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Role of Cs promotion of Ag/AlOOH catalysts for the epoxidation of 1,3-butadiene: effects on surface acidity and basicity

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Abstract

The epoxidation of 1,3-butadiene to epoxybutene (EpB) was performed in a plug flow reactor using a boehmite-supported silver catalyst with molecular oxygen as the oxidant. Unpromoted silver catalysts exhibited optimum catalytic activity at a silver loading of 15 wt%. Using this experimentally determined silver level, a range of Cs nitrate loadings was incorporated on the Ag/boehmite catalyst to determine which catalyst composition provides the optimum activity. For this study, two catalyst preparations were investigated: (1) simultaneous supporting of silver and Cs nitrate and (2) initial supporting of silver followed by the sequential supporting of Cs nitrate. Reactivity studies have shown that catalysts prepared by simultaneously supporting silver and Cs nitrate are not as effective at enhancing EpB production and catalyst stability compared with catalysts prepared by the sequential supporting method. Adsorption microcalorimetry of CO_2 indicates that a portion of the Cs promoter is blocked when simultaneously supporting both Cs and Ag on the support surface. Adsorption microcalorimetry of NH_3 and DRIFTS studies have shown that increased Cs loadings result in a reduction in the number of acidic hydroxyl groups present on the catalyst, producing a catalyst that exhibits less deactivation with time-on-stream.

Keywords: Epoxidation; Silver; Cesium; Promotion; Oxygen; Butadiene; Boehmite

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1. Introduction

Epoxidation is the electrophilic addition of oxygen across a carbon–carbon double bond, resulting in a three-member ring structure that can undergo further chemical transformations to produce desirable oxygenated products, such as ketones, alcohols, and ethers. Much emphasis has been placed on research investigating the epoxidation of ethylene, propylene, and 1,3-butadiene [1–5], because the epoxides of these olefins are useful intermediates for the production of high-volume industrial and consumer products [6]. The preferred epoxidation mechanism uses molecular O_2 as an oxidant, because O_2 is inexpensive and also because capital expenses for constructing commercial manufacturing facilities are lower for processes that use molecular O_2 as the oxidant [5].

Supported silver catalysts have been shown to epoxidize olefins with nonallylic hydrogen when an alkali promoter is doped on the surface [4]. Certain alkali metal salts, including CsCl, RbCl, KCl, and $CsNO_3$, lower the desorption energy of the olefin epoxide when doped to the catalyst surface, dramatically improving activity, selectivity, and catalyst lifetime [4]. In fact, Monnier determined that the addition of an optimum level of promoter increased the activity and selectivity from about 1% butadiene conversion and 50% selectivity for epoxybutene (EpB) to 15% conversion and 95% selectivity, respectively, for the epoxidation of 1,3-butadiene [4].

The literature is replete with instances where adsorption microcalorimetry has been used to improve understanding of silver-based epoxidation catalysts. For example, initial studies were performed investigating the heats of adsorption of dioxygen, ethylene, and butadiene on silver supported on

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alumina [7]. Other studies investigating the enhancing role of Cs have used butadiene as a probe to show that the rate of initial uptake of butadiene, along with the amount of irreversibly adsorbed butadiene, was determined to decrease with increasing levels of $CsNO_3$ promotion [8]. Furthermore, the adsorption of butadiene on the O-covered surface of Ag/Al_2O_3 catalysts promoted with CsCl was almost completely reversible [8]. More recently, NO has been used as a probe for promoted silver catalysts, where uptake measurements have shown that surface oxygen enhanced NO adsorption and that the presence of both Cs and Cl may decrease the surface concentration of nucleophilic oxygen [9]. Despite all of these microcalorimetric studies, however, no one has investigated the role of Cs in enhancing the surface basicity and/or neutralizing support acidity for an epoxidation catalyst.

