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Effects of Cesium and Chlorine on Butadiene Adsorption on Ag/α-Al_2O_3 Catalysts

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Integral heats of adsorption, Q_{ad}, were measured at 300 K for butadiene on unpromoted and promoted Ag/α–Al_2O_3 catalysts with average Ag particle sizes in the range of 250–350 nm. The promoted catalysts mimic those used commercially and were prepared using either $CsNO_3$ to study the effect of cesium or CsCl to study the combined effect of cesium and chlorine, and the Cs content was maintained at either 400 ppm or 1200 ppm. Prior to measurement of either the butadiene uptake or the corresponding energy change, the catalysts were subjected to a pretreatment involving calcination at 523 K for 2 h followed by reduction in H_2 at 473 K for 1 h. The butadiene measurements were made on either a clean reduced or an O-covered Ag surface, with the latter containing either a monolayer or a half-monolayer of oxygen after adsorption at 443 or 300 K, respectively. Butadiene adsorption on reduced Ag surfaces was almost all reversible, but the very low irreversible uptakes gave Q_{ad} values ranging from 130 to 250 kcal/mol, thus indicating that more than molecular adsorption was occurring. For the unpromoted catalyst, the amount of irreversibly adsorbed butadiene increased as the extent of the surface precovered by oxygen increased, and apparent Q_{ad} values for irreversibly adsorbed butadiene on the O-covered surfaces were much lower compared to those for the reduced surface, with the lowest Q_{ad} value of 13 kcal/mol occurring for the surface that was half covered by oxygen at 300 K. The amount of irreversibly adsorbed butadiene on O-covered surfaces decreased only slightly and was the same when the catalyst was promoted with 400 ppm of cesium via either $CsNO_3$ or CsCl; however, Q_{ad} increased to 84 kcal/mol when $CsNO_3$ was used, but decreased to 33 kcal/mol with CsCl, compared to 64 kcal/mol for the unpromoted sample. Both the amount and the Q_{ad} value for irreversibly adsorbed butadiene on O-covered Ag surfaces dropped when the amount of Cs was increased to 1200 ppm, and with the CsCl-promoted catalyst almost all the butadiene was reversibly adsorbed. Adsorption of 1-butene on the unpromoted Ag catalyst indicated lower uptakes compared to butadiene, but much higher heats of adsorption. This implies that certain aspects of the bonding of 1-butene and butadiene on the supported catalyst are different. Differences in the adsorption of 1-butene and butadiene on unsupported Ag were less apparent, possibly due to the low uptakes of butadiene on the low-surface-area Ag powder. Both the high Q_{ad} values and the frequent exothermic tail during calorimetric measurements appear to be associated with butadiene dissociation or dimerization reactions on the Ag surface. © 2002 Elsevier Science (USA)

INTRODUCTION

Silver is used commercially for epoxidation reactions (1), which are carried out on low-surface-area α-Al_2O_3-supported silver catalysts that include promoters such as K and Cs as well as chloride (2–6). The capability of epoxide formation versus complete combustion to carbon dioxide is attributed to the absence of allylic hydrogen in the reactant molecules, such as C_2H_4 and C_4H_6. Although epoxidation reactions have been widely studied, there is limited knowledge about the effect of promoters on reactant adsorption on commercial-type catalysts, particularly those used for butadiene expoxidation because catalysts effective for ethylene epoxidation are not active for the former reaction. In previous work, the influence of cesium and chlorine on oxygen adsorption was examined by promoting an Ag/α-Al_2O_3 catalyst with either $CsNO_3$ (to study the effect of only cesium) or CsCl (to study the combined effect of cesium and chlorine) (7). The present study is focused on the adsorption of 1,3-butadiene on α-Al_2O_3-supported Ag as well as on this catalyst promoted with Cs and Cl.

The heat of adsorption of 1,3-butadiene on alumina-supported silver was reported earlier (8); however, the support used was η-Al_2O_3. Even after sintering at 1273 K in flowing air for 8 days, this support had a surface area of 70 m^2/g, which is much higher than the surface area of commercial catalysts, which routinely use α-Al_2O_3 with a total surface area of around 1 m^2/g. Also, in this earlier study, butadiene adsorption was measured on a catalyst with an average Ag crystallite size of 24 nm, whereas most commercial catalysts have silver particle sizes of 50 nm or larger. It has repeatedly been reported that large silver crystallites are more effective in catalyzing the epoxidation reaction than are small silver crystallites (9–11). One added complication in 8 was the large uptake of butadiene on the pure alumina support, part of which was irreversible, and appropriate

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corrections had to be made to estimate the irreversible heat of adsorption for butadiene on silver.

Anderson *et al.* measured butadiene adsorption on O-covered and clean (reduced) Ag surfaces at both 300 and 443 K (8), with the latter temperature chosen because it is the optimum temperature for achieving monolayer oxygen coverage (12–14). In the present study the catalysts examined closely mimic those used for commercial epoxidation and they contain the full complement of promoters required for optimum butadiene epoxidation at industrially relevant conditions; hence some reaction was possible and expected in the temperature region of 443 K. This prevented uptake measurements of butadiene at 443 K; therefore, all butadiene adsorption studies were conducted at 300 K, but included samples that were reduced as well as oxygen-covered at 300 or 443 K. Based on a comparison of ethylene and butadiene adsorption, Anderson *et al.* concluded that only one double bond in the butadiene molecule was involved during adsorption. In the present study, butadiene and 1-butene adsorption on both an unpromoted Ag catalyst and Ag powder was compared to gain additional information about butadiene bonding.

EXPERIMENTAL

The supported Ag catalysts used for butadiene adsorption studies were those used in an earlier study of oxygen adsorption (7). The catalysts were prepared using a low-surface-area α-Al_2O_3 (Norton Corp., SA 5562), whose surface area was 0.78 m^2/g and which was received in the form of $\frac{1}{4}$-in. rings. The support was mixed with a solution of ethylenediamine, water, and silver oxalate. For promoted catalysts, a known amount of either $CsNO_3$ or CsCl was added to the solution. Following drying for 15 min at 335 K, the catalysts were calcined in a forced air oven at 598 K for 30 min. The nomenclature used for the supported catalysts is the same as that used in the earlier work (7). The unpromoted catalyst is designated UNP-II, while two nominal 400-ppm Cs-promoted catalysts, designated CsN(409) and CsCl(412), and two nominal 1200-ppm Cs-promoted catalysts, designated CsN(1174) and CsCl(1155), were also used. The prefixes CsN and CsCl indicate either $CsNO_3$ or CsCl as the promoter precursor, and the number in parentheses indicates the analyzed cesium content in parts per million. Butadiene adsorption was also carried out on pure alumina and unsupported UHP Ag powder. The Ag powder was 99.9995% purity (Alfa Aesar) and the surface area was found to be 0.2 m^2/g, as measured by the BET method. Measurements of 1-butene adsorption were made on both UNP-II and Ag powder.

