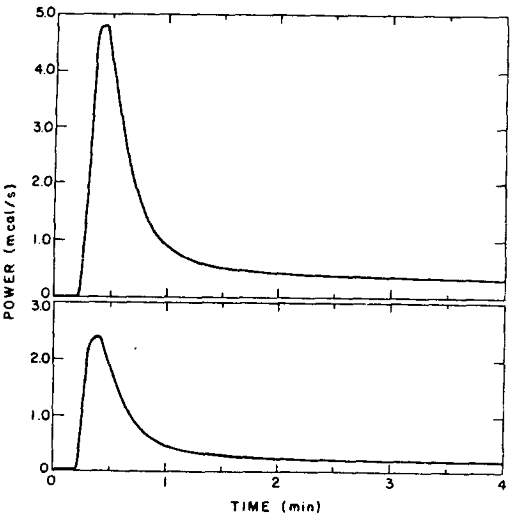

FIG. 6. Calorimeter exotherms for ethylene adsorption on oxygen-covered 18.8% Ag/Al_2O_3(S). T = 443 K, P = 38 torr, Al_2O_3(S) in reference cavity. Upper, initial C_2H_4 adsorption; lower, reversible C_2H_4 adsorption.

TABLE 4

Reported Heat of Adsorption Values for Oxygen on Silver Surfaces

Adsorption temperature (°C)	Ag sample	Initial Q_{ad} (kcal/mol)	Estimated integral Q_{ad} (kcal/mol)	Reference
170	Powder	17		(*12*)
170	Reduced AgO	12–17		(*13*)
170	Ag alloy with Ca and Ni	27–29		(*14*)
100	Powder	46	25	(*15*)
>150	Powder	22–24		(*16*)
110	Powder	125	22	(*17*)
25	Ag (111)	35–45		(*18*)
200	Powder	80	32	(*19*)
25	Ag (110)	40		(*20*)
170	Ag (110)	22		(*21*)
170	Powder	18.4	16	(*22*)
191	Reduced silver carbonate	48	30	(*23*)
227	Ag (111)	40.8		(*24*)
227	Ag (110)	44		(*24*)
200	Ag/SiO_2	70–120	49–92	(*2*)

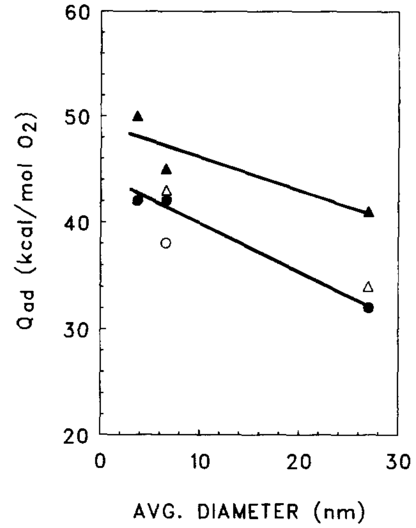

FIG. 8. Heat of adsorption of O_2 on Ag versus average crystallite size. T = 443 K: Series I, △; Series II, ▲. T = 300 K: Series I, ○; Series II, ●. (See Table 1 for details.)

cause the interaction with very small Ag particles could be different (*3*), and turnover frequencies are two orders of magnitude lower on small crystallites although the selectivity is little different (*4*).

The isothermal energy changes and the O_2 uptakes are listed in Table 1. By taking these integral values and the uptakes after 3 min, the Q_{ad} values in Table 1 are obtained. If the Ag dispersions measured by O_2 chemisorption at 443 K are used to determine crystallite size, its influence on the O_2 heat of adsorption is shown in Fig. 8. The Q_{ad} values on the largest Ag crystallites (27 nm) are in excellent agreement with the values of 35–45 kcal mol^{-1} determined on Ag single crystals under UHV conditions (*18, 20, 24*). As expected, values at 300 K are consistently lower than those at 443 K. Despite the greater uncertainty associated with the Q_{ad} values for the smallest crystallites, the results in Fig. 8 indicate that the heat of adsorption of O_2 on Ag exhibits a small but distinct increase as crystallite size decreases below 10 nm, and the increase is observed at both 300 and 443 K. Further study is required to obtain a detailed explanation, but these results may reflect the fact that oxygen chemisorption produces a larger enthalpy change than bulk Ag oxide formation, and subsurface oxygen will be diminished or eliminated in very small Ag particles. Regardless, these smaller Ag crystallites ex-