Although significant progress has been made in improving the conversion and selectivity to EpB using Cs-promoted Ag/Al_2O_3 catalysts, the role of the promoter is not well understood. Optimum promoter levels rely on the promoter compound, the type of support, and the amount of silver on the catalyst surface. Therefore, our efforts here were focused on investigating the role of Cs promotion on the epoxidation of 1,3-butadiene using a variety of Ag/AlOOH catalysts promoted with $CsNO_3$. The goal of this investigation was to determine an optimum $CsNO_3$ loading and then probe various Cs-promoted Ag-supported catalyst surfaces to elucidate how Cs was enhancing catalyst stability and EpB production on a surface acidity/basicity level when using this support. We also investigated different methods for depositing the Cs promoter to determine how conversion was affected. Finally, we further analyzed the Cs-promoted Ag-supported catalysts using adsorption microcalorimetry of CO_2 and NH_3 as probe molecules to help determine the relative number and strength of base and acid sites, respectively, on the catalyst surface, with the aim of gaining a better understanding of cesium's potential role in enhancing surface basicity and neutralizing surface acidity at the catalyst surface.

2. Experimental

2.1. Preparation of promoted Cs and Ag catalysts on boehmite

2.1.1. Simultaneous promotion of Ag and Cs

Initially, 15 ml of distilled-deionized (DDI) water was heated to 50 °C in a 200-ml beaker using a stirring hotplate. This volume of water corresponds to a volume of about 2.7 times greater than the incipient wetness point for aluminum oxide hydroxide, chemical name boehmite (Apyral AOH180DS, Nabaltec), which has a reported surface area between 15 and 18 $m^2\,g^{-1}$. Boehmite, a monohydrate form of alumina ($Al_2O_3 \cdot H_2O$), is a common precursor for the production of various aluminas. Using a TA Instruments Q50 thermogravimetric analyzer (TGA), the stability of the surface hydroxyl groups for the as-received AlOOH was determined by heating a fresh sample in a flow of air to 400 °C at a rate of 5 °C/min to encourage dehydroxylation to water. Less than 2.5% of the total mass was removed during this thermal treatment, indicating that significant dehydroxylation does not occur. The boehmite has a near-neutral surface condition, with a pH of an aqueous solution near 8, which helps reduce the acidity and basicity contributions of the support. In addition, the greater surface area of boehmite provides a catalyst surface with enhanced adsorption capabilities compared with the typically used aluminas, which have surface areas $<2\ m^2\,g^{-1}$ and exhibit small adsorption uptake to probe molecules. Excess water was used to ensure a more uniform surface loading, while aiding dissolution of both the $AgNO_3$ and $CsNO_3$ compounds. Once the temperature of the water reached roughly 50 °C, 2.779 g of $AgNO_3$ (99.8%, Baker), which corresponded to a silver loading of roughly 15 wt%, was added to the water and stirred. Immediately after the silver nitrate was completely dissolved, the desired amount of $CsNO_3$ (99.99%, Acros) promoter was weighed and added to the solution. Once the $CsNO_3$ was completely dissolved, 10.00 g of dry boehmite was added to the solution, and the resulting slurry was stirred continuously by hand. Once no excess water was observed on the catalyst surface, the beaker with the catalyst contents was placed in an oven and dried in air overnight at 90 °C. Catalysts prepared through this "simultaneous" preparation procedure are referred to herein as Cs–Ag/AlOOH.

2.1.2. Sequential promotion of Ag and Cs

As for the simultaneous catalyst preparation procedure, here 15 ml of DDI water was heated to 50 °C in a 200-ml beaker using a stirring hotplate. Next 2.779 g of $AgNO_3$ was added to the water and stirred. Once the $AgNO_3$ salt was completely dissolved, 10 g of dry boehmite was added to the solution, and the resulting slurry was stirred by hand. Once no excess water was observed on the catalyst surface, the beaker with the catalyst contents was placed in an oven and dried in air overnight at 90 °C.

Once the catalyst was dry, the catalyst was size-separated to <40 mesh and transferred into a coarse-fritted glass calcination tube for thermal treatment. The optimum catalyst pretreatment conditions suggested by Badani and Vannice [8] were followed to treat the catalyst. The catalyst was heated from room temperature to 250 °C in nitrogen (UHP, Praxair) for 90 min, after which time an oxidizing atmosphere of makeup air, consisting of 20% O_2 (UHP, Praxair) in N_2, was passed over the catalyst for 2 h. After this oxidizing step, the catalyst was cooled to 200 °C in 30 min in flowing nitrogen. Once the catalyst was at a constant temperature, a reducing atmosphere consisting of 20% H_2 (UHP; Praxair) in N_2 was introduced to the catalyst for 1 h. The catalyst was subsequently cooled to room temperature in flowing N_2. This yielded a boehmite-supported silver catalyst, denoted herein as Ag/AlOOH.