The butadiene volumetric uptakes were measured in the same system as that used for oxygen chemisorption in the previous work (7). The stainless steel adsorption system was equipped with a Balzers turbomolecular pump, and isotherm pressures were measured with an MKS Baratron capacitance manometer. Sample temperatures were regulated by a furnace and temperature controller (Theall Engineering). The energy changes were monitored utilizing a Perkin–Elmer DSC-2C differential scanning calorimeter operated isothermally. Before energy change measurements, the calorimeter was calibrated on sensitivity scales of 5 and 10 mcal/s with two indium samples of 5.28 and 8.00 mg using either Ar or He as a carrier gas. The calculated calibration constant relating the area under the exotherm to the energy change in millicalories was found to be 0.0919 ± 0.0003. The resultant energy changes during butadiene adsorption were measured at a sensitivity scale of 0.5 mcal/s. For both the adsorption and calorimetric systems, gas flows were regulated by mass flow controllers (Tylan, Model FC-260). The nonhydrocarbon gases used were He (99.999%), Ar (99.999%), O_2 (99.999%), and H_2 (99.999%)—all from MG Scientific Gases. These gases were passed through drying tubes (Supelco, Inc.) while Ar, He, and H_2 were also passed through Oxytraps (Alltech Assoc.). The hydrocarbon gases, i.e., 1,3-butadiene (99.0%) and 1-butene (99.0%), were used without purification.

For each cycle during calorimetric and volumetric measurements, the catalyst sample was subjected to a low-temperature (LT) pretreatment as follows:

(1) Heat in 50 cm^3/min of inert (Ar/He) to 523 K.

(2) Switch to 20% O_2, maintaining constant total flow and calcine for 2 h at 523 K.

(3) Purge with inert gas and cool to 473 K.

(4) Switch to 20% H_2 and reduce for 1 h at 473 K.

(5) For chemisorption measurements, evacuate the sample for 30 min at 473 K while for calorimetric measurements, instead of evacuation, purge with an inert gas (Ar/He).

The butadiene studies were conducted using either a clean, reduced, or O-covered Ag surface. For studies on reduced Ag surfaces, following the LT pretreatment the catalyst was cooled to 300 K and exposed to butadiene. For O-covered Ag surfaces, following the pretreatment the catalyst was exposed to oxygen for 1 h at either 443 or 300 K. For the volumetric measurements, each oxygen isotherm was measured over a total oxygen exposure time of around 1 h, and the catalyst was then evacuated and cooled to 300 K for butadiene adsorption. The butadiene isotherms were measured using an initial pressure of around 50 Torr (760 Torr = 1.013 bar). The first point in the isotherm was measured after 20 min of exposure while additional data points were collected at incremental butadiene pressures after 5 min of stabilization. Following completion of the first isotherm, the sample was evacuated for 30 min and a second isotherm was measured to determine the reversible butadiene uptake using the same procedure as that employed during the measurement of the total butadiene uptake. Prior to measurement of the first data point in the isotherm, the uptake after 1 min of butadiene exposure was noted. Additional cycles of butadiene adsorption were made on the same catalyst sample by applying the LT pretreatment procedure between cycles.

The calorimetric studies were carried out on a separate fresh batch of catalyst at a butadiene pressure of 50 Torr. As mentioned in previous work, baseline fluctuations were minimized by equalizing the pressure drops on the sample and the reference sides of the differential scanning calorimetry (DSC), by matching the sample and reference pans, and by using the proper mixture of Ar and He in the makeup carrier gas stream to match the thermal conductivity of the C_4H_6/Ar mixture (7). A base carrier gas of pure Ar was mixed with a flow of 3 cm^3/min of butadiene to give a partial pressure of 50 Torr of C_4H_6. The experimental conditions used were "identical" to those used for the volumetric measurements to ensure that the catalyst was in a similar state after any given cycle. To measure butadiene exotherms on oxygen-covered Ag surfaces, the catalyst was exposed to 50 Torr of oxygen for 1 h at either 443 or 302 K after the catalyst pretreatment and then purged, and butadiene exotherms were measured at 302 K, a temperature slightly higher than room temperature, to ensure a constant temperature profile necessary for flat baseline behavior.

The first exotherm corresponding to total butadiene uptake was measured using 70–80 mg of catalyst on the sample side and an equal weight of nonporous glass beads on the reference side. After this initial exotherm, the catalyst was purged for 30 min in a flow of 50 sccm of argon, and a second exotherm, associated with reversible butadiene adsorption, was measured under identical conditions. To calculate the heat of adsorption for irreversible butadiene adsorption, a "difference exotherm" was obtained by subtracting the second exotherm from the first exotherm, which corrected for any energy changes due to reversible uptake or baseline fluctuations during the switch. The difference exotherm consists of an initial pronounced peak followed by either a slow decline or, in some cases, a "flat" baseline with a positive offset. The peaks were recorded and integrated over the first minute, then recording and integration continued until either the baseline dropped below a value of 0.1 or it became flat. This latter value from DSC measurements is denoted as "bc" (baseline corrected), and it is assumed that the flat baseline behavior is due to some surface phenomena unrelated to the butadiene adsorption. The possible sources and nature of these phenomena are discussed later in this paper.

The heat of adsorption, Q_{ad}, for irreversible butadiene adsorption was calculated by dividing the exothermic heat monitored by DSC with the appropriate volumetric uptake. The volumetric uptake for the first minute was calculated by determining the difference in uptakes (after 1 min) at 50 Torr between the first and second isotherms.

Consequently, based on 1-min data,

$$Q_{\mathrm{ad}}\ (1\ \mathrm{min}) = \frac{\text{heat evolution during initial minute in difference exotherm}}{\text{volumetric uptake during initial minute}}.$$

In addition, a Q_{ad} value based on equilibrium adsorption was also determined, i.e.,

$$Q_{\mathrm{ad}}\ (\mathrm{bc}) = \frac{\text{heat evolution of difference exotherm after baseline correction (bc)}}{\text{equilibrium irrreversible uptake}}.$$

It should be emphasized that these Q_{ad} values do not necessarily imply molecular butadiene adsorption but rather reflect all surface chemistry that may occur during the adsorption process.

The Q_{ad} values for reversible adsorption was calculated at a butadiene pressure of 50 Torr. This was based on the second exotherm and the butadiene uptake at 50 Torr during the second isotherm. However, these exotherm values were not corrected for any baseline fluctuation during the initial switch or baseline drift due to a mismatch in gas composition/pressure. The values for reversible adsorption were calculated only to ensure that they were in a reasonable range for a reversible phenomenon at 300 K. The heat of adsorption of 1-butene was measured on both the Ag powder and the UNP-II catalyst using exactly the same procedure as that detailed for 1,3-butadiene.