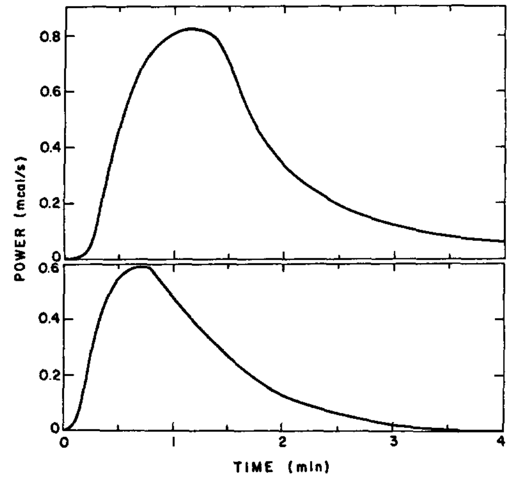

FIG. 7. Calorimeter exotherms for butadiene adsorption on 18.8% Ag/Al_2O_3(S). T = 300 K, P = 38 torr, glass beads in reference cavity. Upper, initial C_4H_6 adsorption; lower, reversible C_4H_6 adsorption.

hibit higher Q_{ad} values as well as lower turnover frequencies (*4*); therefore, it is possible that stronger Ag–O bond strengths result in lower specific activities. This conclusion is also supported by the study of Auroux and Gravelle (*2*).

Ethylene Adsorption

The Q_{ad} values calculated for ethylene on pure alumina and Ag surfaces are listed in Table 2. On pure alumina, C_2H_4 adsorption was reversible (Fig. 3a) and the average Q_{ad} of 10.1 kcal mol^{-1} is quite resonable and consistent with Q_{ad} values of 10–14 kcal mol^{-1} reported for C_2H_4 on MoO_3/Al_2O_3 catalysts (*25*). A value of 18 kcal mol^{-1} for C_2H_4 adsorption on an *unreduced* Ag–X zeolite has also been determined (*26*).

We emphasize that the extraction of heat of adsorption values for C_2H_4 on clean Al_2O_3(S)-supported Ag surfaces was complicated by the significant amount of reversible adsorption on the support, a Q_{ad} value on the alumina comparable to that on the silver, and uncertain cancellation of adsorption on the support by the reference Al_2O_3(S) because of the high Ag loading in the Ag/Al_2O_3(S) sample. This prevented a quantitative determination of Q_{ad} at 300 K because these runs were not conducted with the nonporous beads as the reference, and it can only be said that this value is low. However, at 443 K the amount of C_2H_4 on alumina was very small and the extrapolated zero-pressure value was zero (see Fig. 3a); therefore, an estimate of Q_{ad} could be obtained if the amount of ethylene adsorbed on the Al_2O_3(S) surface in the catalyst was assumed to be identical to that adsorbed on the pure support. This value of 10 kcal mol^{-1} has much uncertainty associated with it, but it is near the Q_{ad} of 8.9 kcal mol^{-1} reported by Campbell and Paffett after adsorption at 134 K on a Ag(110) surface (*1*).

Fortunately, C_2H_4 adsorption on an oxygen-covered surface is much greater and also stronger (*1, 27,28*), and the significant irreversible uptakes allowed Q_{ad} values of 5.2 ± 2.6 kcal mol^{-1} and 64 ± 11 kcal mol^{-1} at 300 and 443 K, respectively, to be determined. The integral value at 300 K is low but not unreasonable compared to the initial value of 10.7 kcal mol^{-1} reported for C_2H_4 adsorbed at 134 K on an O-covered Ag(110) surface (*1*), and it is also in reasonable agreement with the range of 8–13 kcal mol^{-1} determined by Akimoto *et al.* for C_2H_4 on O-covered Ag powder at 273 K using a chromatographic technique (*28*). Perhaps the most interesting aspect of this study of ethylene adsorption is the dramatic increase in the adsorption exotherm when the temperature is increased to 443 K. The Q_{ad} value of 64 kcal mol^{-1} implies that the interaction between C_2H_4 and an O-covered Ag surface is markedly strengthened; however, no gas-phase products were detected by mass spectroscopy, and thus whatever species formed remained on the surface. This behavior is consistent with a model in which the C=C bond in the initial weakly π-bonded molecule is broken and a much more strongly bound species is formed by an interaction between C and O atoms. As monolayer oxygen coverage on this catalyst was 102 μmol O_{ad}/g catalyst (118 μmol O_{ad}/g dry catalyst), the C_2H_4 coverage on this surface constitutes about one-half a monolayer. If the preadsorbed oxygen layer is formed at 300 K instead (Table 1), then after ethylene adsorption on this surface the $C_2H_{4\,ad}/O_{ad}$ ratio is one-third. Thus there are at least two surface oxygen atoms per ethylene molecule to react to form a strongly adsorbed intermediate at 443 K. Further evidence of such an intermediate is provided by a recent CP MAS NMR study of $^{13}C_2H_4$ adsorbed on oxygen-covered Ag/Al_2O_3, which has provided spectra with chemical shifts indicative of acetate species (*11*).