The Ag/AlOOH catalyst was now ready for the sequential addition of the $CsNO_3$ promoter. Once again, 15 ml of DDI water was heated to 50 °C in a 200-ml beaker using a stirring hotplate. The desired amount of $CsNO_3$ was added to the water and the solution was stirred until the promoter salt was completely dissolved. Next, the thermally treated Ag/AlOOH catalyst was added to the solution, which was stirred by hand. Once no excess water was observed on the catalyst surface, the beaker with the catalyst contents was placed in an oven and dried in air overnight at 90 °C. Catalysts prepared via this "sequential" preparation procedure are referred to herein as Cs/Ag/AlOOH.

2.2. *Gas-phase epoxidation of 1,3-butadiene*

The gas-phase epoxidation of 1,3-butadiene was carried out in a continuous-flow, fixed-bed reactor. Roughly 0.50 g of size-separated catalyst (+30/−40) was supported by glass wool in a 0.25-inch o.d. stainless steel reactor tube sheathed by a 1-inch o.d. brass rod, which served as a heat sink to provide better temperature uniformity throughout the reaction zone.

The thermal treatment steps outlined in Section 2.1.2 for the preparation of Ag/AlOOH were also used to activate each catalyst before reaction. The oxidation/reduction treatment steps decomposed the supported silver nitrate salt to metallic silver and decomposed the $CsNO_3$ to produce a Cs oxide, which is believed to be the Cs species produced [10]. Initial oxidation of the catalyst occurred at 250 °C in a flow of makeup air over 2 h, and subsequent reduction of the catalyst occurred at 200 °C in a flow of 20% H_2 in N_2 for 1 h.

Reactor conditions and reactant flow rates were similar to those reported by Monnier [5]. The reactor was operated at atmospheric pressure and a constant temperature of 200 °C. A reactant mixture of 1,3-butadiene (99+%, Aldrich), O_2, and N_2 was passed over the catalyst bed, where nitrogen acted as an inert diluting agent. A total feed rate of 100 sccm was used. The ratio of 1,3-butadiene:O_2:N_2 molar flow rates was 10:20:70. All stainless steel tubing downstream from the reactor was heat-traced using flexible Thermolyne electric heating tapes to ensure that all products remained in the vapor phase. The reaction was performed under differential conditions with conversions $<5\%$. The product stream was analyzed by flame ionization detection using a Thermoquest Trace gas chromatograph (GC) fitted with a Supelcowax column, in which EpB was the primary organic product identified. Sampling to the GC at 9.1-min intervals was automated using an air-actuated six-port, two-position, Valco gas-sampling valve.

2.3. *Adsorption microcalorimetry of CO_2 and ammonia*

Adsorption microcalorimetry of acidic CO_2 and basic NH_3 was performed using a Calvet-type microcalorimeter. The microcalorimetry unit consisted of an aluminum block with two integral thermoelectric enclosures (model CR-100-1, International Thermal Instrument Co.). A high-temperature silicone oil (Acros Organics) was used to ensure good thermal contact between the cell wall and the inner wall of the cavity of the microcalorimeter. The microcalorimeter unit was located in a well-insulated forced-air oven to isolate the system from the environment.

First, the catalyst to be investigated was thermally treated external to the microcalorimeter system using the thermal treatment related to the specific preparation procedure, as outlined in Section 2.1. Immediately after completion of the reduction step, approximately 2.0 g of catalyst was transferred into a sample cell to form a catalyst bed a few millimeters thick. The sample was subsequently outgassed under dynamic vacuum at 250 °C for 8 h, then cooled to room temperature for gas adsorption. Once pretreatment was completed, the gas-dosing manifold was charged with CO_2 (UHP, Linweld) or NH_3 (anhydrous, 99.99+%; Aldrich). For the studies involving CO_2 adsorption, the initial manifold pressure was normalized to the mass of AlOOH present in the sample. Manifold pressures were measured using a 615A high-accuracy Baratron absolute pressure sensor (MKS Instruments). A LabView programmed virtual instrument was used to control the sequential dosing of gas to the sample and to record the evolved heat and manifold pressures needed to determine the total heat of adsorption and the amount adsorbed. The dry catalyst mass was used to determine the differential heats of adsorption as a function of CO_2 and NH_3 uptake per gram of boehmite and catalyst, respectively.