RESULTS

The Ag/α-Al_2O_3 catalysts were analyzed for Ag loading by ICP–AAS (inductively coupled plasma–atomic absorption spectroscopy), for Cs content by AAS, and for Cl content by XRF (X-ray fluorescence). The Ag particle size distribution was determined by scanning electron microscopy SEM. In addition the catalysts were characterized by a series of oxygen chemisorption and hydrogen titration experiments. Table 1 lists the elemental analyses, average Ag particle sizes, and total and reversible oxygen uptakes. Oxygen uptake values are reported for the stabilized catalysts, i.e., those given several pretreatment cycles, while butadiene adsorption was done with a fresh catalyst; however, the oxygen uptakes give a good indication of the available surface area for each catalyst. Also reported in Table 1 is the oxygen uptake on stabilized Ag powder and pure α-Al_2O_3.

The butadiene uptake on the pure support was measured following the LT pretreatment, and Fig. 1 shows that almost all the butadiene uptake on alumina is reversible. For the unpromoted Ag catalyst (UNP-II), the butadiene uptakes were measured on both the clean, reduced, and O-covered surfaces. The latter were formed by O_2 adsorption at either 443K, designated O(443), or 300 K, designated O(300). The O(443) surface has a monolayer coverage of oxygen while the O(300) surface has about half a monolayer of oxygen.

TABLE 1

Characterization of Catalysts Used for Measurement of Heats of Adsorption at 300 K

Catalyst	Silver[a] (%)	Cesium[b] (ppm)	Cl[c] (ppm)	Ag crystallite size[d] (nm)	O_2 uptake[e] (μmol/g cat) Irrev.	Total
α-Al_2O_3	0	0	0	—	0	0
Ag powder	—	—	—	—	2.5 ± 0.1	2.5 ± 0.1
UNP-II	14.9	0	0	275	3.0 ± 0.1	3.0 ± 0.1
CsN(409)	15.5	409	0	283	3.3 ± 0.1	3.5 ± 0.2
CsCl(412)	14.4	412	130	247	2.2 ± 0.1	2.4 ± 0.1
CsN(1174)	10.8	1174	0	354	1.9 ± 0.1	2.7 ± 0.2
CsCl(1155)	14.5	1155	308[d]	296	1.8 ± 0.2	2.0 ± 0.1

[a] Analyzed using ICP–AAS.
[b] Analyzed using AAS.
[c] Analyzed using XRF.
[d] Average size from SEM analysis.
[e] From Ref. 7.

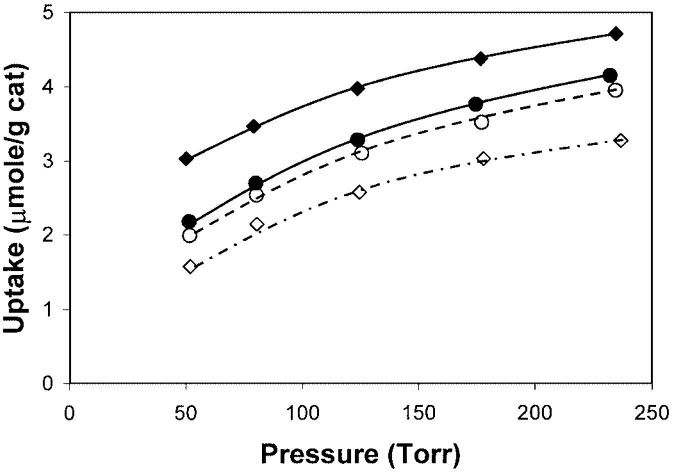

FIG. 2. Butadiene isotherms 300 K on unpromoted Ag/α-Al_2O_3 (UNP-II) after a low-temperature pretreatment: (◆) total uptake on O(443) surface, (◇) reversible uptake on O(443) surface, (●) total uptake on reduced surface, (○) reversible uptake on reduced surface.

Figure 2 shows the butadiene isotherms at room temperature for the reduced and O(443) surfaces of the UNP-II catalyst. With the reduced surface there is a small amount (0.2–0.3 μmol/g of catalyst) of butadiene that is irreversibly adsorbed. By comparison, on the O(443) surface with a full monolayer of oxygen, the total butadiene uptake increased while the reversible uptake decreased, which resulted in a significant increase of irreversible butadiene adsorption. Note that the reversible uptake of butadiene on the O(443) surface is similar to the reversible butadiene uptake on the α-Al_2O_3 support (Fig. 1), indicating that the reversible butadiene adsorption on the O(443) surface is principally due to adsorption of butadiene on the α-Al_2O_3 surface. In separate cycles with an O(300) surface, the irreversible butadiene uptake was lower compared to the O(443) surface but was still much larger than that observed for the reduced Ag surface, thereby illustrating the role of preadsorbed oxygen in butadiene adsorption. The volumetric uptakes for the unpromoted catalysts are listed in Table 2, and they include the irreversible uptake during the initial 1-min period, the equilibrium irreversible uptake, and the reversible uptake measured at a butadiene pressure of 50 Torr. The total uptake at 50 Torr is the sum of the equilibrium irreversible

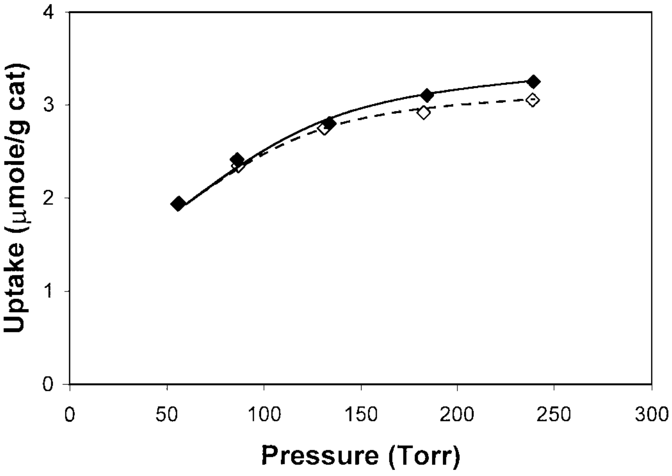

FIG. 1. Butadiene isotherms at 300 K on α-Al_2O_3 support after a low-temperature pretreatment: (◆) total uptake, (◇) reversible uptake.