Butadiene Adsorption

The butadiene isotherms for Al_2O_3 were well behaved, exhibited Henry's law behavior above 25 torr, and demonstrated large amounts of adsorption at 300 K, almost all of which was reversible. The reversible adsorption on Al_2O_3 decreased markedly at

443 K while the irreversibly adsorbed butadiene increased somewhat, as shown in Table 3. As with ethylene, adsorption increased significantly on oxygen-covered Ag surfaces, and the irreversible uptake of butadiene at 300 K was nearly the same as that of ethylene (65 vs 56 μmol/g catalyst), again giving one-half monolayer. However, in contradistinction with C_2H_4, sizeable amounts of butadiene also adsorbed irreversibly on the clean Ag surface.

Calculated heats of adsorption for butadiene are also listed in Table 3. On pure Al_2O_3, the first exotherm at 300 K gave a heat of adsorption of 10.9 kcal mol^{-1} and the second one gave 9.7 kcal mol^{-1}; thus these values are quite similar to those for ethylene and agree well with a Q_{ad} of 8 kcal mol^{-1} for butadiene on SiO_2 (*29*) and values of 8–15 kcal mol^{-1} on other oxide surfaces (*30, 31*). At 443 K, more strongly bonded species are favored and C_4H_6 adsorption on clean Al_2O_3 gave an overall Q_{ad} of 13.1 kcal mol^{-1}, while readsorption after evacuation gave 8.8 kcal mol^{-1}. Both sets of data imply that there is a low concentration of sites on this amorphous Al_2O_3 surface that can coordinate C_4H_6 very strongly, and Q_{ad} values of 82 and 23 kcal mol^{-1} for this irreversibly adsorbed butadiene can be calculated at 300 and 443 K, respectively.

No measurements of Q_{ad} values for butadiene on any metal surface are available in the literature; however, a value of 13 kcal mol^{-1} on Ag(111) has recently been reported (*32*). Also, in their SERS study of this molecule on silver films Itoh *et al.* reported more than one adsorbed state, with the strongest interaction associated with Ag^+ sites induced by preadsorbed oxygen (*33*). Because of the alteration by the silver of both the total and reversible C_4H_6 uptakes on the alumina support, determination of Q_{ad} values was not straightforward, as it was with O_2 adsorption. However, with certain assumptions, such values can be calculated (*10*). The most meaningful values are those obtained from the series of experiments with glass beads in the reference cavity. Only the assumption that the irreversible adsorption on the Al_2O_3(S) remains unaltered by the Ag is required to allow the uptake values in Table 3 to be used in the following energy balance to calculate the irreversible heat of adsorption of C_4H_6 on Ag,

$$(\text{Irrev. Ads.}_{\text{Ag}})\,(Q_{\text{Ag,Irrev.}}) + (\text{Irrev. Ads.}_{\text{Al}_2\text{O}_3})(Q_{\text{Al}_2\text{O}_3,\text{Irrev.}}) = (\text{Total }\Delta E) - (\text{Rev. }\Delta E),$$

where the first term represents the exotherm from irreversible adsorption on the Ag and the second term represents the exotherm from irreversible adsorption on the Al_2O_3. This gives values of 35 kcal mol^{-1} on clean Ag at 300 K and 21 and 65 kcal mol^{-1} on O-covered Ag at 300 and 443 K, respectively, as shown in Table 3. Because the contribution from the support is relatively small, even if all the irreversible uptake is attributed to the Ag, these values do not change much.

The Q_{ad} values estimated from the series of runs with Al_2O_3(S) as the reference material are more uncertain because more assumptions are required, and the ensuing energy balance is more complicated (*10*). However, if no irreversible adsorption is assumed to occur on the catalyst support and the reversible adsorption on the catalyst support is assumed to be unaltered, estimates of Q_{ad} values on Ag and O-covered Ag can be made. These can only be considered as *minimum* estimates because the isotherms showed that adsorption on the support can be decreased by the presence of the Ag. Indeed, if reductions in the reversibly adsorbed butadiene on alumina are also considered, these values increase further (*10*). Both the calculated Q_{ad} values and the minimum estimates are tabulated in Table 3.