2.4. *Diffuse reflectance infrared spectroscopy*

Diffuse reflectance infrared spectroscopy (DRIFTS) was performed using a Thermo Nicolet Nexus 670 Fourier transform infrared spectrophotometer equipped with a Smart Collector and high-temperature, high-pressure in situ chamber (Spectra-Tech). In the DRIFTS chamber, a series of background spectra of KBr were taken from 50 to 250 °C under a helium atmosphere. Each sample was prepared by taking 3.0 mg of each catalyst and diluting it into 27 mg of KBr to produce a 10% sample by weight, which was subsequently ground into a fine, homogeneous powder and loaded into the DRIFTS chamber. Under a flow of helium (160 sccm), the sample was heated at a rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$ to 180 °C and held at that temperature for 1 h, after which time a spectrum was recorded. To minimize potential contamination from the He stream, a liquid nitrogen trap was placed on the inlet line to prevent trace amounts of water from entering the system. Likewise, an oxygen trap was added to remove trace amounts of O_2 from the He.

3. Results and discussion

3.1. Determination of optimum silver loading on boehmite

Minahan reported that the best support for Ag-supported catalysts is alumina, because of its low surface area and low acidity, which minimizes the complete oxidation of the olefin and epoxide product [1]. Monnier reported that a support with a surface area $<2\ \mathrm{m^2\,g^{-1}}$ is needed to prepare an effective Ag-supported catalyst and that the optimum silver loading on an unpromoted Ag-supported catalyst is between 12 and 15 wt% silver [11]. But performing studies that involve adsorption of gaseous molecules is difficult when using these low-surface-area supports, because of the high sensitivity required to accurately measure the low uptake associated with these surfaces, which in some instances can be $<1\ \mathrm{m^2\,g^{-1}}$. The higher surface area of the boehmite used here provided a catalyst surface with better adsorption capabilities than α-alumina, but not so high that meaningful comparisons to lower-surface-area aluminas cannot be made.

Initially, several supported silver catalysts were prepared with silver loadings ranging from 10 to 20 wt%, to verify that the optimum silver loading on the Nabaltec boehmite used here (which had a surface area roughly 10 times greater than typically used α-aluminas) was consistent with Monnier's findings. These catalysts were subsequently investigated for epoxidation activity. Silver loadings of 10 and 12.5 wt% on boehmite showed little appreciable activity toward EpB production; a loading of 15 wt% Ag on AlOOH showed the greatest reactivity. Likewise, pure AlOOH was inactive for the epoxidation reaction. Moreover, silver loadings above 15 wt% exhibited less reactivity than the 15 wt% Ag-supported catalyst. Thus a loading of 15 wt% silver on AlOOH was verified as the optimum silver loading for this AlOOH sample. On a per-mass basis, this optimum silver loading is consistent with the optimum silver loading observed on α-alumina supports [8,9]. After about 2 h of time-on-stream (TOS), no Ag/AlOOH epoxidation catalyst investigated exhibited any activity for EpB production.

3.2. Determination of optimum Cs loading on Ag/AlOOH

We investigated the effects of Cs promoter loading at the optimum 15 wt% silver loading. The promoter loading level is the primary factor affecting the conversion to epoxide and catalyst stability. Although a certain interaction effect between the Ag loading and Cs promotion level could occur, determining the exact optimum catalyst composition using boehmite as a support is beyond the scope of this work. An optimum Cs loading stabilizes the Ag-supported catalyst and optimizes its selectivity to the epoxide product, reducing the deactivation observed with an unpromoted catalyst. Badani and Vannice [2] and Monnier et al. [11] reported an optimum Cs-promotion level for Ag-supported catalysts in the range of 400–1200 ppm (0.04–0.12 wt%) whenever CsCl is used as the alkali promoter salt. As a result, the Cs nitrate promotion levels between 0.04 and 0.22 wt% were initially prepared via the simultaneous preparation method in this study.