TABLE 2

Effects of $CsNO_3$ and CsCl Promotion on Butadiene Adsorption on O-Precovered and Reduced Ag Surfaces

		Uptake[a]			Q_{ad} (kcal/mol C_4H_6)		
		Irrev.		Rev.	Irrev.		Rev.
Catalyst	Surface	1 min	Equil		1 min	bc	
α-Al_2O_3	Red	0	0	1.9	—	—	6.6
α-Al_2O_3	Ox (443)	—	0	2.2	—	—	—
(1000 ppm Cs)	Red	—	∼0	2.2	—	—	—
Unpromoted	O(443)[b]	1.4	1.5	1.5	65	64	11
(UNP-II)	Red	0.2	0.2	2.0	175	210	8
	O(300)	0.6	0.7	1.6	nc[c]	13	9
$CsNO_3$-promoted	O(443)[b]	1.2	1.3	1.9	81	84	9
(409 ppm Cs)	Red	0.2	0.2	2.6	130	150	7
	O(300)	1.0	1.0	2.1	14	14	7
CsCl-promoted	O(443)[b]	0.7	1.3	2.1	35	33	9
(412 ppm (Cs)	Red	0.1	0.3	2.1	90	37	11
$CsNO_3$-promoted	O(443)[b]	0.7	1.1	1.5	25	19	9
(1174 ppm Cs)	Red[b]	0.1	0.3	2.5	250	130	6
CsCl-promoted	O(443)	0.02	0.07	1.7	na[c]	5	4
(1155 ppm Cs)	Red	0.0	0.1	1.3	na[c]	10	9

[a] Total uptake at 50 Torr = Irrev. Equil. + Rev.
[b] Average of two runs.
[c] Not available.

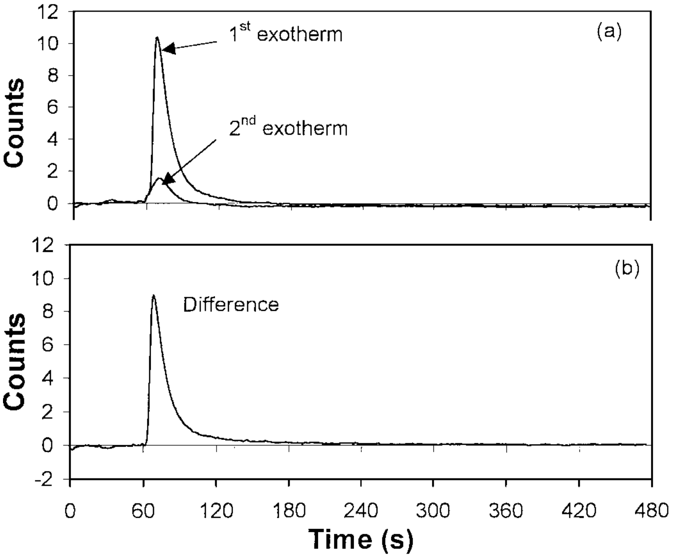

FIG. 3. Exotherms during butadiene adsorption at 300 K on an O(443) surface of unpromoted Ag/α-Al_2O_3 (UNP-II) with $P_{C_4H_6} =$ 50 Torr: (a) first and second exotherms, (b) difference exotherm.

uptake and the reversible uptake at 50 Torr. Also included in Table 2 are similar measurements for the catalysts promoted with approximately 400 ppm Cs and 1200 ppm Cs as either $CsNO_3$ or CsCl.

The calorimetric results in Table 2 were made using the same set of cycles at a butadiene partial pressure of 50 Torr. Figure 3a shows the first and second exotherms obtained at 302 K with an O(443) surface of the unpromoted Ag catalyst, and Fig. 3b shows the difference exotherm, which exhibits an initial well-defined peak followed by a slow decline. Figure 4 shows the difference exotherm for butadiene adsorption on the reduced surface of the unpromoted catalyst, which exhibits a flat baseline with a positive offset following the initial peak. The continuing positive offset could not be justified by any corresponding time-dependent butadiene uptake, which suggests the difference exotherm was caused by some slow exothermic process other than adsorption. This assumption is supported by comparison with the butadiene uptake data in Table 2, which show that butadiene uptake values for the unpromoted and reduced sample are very similar for both 1-min and equilibrium periods of time. For comparative study, the difference exotherm was integrated over the initial 1-min period and then continued to the point that the baseline either dropped below 0.1 count (arbitrary units) or the baseline became flat, and apparent heats of adsorption for irreversibly adsorbed butadiene were calculated based on both the 1-min values and the baseline-corrected (bc) values. For small energy changes where the peaks were integrated for a period of less than a minute for the bc values, Q_{ad} values based on 1-min data were not reported. The heats of adsorption for reversible adsorption were calculated based on the second exotherm without any additional corrections. The resultant Q_{ad} values for the unpromoted Ag catalyst and the catalysts promoted with ~400 ppm or ~1200 ppm Cs are also listed in Table 2. On the reduced unpromoted surface, the small irreversible uptake of butadiene has a very high Q_{ad}. When the surface is partially covered with oxygen, i.e., after O_2 adsorption at 300 K, the irreversible butadiene uptake increases significantly and the Q_{ad} decreases markedly. With monolayer coverage of oxygen, the irreversible uptake increases further and Q_{ad} increases compared to Q_{ad} on the partially covered surfaces, but the latter is still much lower than that observed with the reduced surface. The uncertainty is much higher for Q_{ad} of irreversibly adsorbed butadiene on a reduced Ag surface because of both the extremely low coverages (0.2 μmol of C_4H_6/g of catalyst) and the correspondingly lower heat generation during adsorption (note the y-coordinates in Figs. 3b and 4).

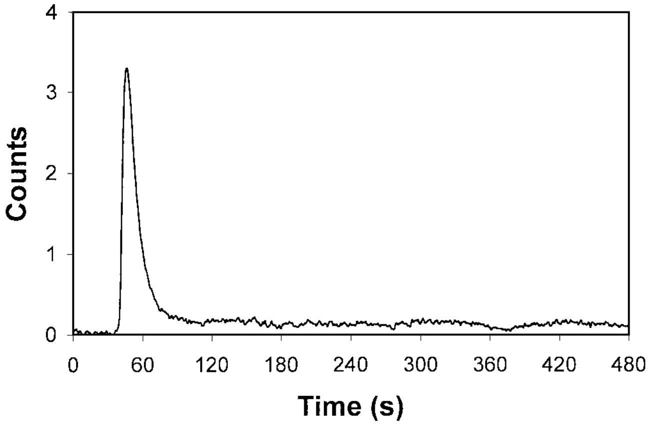

FIG. 4. Difference exotherm during butadiene adsorption at 300 K on a reduced surface of unpromoted Ag/α-Al_2O_3 (UNP-II) with $P_{C_4H_6} =$ 50 Torr.