The variances between the minimum values estimated using pure Al_2O_3(S) as the reference material and those obtained with glass beads as the reference are almost certainly caused by a change in the amount of C_4H_6 adsorbed on the Al_2O_3. This could be caused either by the presence of the Ag or possibly by the repeated cycling of the

Al_2O_3(S) reference or both; consequently, the values obtained with the glass beads may be somewhat preferable. Regardless, each set mirrors the same trend—Q_{ad} values for butadiene on O-covered Ag at 300 K appear to be lower than Q_{ad} values on clean Ag, but adsorption at 443 K greatly increases the heat of adsorption on O-covered Ag, whereas it may even decrease Q_{ad} on clean silver. The value for butadiene of 9 kcal mol^{-1} at 443 K on clean Ag is in good agreement with that of 13 kcal mol^{-1} on Ag(111) reported by Apai *et al.*(*32*); however, those determined at 300 K are noticeably higher.

When the values for butadiene are compared to those for ethylene, they are found to be quite similar on clean silver at 443 K (9 vs 10 kcal mol^{-1}, respectively), but Q_{ad} values for C_4H_6 at 300 K are higher than the literature value of 9 kcal mol^{-1} for C_2H_4 obtained after low temperature adsorption (*1*). On O-covered Ag, the Q_{ad} value of 21 kcal mol^{-1} for butadiene is noticeably higher than our value of 5.2 kcal mol^{-1} for ethylene although it is more similar to the maximum value of 13 kcal mol^{-1} reported by Akimoto *et al.* (*28*). At 443 K on an O-covered Ag surface, the Q_{ad} values for butadiene and ethylene are the same (65 vs 64 kcal mol^{-1}), thus implying that very similar bonding occurs with either molecule on this surface, presumably involving only one C=C double bond.

SUMMARY

Integral heats of adsorption for O_2 chemisorption on alumina-supported Ag were obtained using a modified differential scanning calorimeter. On large particles with an average size of 27 nm, the values of 34–41 kcal mol^{-1} at 443 K agreed well with those reported on Ag single crystals and, under a given set of conditions, Q_{ad} values increased from 40 kcal mol^{-1} on the largest crystallites to 50 kcal mol^{-1} on the smallest (3.7 nm). The heat of adsorption was lower at 300 K (32 kcal mol^{-1}), but showed the same trend with decreasing crystallite size as it increased to over 40 kcal mol^{-1}.

Ethylene adsorption on alumina was completely reversible and gave a Q_{ad} value of 10.1 kcal mol^{-1}; thus the heat of adsorption is comparable to that reported for C_2H_4 on a Ag(110) surface. This, coupled with the sizable adsorption on the alumina support, precluded any quantitative determination of Q_{ad} for C_2H_4 on clean silver at 300 K, but a value of 10 kcal mol^{-1} at 443 K was estimated. Values of 5.2 kcal mol^{-1} at 300 K and 64 kcal mol^{-1} at 443 K could be readily obtained for O-covered Ag because of the markedly enhanced irreversible adsorption. The high value at 443 K implies partial decomposition and reaction to form a strongly adsorbed, oxygen-containing species as no products desorbed.

Butadiene gave overall heats of adsorption on Al_2O_3 of 10.9 and 13.1 kcal mol^{-1} at 300 and 443 K, respectively, and also exhibited some irreversible adsorption. The presence of Ag altered the adsorption capacity on the support, which further complicated the interpretation of the exotherms; however, on clean Ag a value of 35 kcal mol^{-1} at 300 K could be calculated and a minimum value of 18 kcal mol^{-1} was estimated from a different set of experiments. At 443 K the Q_{ad} for butadiene on clean Ag decreased to 9 kcal mol^{-1}. On oxygen-covered Ag a somewhat lower value of 21 kcal mol^{-1} was obtained at 300 K but again a high value of 65 kcal mol^{-1} was measured at 443 K. At 300 K butadiene adsorbs more strongly than ethylene on clean silver but the two values are quite similar at 443 K. On O-covered Ag at 443 K, the high Q_{ad} values for C_2H_4 and C_4H_6 are again nearly identical and imply a strong interaction with surface oxygen at temperatures approaching reaction conditions and a similar bonding mode, presumably involving the rupture of only one C=C double bond.

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