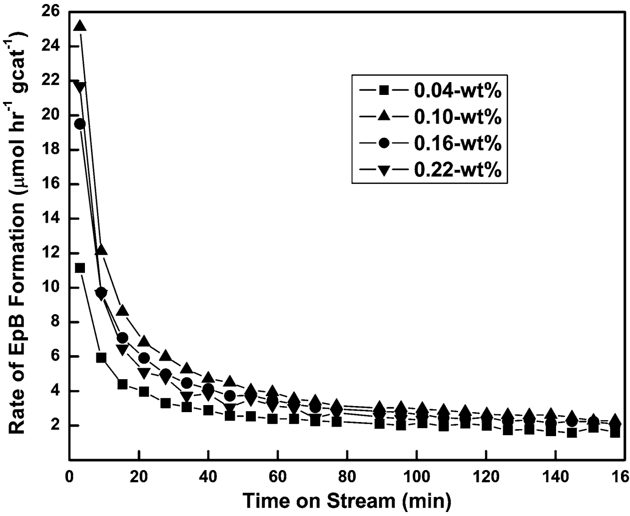

Fig. 1. 1,3-Butadiene epoxidation activity at 200 °C for various Cs–Ag/AlOOH catalysts.

Fig. 1 shows how the rate of EpB formation changed with time for each simultaneously promoted Cs-Ag/AlOOH catalyst. The figure illustrates that all Cs–Ag/AlOOH catalysts exhibited the same rate of EpB formation after approximately 80 min of TOS, which was about $2.5\ \mathrm{\mu mol\,h^{-1}\,g_{cat}^{-1}}$. Over this range of Cs promotion, which gives the optimum catalyst for the epoxidation of 1,3-butadiene for Ag supported on α-alumina, no enhancement in catalyst reactivity was observed when the Cs promotion level was increased. It appears that at these loadings, simultaneously supporting silver and Cs on boehmite using the method described here (the primary catalyst preparation method described in the literature [1,8,12,13]), does not effectively disperse the Cs in locations where the Cs promoter can enhance the stability of the catalyst. Thus the Cs must be located in positions that do not promote the silver, either being blocked by the silver itself or contributing to neutralization of surface acidity associated with the support. In either case, the Cs is not located on the silver surface.

It appears that the surface composition remains comparable regardless of the initial amount of Cs nitrate during the catalyst preparation over this range of Cs promotion. The large number of silver particles may block much of the Cs promoter when the two species are incorporated onto the support simultaneously, or the Cs may be far removed from the silver, interacting with the support by neutralizing surface acidity associated with surface hydroxyl groups as other alkali and alkaline earth oxides do at these lower loadings [14–17]. Thus the loading of Cs nitrate was not effective at promoting the silver surface when deposited simultaneously with silver nitrate during the catalyst synthesis over

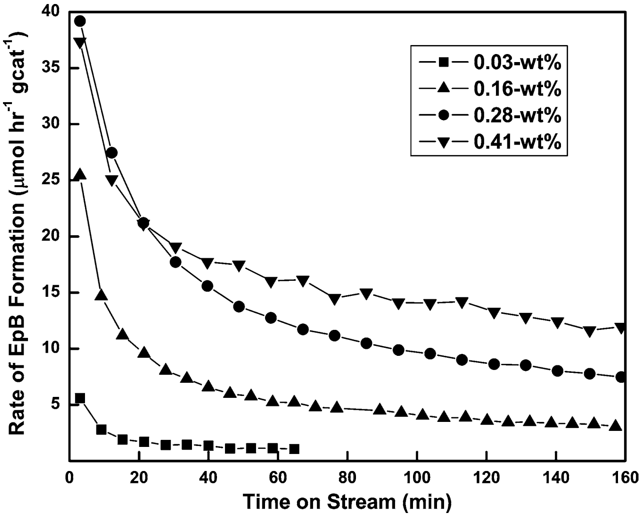

Fig. 2. 1,3-Butadiene epoxidation activity at 200 °C for various Cs/Ag/AlOOH catalysts.