For the two catalysts with low Cs loadings, Table 1 shows that the Cs(409) catalyst had an uptake of oxygen about 10% higher than that on the unpromoted (UNP-II) catalyst, while the CsCl(412) catalyst exhibited an oxygen uptake about 25% lower than that of the unpromoted catalyst. The data for the CsN(409) catalyst suggest that little or no Cs is present on the surface and that Cs lowers the average Ag crystallite size and/or increases the reducibility of Ag after calcination, such that the total uptake of O_2 actually increases. The CsCl-promoted sample, however, clearly indicates that some of the Cl moderator is present on the surface of the Ag catalyst and blocks oxygen adsorption sites. This behavior is consistent with surface science studies (15, 16). The butadiene adsorption data in Table 2 must be interpreted within this context. The reversible butadiene adsorption is comprised of that on both the Ag and the α-Al_2O_3. Addition of only Cs increased the reversible uptakes by 25–30% after reduction and decreased the overall Q_{ad} value for reversible adsorption by 1–2 kcal/mol compared to the unpromoted catalyst. This latter decrease

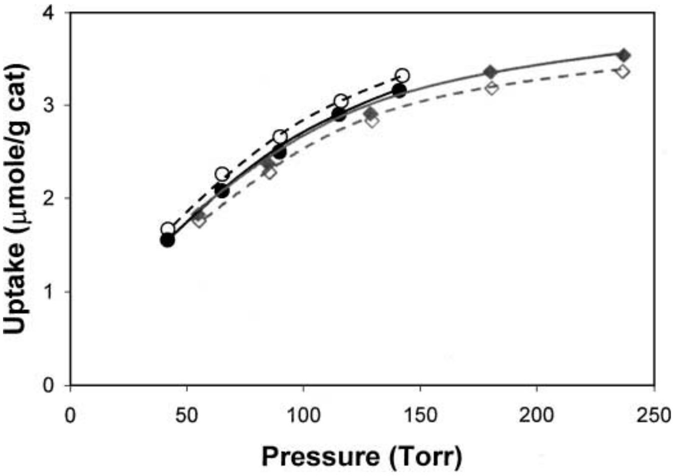

FIG. 5. Effect of five successive low-temperature pretreatment cycles on butadiene isotherms at 300 K for O-covered CsCl(1155): (◆) total uptake after one cycle, (◇) reversible uptake after one cycle, (●) total uptake after five cycles, (○) reversible uptake after five cycles.

implies that Cs facilitates the desorption of butadiene from Ag sites, i.e., the binding energy is lowered on these Ag surfaces. In contrast, when Cl is also present, the reversible butadiene uptake is either unaffected or decreased, but a concomitant increase occurs in the heat of adsorption, as indicated by the CsCl(412) and (1155) samples. The uptakes on α-Al_2O_3 and Cs-promoted α-Al_2O_3 indicate that the presence of only Cs may increase reversible butadiene adsorption slightly on the support; however prior exposure to O_2 at 443 K does not influence adsorption on the support. This latter pretreatment increased the reversible heat of adsorption on UNP-II and the two Cs-only samples, whereas Q_{ad} decreased when Cl was also present. For the O(443) surfaces in Table 2, all reversible uptakes of butadiene fell within a certain range, which suggests that the higher promoter loadings do not noticeably change the amount of reversible butadiene adsorption. This was verified by butadiene adsorption on α-Al_2O_3 promoted with 1000 ppm Cs, as shown in Table 2. This does not necessarily mean that in all cases the reversible uptake of butadiene occurs on the Al_2O_3 support because the Q_{ad} values in Table 2 for reversible adsorption show that the promoted samples have lower values, and hence different adsorption characteristics.

The difference in Q_{ad} values between UNP-II and the high Cs-promoted samples is much more dramatic for irreversible adsorption, as the irreversible heats of adsorption for the promoted samples are much lower than for UNP-II, indicating the Cs and Cl have greatly modified the nature of butadiene adsorption. Comparison of the data in Table 2 indicates that Cl has the greater impact on the strength of irreversible butadiene adsorption. Because earlier studies on the adsorption of oxygen on CsCl(1155) had shown that the catalyst required three to four cycles of low-temperature pretreatment/adsorption to give stable uptakes (7), a catalyst was given the same number of cycles and exposed to butadiene following the final O(443) treatment. The data shown in Fig. 5 indicate that multiple pretreatment cycles do not change the nature of butadiene adsorption on catalysts with high CsCl loadings. For irreversible adsorption on both of the reduced Ag surfaces promoted only with Cs, the heats of adsorption are still very high, although lower than that for the unpromoted catalyst (UNP-II). In comparison, the presence of Cl decreased the irreversible Q_{ad} values markedly, as shown by the results for CsCl(412) and CsCl(1155). Irreversible uptakes were higher on O-covered Ag surfaces and the presence of only Cs again decreased irreversible Q_{ad} values, relative to the comparable reduced surface. As with the reduced samples, the copresence of Cl significantly reduced the Q_{ad} further, with the most dramatic effect provided by CsCl(1155). The CsCl(412) catalyst had a lower rate of initial butadiene uptake (1 min vs equilibrium) when compared to the corresponding data for the unpromoted and CsN(409) samples; thus, the presence of Cl also appears to change the rate of butadiene adsorption on the reduced and O(443) surfaces. Consistent with this slow butadiene uptake, the difference exotherm for the O(443) surface was much broader, as shown by the first exotherm and the difference exotherm for CsCl(412) in Fig. 6. The total exotherm has an initial sharp peak followed by a broad, slow decline, and much of the initial peak is accounted for by the second exotherm; hence the difference exotherm is a very broad peak. The data in Table 1 show similar irreversible oxygen uptake values for CsN(1174) and CsCl(1155), which suggests that at these higher loadings the presence of Cl did not modify oxygen chemisorption significantly. This is somewhat unexpected because similar measurements for CsN(409) and CsCl(412) indicated that the presence of Cl substantially lowered the amount of

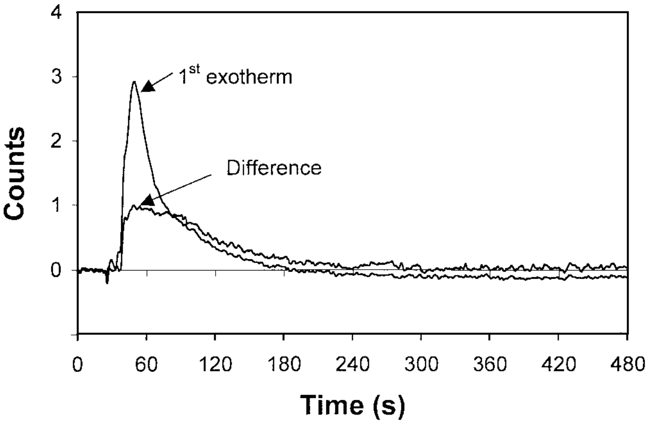

FIG. 6. Difference exotherm and first exotherm during butadiene adsorption at 300 K on an O-covered surface of CsCl(412) with $P_{C_4H_6} = 50$ Torr.

irreversibly adsorbed oxygen. However, the amount of reversible plus irreversible oxygen adsorbed on CsN(1174) and CsCl(1155) does indicate that the presence of Cl lowers the total amount of oxygen uptake, which is approximately 25% lower on CsCl(1155) than on CsN(1174). The butadiene uptakes in Table 2 show that the higher promoter loadings markedly suppress irreversible butadiene adsorption compared to that on UNP-II. The values for irreversibly adsorbed butadiene in Table 2 indicate that with the O(443) surfaces there is a good agreement between the 1-min and equilibrium Q_{ad} values, which marginally increase when the catalyst is promoted with 409 ppm $CsNO_3$, but significantly decrease in the presence of chloride. For reduced surfaces, the Q_{ad} values are very high for the small amount (<0.3 μmol/g of catalyst) of irreversibly adsorbed butadiene that occurs, and there is significant discrepancy between the 1-min and bc values. This is attributed to a lower rate of uptake on the reduced catalyst, which complicates the estimation of initial (1 min) heats of adsorption; thus, for the reduced samples, the Q_{ad} values from the bc method are preferred for comparisons. Based on these bc values, heats of adsorption are higher for the reduced surfaces compared to their O-covered counterparts. The heat of adsorption significantly decreases when Cl is present and, for this case, the Q_{ad} values are similar for both the reduced and O-covered surfaces.

The promoted catalysts also have varying and usually lower oxygen coverages compared to their unpromoted counterpart. The butadiene coverage on an O-covered surface may depend on the amount of oxygen preadsorbed as well as on other effects of the promoters. Table 3 lists the amount of total and irreversible butadiene uptakes for the O(443) surface of different catalysts along with the irreversible oxygen coverages. The total butadiene uptakes are similar for the unpromoted and 400 ppm Cs-promoted catalysts but are lower for the 1200 ppm Cs-promoted catalysts; however, the total butadiene coverage has less relevance since part of it is adsorbed on the alumina and it is difficult to estimate the amount adsorbed only on silver. The irreversible butadiene uptakes on the O-covered surfaces do not differ markedly except for the CsCl(1155) catalyst, for which irreversible adsorption was decreased to near zero. Since CsCl(412) had a lower oxygen uptake, the ratio of irreversible butadiene uptake to oxygen is highest for this catalyst; in contrast, for CsCl(1155) almost all the butadiene was reversibly adsorbed.

TABLE 3

Ratio of Butadiene Uptake to Irreversible Oxygen Uptake on α-Al_2O_3-Supported Ag Covered with a Monolayer of Oxygen

	O_2 uptake[a] (μmol/g)	Butadiene uptake (μmol/g cat)		$(C_4H_6)_{irrev}$	$(C_4H_6)_{tot}$
Catalyst	(Irrev.)	Irrev.	Total	O	O
Ag powder	2.5	0.5	0.9	0.10	0.18
UNP-II	3.0	1.5	3.0	0.25	0.50
CsN(409)	3.3	1.3	3.2	0.20	0.48
CsCl(412)	2.2	1.3	3.4	0.30	0.77
CsN(1174)	1.9	1.1	2.6	0.29	0.68
CsCl(1155)	1.8	0.07	1.7	0.02	0.47

[a] From Ref. 7.

TABLE 4

Comparative Adsorption of 1-Butene and 1,3-Butadiene on O-Covered and Reduced Surfaces of UNP-II at 300 K

		Uptake (μmol/g cat)			Q_{ad} (kcal/mol)		
		Irrev.		Rev.	Irrev.		Rev.
Olefin	Surface	1 min	Equil.		1 min	bc	
1-Butene	O(443)[a]	0.8	1.0	1.3	130	130	11
	Red	0.2	0.3	1.8	140	500	5
	O(300)	0.2	0.3	1.4	na	13	9
Butadiene	O(443)[a]	1.4	1.5	1.5	65	64	11
	Red	0.2	0.2	2.0	175	210	8
	O(300)	0.6	0.7	1.6	na	13	79

[a] Average of two runs.

From the butadiene uptake data for O-covered surfaces, it is not clear whether one or both double bonds are involved in bonding; thus, to better understand butadiene bonding on a silver surface, 1-butene adsorption studies were carried out on the unpromoted catalyst. Table 4 lists the 1-butene uptakes and Q_{ad} values for the unpromoted catalyst. The irreversible and total 1-butene uptakes on a reduced surface are similar to those observed for butadiene. The total and the irreversible uptakes for 1-butene on an O(443) surface are considerably lower compared to those for butadiene, but the integral Q_{ad} values for irreversible adsorption are double those obtained with butadiene. This implies that the nature of bonding for 1-butene and butadiene on an unpromoted, oxygen-covered Ag surface is very different.

Butadiene and 1-butene adsorption was also conducted on unsupported Ag powder after similar pretreatment conditions, and Table 5 lists the uptakes and Q_{ad} values for both compounds. The amount of butadiene adsorbed on Ag powder was much smaller than that adsorbed on the UNP-II catalyst, and the reversibly adsorbed butadiene was only 15–20% that obtained with the UNP-II catalyst. This is partly because of the lower specific surface area of the unsupported powder and partly because much of the reversible adsorption on the supported catalysts is attributable to the alumina support. The apparent heats of adsorption for reversibly adsorbed butadiene on the unsupported Ag powder are around 20 kcal/mol. These values are unreasonably high for a reversible adsorption process and imply that a significant fraction of the area under the

TABLE 5

Butadiene and 1-Butene Adsorption on O-Covered and Reduced Surfaces of Ag Powder at 300 K

		Uptake (μmol/g cat)			Q_{ad} (kcal/mol)		
		Irrev.		Rev.	Irrev.		Rev.
Olefin	Surface	1 min	Equil.		1 min	bc	
Butadiene	O(443)[a]	0.4	0.5	0.4	60	50	20
	Red	0.2	0.3	0.3	30	20	20
1-Butene	O(443)[a]	0.3	0.5	0.3	90	70	20
	Red	0.1	0.2	0.4	50	40	20

[a] Average of two runs.

second exotherm for reversible butadiene adsorption may be due to baseline fluctuations at this high sensitivity in the calorimeter. Alternatively, this high value could reflect the presence of slow exothermic surface reactions. The heat of adsorption of butadiene on the O(443) surface of Ag powder is close to that observed for the unpromoted catalyst, but on the clean surface it is much lower. The uptake of 1-butene on Ag powder was slightly lower than that for butadiene, but the Q_{ad} values for 1-butene are slightly higher; however, the difference is not as significant as that with the unpromoted UNP-II catalyst.