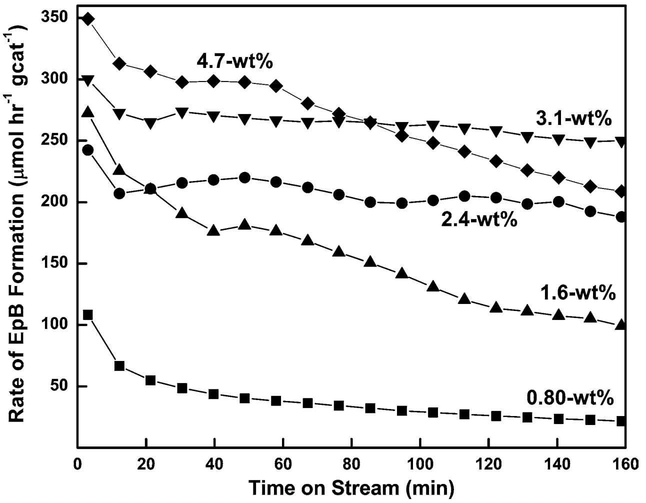

Fig. 3. Determination of the optimum Cs-promotion level for the epoxidation of 1,3-butadiene at 200 °C for Cs/Ag/AlOOH catalysts.

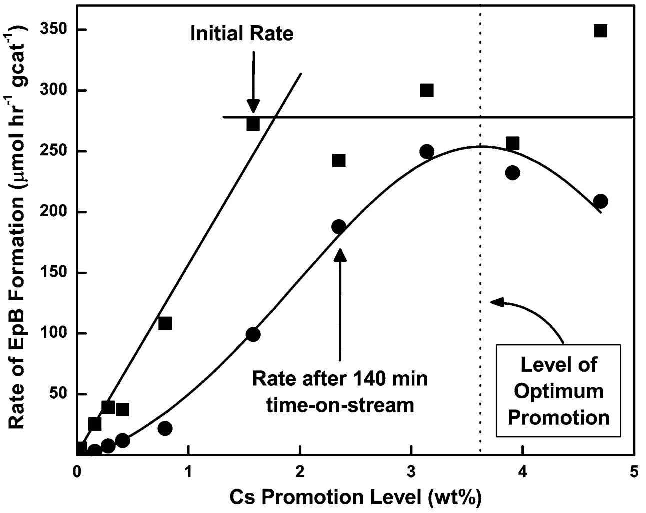

Fig. 4. Effect of Cs-promotion level on the EpB rates of formation for various Cs/Ag/AlOOH catalysts. The initial rate of formation of EpB is taken after a time-on-stream of 3 min.

the expected optimum promotion levels that used lower surface area α-alumina.

Consequently, we prepared Cs/Ag/AlOOH catalysts with $CsNO_3$ promotion levels between 0.04 and 0.41 wt% to determine whether the sequential loading of silver followed by Cs nitrate resulted in more effective Cs-promoted catalysts for epoxidation over a similar range of Cs promotion. Fig. 2 shows how the rate of EpB formation changed over time for each sequentially prepared Cs/Ag/AlOOH catalyst. As $CsNO_3$ promotion levels neared 0.16 wt% Cs, the rate of EpB formation was comparable to the rate exhibited by every simultaneously promoted catalyst investigated. But at higher Cs promotion levels, a clear reduction in catalyst deactivation during TOS was observed when using the sequential preparation procedure that was not observed for the simultaneously prepared catalysts. Furthermore, after 160 min of TOS, the rate of EpB formation increased to a value near 15 $\mu mol\, h^{-1}\, g_{cat}^{-1}$, for a Cs loading of 0.41 wt%, which was almost three times the rate exhibited by each simultaneously prepared Cs–Ag/AlOOH catalyst investigated. Thus it appears that sequentially supporting Cs nitrate after supporting silver more efficiently promotes the silver surface when preparing a silver-based epoxidation catalyst.