DISCUSSION

It is important to stress that commercial ethylene epoxidation catalysts are not effective for butadiene epoxidation; consequently, references to studies of the former reaction have been minimized. The adsorption of 1,3-butadiene on silver surfaces has been studied previously. On Ag(111) at 25–30 K, it was reported that the adsorbate lies parallel to the surface, and an increase in temperature to 90 K resulted in tilting of the molecular plane with the C=C bonds remaining parallel to the surface (17). Madix and coworkers studied the orientation of 1,3-butadiene on Ag(110) using NEXAFS, found that butadiene bonds to the Ag(110) surface with its σ_h plane lying parallel to the plane of the surface, and reported that molecular desorption occurred at 227 K (18). Itoh and coworkers studied adsorption of butadiene on cold evaporated silver films (19–21) and reported that the adsorbate takes on a structure with one of the C=C bonds coordinated to a positively charged site on the silver film at 120 K whereas a structure with both C=C bonds coordinated to positively charged sites occurred at 180 K. Schiøtt and Jørgensen examined the interaction of 1,3-butadiene with atomically adsorbed oxygen on an Ag(110) surface and, using extended Hückel tight-binding methods, calculated that at low O-coverages the interaction of both of the terminal carbon atoms with surface oxygen is favored (22). This intermediate shows a preference for 1,4 ring closure, rather than 1,2 ring closure, leading to 2,5-dihydrofuran instead of vinyl epoxide. Madix and coworkers also reported formation of 2,5-dihydrofuran during reaction of 1,3-butadiene with atomically adsorbed oxygen on Ag(110) (23, 24). However, Monnier showed that expoxidation of nonallylic olefins such as butadiene can be carried out using promoted, supported silver catalysts to form 3,4-epoxy-1-butene, which suggests that the interaction of butadiene with the Ag surface is through just one of the localized C=C double bonds (1). The author proposed that the formation of 2,5-dihydrofuran proceeded by the isomerization of 3,4-epoxy-1-butene to form 2,5-dihydrofuran. Considering the relevance of 1,3-butadiene expoxidation, the present study focuses on the measurement of heats of adsorption for 1,3-butadiene on reduced (clean) and O-covered promoted and unpromoted silver surfaces.

Q_{ad} values for butadiene on silver supported on sintered η-Al_2O_3 were reported earlier (8), but the silver particle size was an order of magnitude smaller than the Ag particle size utilized in the present study. For the O(300) surface, the Q_{ad} value for the UNP-II catalyst is similar to the value of 21 kcal/mol reported in earlier work (8). The values for the O(443) surface cannot be compared because in the previous study the heat of adsorption of butadiene on the O(443) surface was measured at 443 K. The irreversible heat of adsorption of butadiene on the reduced Ag surface in the UNP-II catalyst is much higher than that reported earlier for smaller Ag particles. This implies that on these large supported Ag crystallites a small number of surface sites can bind butadiene very strongly and can facilitate butadiene dissociation. Ongoing Fourier transform IR studies have identified surface groups containing C–H, C=C, and C=O stretching frequencies after purging in He at 300 K, but no molecular 1,3-butadiene (25). When the surface was partially covered with oxygen at room temperature, the amount of irreversibly adsorbed butadiene increased and the binding energy simultaneously decreased. Thus it appears that oxygen may cover the high-binding energy sites on the clean reduced surface and, at the same time, lead to the formation of new Ag–O butadiene adsorption sites. For the ethylene–Ag(111) system, Grant and Lambert observed that there was no detectable ethylene adsorption on clean Ag(111) at 300 K, but ethylene did chemisorb on a surface presaturated with oxygen at 300 K (26). In the present study, when the surface of the unpromoted catalyst was covered with a monolayer of oxygen at 443 K, the irreversible adsorption increased and the integral heat of adsorption for butadiene decreased compared to that obtained with a reduced surface. The larger Q_{ad} values for butadiene on an Ag surface covered by a monolayer of oxygen, rather than half a monolayer, may be due to the presence of a more weakly bonded oxygen species that readily interacts with butadiene, i.e., high heats of adsorption obtained with the O(443) surface compared to the O(300) surface may reflect the different ratio of surface and subsurface oxygen. The increased inventory of both surface and subsurface oxygen may increase the electrophilicity of the oxygen adlayer (27). If this is so, the presence of a Cl moderator might have the same effect as the surface/subsurface oxygen in increasing the electrophilicity of the oxygen adlayer. However, an investigation of Table 2 shows that promotion by CsCl does not result in higher Q_{ad} values when compared to the Q_{ad} values for UNP-II, but it is possible that the presence of Cs along with Cl changes the interaction between Cl and Ag. It is now widely accepted that weakly bonded electrophilic oxygen leads to epoxide formation by reaction with the π-orbitals of chemisorbed ethylene, while strongly bound, bridging oxygen preferentially attacks C–H bonds and leads to nonselective oxidation (28–31). Another possibility is that the surface structure is different after different pretreatments, which in turn may affect the butadiene bonding and lead to different Q_{ad} values. Grant and Lambert reported that during their temperature-programmed reduction experiments, the clean Ag(111) surface showed formation of only carbon dioxide but was activated toward selective epoxidation in the presence of dissolved oxygen (26). Thus different pretreatments may lead to different reactivity of the surface toward olefins and, hence, different apparent Q_{ad} values for irreversible adsorption.

The irreversible butadiene uptake was very small (<0.3 μmol/g of catalyst) on all these reduced Ag surfaces. For the unpromoted and $CsNO_3$-promoted catalysts, the amount of reversibly adsorbed butadiene was higher on the reduced surface compared to that on their O-covered counterparts; however, for the reduced Cl-containing surfaces, the amount of reversibly adsorbed butadiene was very similar to that on O-covered surfaces. Further, the heat of adsorption of irreversibly adsorbed butadiene on the reduced, Cl-containing surfaces is comparable to that observed with its O-covered counterpart, particularly for the bc cases. This is unlike the behavior of the unpromoted and $CsNO_3$-promoted supported Ag, in which the reduced surface shows the presence of very high energy sites compared to the O-covered surface, with Q_{ad} (bc) values ranging from 130–250 kcal/mol. These observations indicate that on reduced Ag surfaces Cl occupies sites that are otherwise available for reversible butadiene adsorption in the absence of oxygen. Further, the presence of Cl suppresses the high-energy binding sites. The effect of Cl on butadiene adsorption is more prominent with O-covered surfaces. For equivalent amounts of cesium, Q_{ad} is much lower in the presence of chlorine. One possibility for this effect may be that Cl on the Ag surface interacts with the adsorbed butadiene, perhaps at the nonbonded end of a localized, bound butadiene molecule in a repulsive manner, since both Cl and C=C are electron-rich moieties and susceptible to repulsive interactions.

The effects of high Cs loading on butadiene adsorption are also quite interesting when compared to similar data for the unpromoted catalyst. For the two $CsNO_3$-promoted catalysts after O_2 adsorption at 443 K, the amount of irreversibly adsorbed butadiene decreases slightly as the Cs content increases compared to the unpromoted catalyst, and the Q_{ad} values are significantly lower compared to the reduced samples, especially for CsN(1174). The decrease in irreversibly adsorbed butadiene tends to track the decrease in irreversibly adsorbed oxygen; hence the ratio of the two is similar to that observed for the unpromoted catalyst, as shown in Table 3. The amount of reversibly adsorbed butadiene on either CsN(409) or CsN(1174) is considerably higher than that on the unpromoted catalyst. In the case of the unpromoted catalyst, most of the reversibly bound butadiene was attributed to the Al_2O_3 support, as verified by the results for α-Al_2O_3 in Table 1. The results for butadiene adsorption on Cs-promoted α-Al_2O_3(1000) indicate that the reversible butadiene uptake is independent of the reduction or oxidation pretreatment and that no irreversible adsorption occurs within experimental uncertainty. A comparison of CsN(1174) to this Cs-promoted Al_2O_3 implies that the presence of the silver may increase the reversible adsorption somewhat on the reduced catalyst but decrease reversible adsorption after exposure to oxygen at 443 K. Consequently, a significant amount of the increase in reversible adsorption on CsN(1174) relative to UNP-II can be attributed to weakly bound butadiene on the Ag surface. This suggests that high Cs loadings lower Q_{ad} for adsorbed butadiene, which is consistent with the conclusion of Monnier that high levels of Cs on catalysts optimized for epoxybutene formation lower the desorption energy of epoxybutene from the Ag surface (1). The Cs in this case should be expected to behave in the same manner, specifically to lower the Q_{ad} for adsorbed butadiene to the point where much of the adsorbed butadiene is so weakly bound that it becomes reversibly adsorbed.

Experiments conducted with 1-butene reveal considerable insight into the bonding of butadiene. The data in Table 4 indicate that both irreversible and reversible adsorption of butadiene is higher than that for 1-butene, particularly on oxygen-pretreated surfaces, which are the more relevant surfaces at reaction conditions. Because 1-butene can bond only through one localized double bond, the fact that butene uptake is lower than the butadiene uptake strongly suggests that butadiene is also adsorbed through one localized double bond. If butadiene were bonded through two localized double bonds or across the end of the butadiene molecule, the total uptake of butadiene would almost certainly be lower than for 1-butene. The corresponding lower Q_{ad} values for butadiene relative to 1-butene for the O(443) pretreated surface also suggest that the higher butadiene coverage results in some repulsive interaction effects between adsorbed butadiene molecules, which lowers the measured heat of adsorption. Certainly, it is easier to envision repulsion effects between terminal, nonbonded C=C bonds of adjacent molecules of butadiene than terminal, nonbonded ethyl groups of adjacent molecules of 1-butene.

If this picture is correct, then what drives the adsorption of butadiene to such high coverages during adsorption experiments? The answer may be either dimerization of two adsorbed butadiene molecules or dissociation of butadiene to form various carbonaceous species on the surface. It is well-known that butadiene undergoes a 4 + 2 Diels–Alder reaction to give 4-vinyl-2-cyclohexene (32–34), and dimerization to form vinyl cyclohexene can occur at room temperature. For instance, commercial cylinders of butadiene often contain vinyl cyclohexene concentrations as high as 5% if the cylinders have been filled for some time and allowed to sit under ambient conditions (35). However, for facile Diels–Alder reactions to occur, the dienophile (terminal C=C bond of butadiene) needs to be activated so that 1,4-electrophilic addition across the ends of the second butadiene molecule is facile. This is typically accomplished by using a catalyst that makes the C=C bond of the dienophile somewhat electron deficient and more electrophilic. Adsorption of butadiene should provide such a role in changing the electron density of the nonbonded, terminal C=C bond to make it electrophilic enough to readily add to a second molecule of butadiene. Indeed, this reaction has been found to occur on an Ag(110) surface (18, 23). Dimerization to form 4-vinyl-1-cyclohexene may also explain the long declining tail or the positive offset in the exotherms observed in some of the calorimetric measurements because this reaction is exothermic and slow enough under these conditions to give the "tailing" or "positive offset" experimentally observed in some of the measurements. Low concentrations of vinylcyclohexene would be difficult to detect with diffuse reflectance Fourier transform, but we have been able to verify the presence of surface groups containing C=C, C–H, and CO_2^- bonds (25); therefore, these high heat-of-adsorption values may represent extensive dissociation of butadiene on the surface.

SUMMARY

Integral heats of adsorption for butadiene were measured at 300 K on large Ag crystallites dispersed on low-surface-area Ag/α-Al_2O_3, and Q_{ad} values were obtained for both the reduced and the O-covered surfaces of these catalysts, some of which were promoted by Cs and Cl. For the unpromoted UNP-II catalyst, the irreversible uptake of butadiene on the reduced surface was very low but with a very high apparent heat of adsorption. When the surface of the unpromoted catalyst was covered with about a one-half monolayer of oxygen, the irreversible uptake of butadiene increased but the resultant heat of adsorption became very low. As the oxygen coverage increased to that of a monolayer, both the irreversible butadiene uptake and the heat of adsorption increased, but the latter was still lower than that for clean Ag. The amount of irreversibly adsorbed butadiene on the reduced surfaces of the promoted catalysts was also very low but, unlike the $CsNO_3$-promoted and the UNP-II catalysts, Q_{ad} values for irreversibly adsorbed butadiene on reduced CsCl-containing surfaces were comparable to those for the oxygen-covered surface. On Ag surfaces with a monolayer of oxygen, the amount of irreversibly adsorbed butadiene on the two 400-ppm Cs-promoted catalysts was almost the same as that observed for the unpromoted catalyst. The rate of initial uptake of butadiene and the heat of irreversibly adsorbed butadiene, however, were much lower for the 400-ppm CsCl-promoted catalyst. Both the amount of irreversibly adsorbed butadiene and its Q_{ad} value on an O-covered surface decreased further for the two 1200-ppm Cs-promoted catalysts, and for the CsCl(1155) catalyst, almost all the butadiene adsorbed on the O-covered surface was reversible. The adsorption of 1-butene on the unpromoted Ag catalyst indicated a different nature of bonding compared to butadiene adsorption. The amount of irreversibly adsorbed 1-butene on an O-covered surface was about half that observed for butadiene whereas the Q_{ad} value was almost twice that obtained for butadiene. In contrast, these differences in the uptake and the heat of adsorption between 1-butene and butadiene were small when the Ag powder was used. The results for butadiene may be influenced by a Diels–Alder dimerization reaction occurring on some of the Ag surfaces; thus the very high Q_{ad} values that are obtained with both unpromoted and Cs-promoted reduced Ag surfaces appear to be associated with butadiene dissociation to various surface species, and the exotherms represent more than molecular adsorption.

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