We prepared additional Cs/Ag/AlOOH catalysts with higher levels of Cs (0.80–19.0 wt% Cs nitrate) using the sequential preparation method, to determine the optimum Cs promotion level for maximum EpB production and minimum deactivation when using the higher-surface-area AlOOH support. Fig. 3 shows how the rate of EpB formation was affected with TOS for each sequentially prepared Cs/Ag/AlOOH catalyst in this range of $CsNO_3$ promotion. Up to a Cs loading of 3.1 wt%, increased Cs loadings resulted in an increase in the rate of EpB formation at longer TOS. However, Cs promotion above this level resulted in a decreased rate of EpB formation for longer TOS (e.g., 4.7 wt% in Fig. 3), despite exhibiting higher initial rates. Eventually, the addition of too much Cs (i.e., around 19.0 wt% Cs; not shown) produced a catalyst with no epoxidation activity, most likely due to the larger amounts of Cs blocking the active silver sites.

Fig. 4 summarizes the rates of EpB formation for each Cs/Ag/AlOOH catalyst investigated after 3 (initial) and 140 min of TOS. The initial rate of EpB formation followed a linear relationship with increased Cs loading up to 1.5 wt%. At loadings above this value, the initial rate began to level off. In contrast, the rate of EpB formation at 140 min of TOS followed a Gaussian-shaped relationship with increased Cs loadings. Analysis of this curve indicates that a Cs nitrate promotion level of roughly 3.4 wt% appears to be the optimum Cs level for sequentially prepared Cs/Ag/AlOOH catalysts for the Nabaltec boehmite used here. To produce a stable silver-based epoxidation catalyst, the higher surface area of the AlOOH support used herein appears to require a greater amount of Cs promoter compared with those catalysts that use α-alumina as the support, despite the fact that an identical silver loading of 15 wt% is optimal when using either support. Thus more Cs per square meter of surface area would be needed for supports with higher surface area to produce uniform Cs-induced electric fields (as proposed by Linic and Barteau [18]) that stabilize the transition state responsible for epoxidation compared with combustion. In fact, Monnier et al. [19] have shown, using X-ray photoemission spectroscopy, that an even distribution of Cs on a supported silver surface is necessary for producing an effective silver-based epoxidation catalyst with minimal deactivation.

3.3. Adsorption microcalorimetry of CO_2 and NH_3

After determining the optimum Cs promotion level for the Cs/Ag/AlOOH catalysts, we conducted further investigations to better understand the role of Cs as a promoter. We performed adsorption microcalorimetry on various simultaneously and sequentially Cs-promoted Ag/AlOOH catalysts of identical composition using CO_2 as a probe molecule. We chose CO_2 as the probe because this slightly acidic molecule adsorbs on the basic Cs oxide sites created during the oxidizing atmosphere catalyst pretreatment step [20,21], providing an indication of the strength and degree of exposed Cs oxide sites located at the surface. To better understand whether Cs reduces the surface acidity of the support, we normalized the adsorption microcalorimetry results herein to the mass of the AlOOH present in the sample.

We initially used CO_2 to probe the surface of both boehmite and a 15 wt% Ag/AlOOH catalyst before Cs incorporation, to determine whether the presence of Ag enhances CO_2 uptake, as reported by Liu et al. [22]. The initial heat of adsorption, normalized to the mass of boehmite present in the sample, was roughly 100 $kJ\,mol^{-1}$ for each sample, indicating that incorporating silver on the surface does not enhance the adsorption strength for CO_2. Bordawekar et al. [16] reported a similar value of approximately 100 $kJ\,mol^{-1}$ for the initial heat of adsorption of CO_2 on alumina. In addition, as seen in Fig. 5, the total uptake for the 15 wt% Ag/AlOOH was less than that for pure boehmite, indicating that some of the surface adsorption sites for CO_2 are blocked by this loading of silver and that CO_2 does not appear to adsorb on silver in significant quantities. Because no enhancement of the initial adsorption energy was observed and no increased CO_2 uptake was found, it appears that titration of surface oxygen on the silver surface does not occur, and that we are able to effectively investigate adsorption enhancements due solely to the incorporation of Cs.

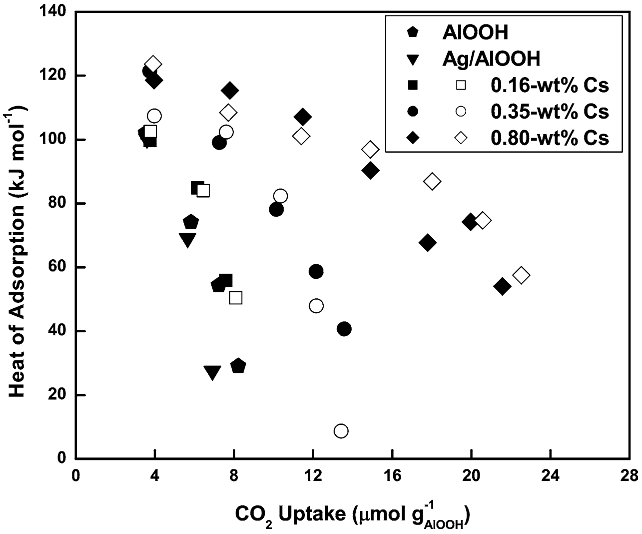

Fig. 5. Effect of Cs-promotion and catalyst preparation method on the differential heat of adsorption as a function of CO_2 uptake at 25 °C for various epoxidation catalysts, normalized to the mass of AlOOH. Open symbols correspond to catalysts prepared via the "simultaneous" preparation method and filled symbols correspond to those prepared via the "sequential" method.

Table 1
Initial heats of CO_2 adsorption, normalized to the mass of AlOOH, for various simultaneously and sequentially Cs-promoted Ag/AlOOH catalysts

	Initial ΔH_{ads} (kJ/mol)	
Cs-promotion (wt%)	Simultaneous (Cs–Ag/AlOOH)	Sequential (Cs/Ag/AlOOH)
0.00	100.2	
0.16	102.6	99.7
0.35	107.4	121.5
0.80	123.6	118.6

Table 1 summarizes the initial heats of adsorption of CO_2 on each catalyst investigated using adsorption microcalorimetry. We normalized the initial heats of adsorption of CO_2 for every catalyst to the mass of the boehmite support. We determined that CO_2 had an initial heat of adsorption of 102.1 $kJ\,mol^{-1}$ on boehmite. As seen in Table 1, the initial CO_2 heat of adsorption for every catalyst characterized was roughly between 100 and 120 $kJ\,mol^{-1}$. The adsorption capacity of the catalysts is small, because of the low surface area of the boehmite; thus the catalyst surface is completely saturated with CO_2 after only a few doses. It is noteworthy to state that these microcalorimetric studies would be significantly more difficult to perform for a catalyst produced using an α-alumina support with $<2\ m^2\,g^{-1}$ surface area, because the total uptake would be significantly lower, perhaps even resulting in a surface saturated with only one dose, and energetic changes as a result of Cs incorporation would be quite difficult to resolve. As shown in Fig. 5, CO_2 uptake was approximately 3 times greater for the highest Cs-loaded catalyst investigated (0.80 wt% Cs/Ag/AlOOH) compared with the unpromoted Ag/AlOOH catalyst and boehmite. In fact, the general trend was that CO_2 uptake increased with increased Cs loading, indicating that the Cs promoter is indeed located at the surface. This trend was observed for higher loadings of Cs promotion as well (not shown).

Simultaneously and sequentially promoted Ag/AlOOH catalysts with Cs loadings <0.16 wt% had roughly the same initial heats of adsorption as boehmite (i.e., ∼100 kJ/mol), indicating that Cs oxide sites at these lower loadings were possibly being blocked by silver or were neutralizing residual acidity associated with the boehmite support. Furthermore, when the Cs loading for simultaneously and sequentially Cs-promoted Ag/AlOOH catalysts approached 0.35 wt%, a clear increase was observed in the initial heats of adsorption compared with an unpromoted Ag/AlOOH catalyst.

The sequentially prepared Cs-promoted Ag/AlOOH catalyst exhibited an initial heat of adsorption of about 120 kJ mol^{-1}, which was higher than that for the simultaneously prepared Cs-promoted Ag/AlOOH catalyst. We have shown that this higher adsorption energy corresponds to CO_2 adsorption on supported Cs oxide sites [23] and indicates that the entire dosing volume of CO_2 was adsorbed on Cs oxide present at the surface. However, the observed 107.4 kJ mol^{-1} heat of adsorption for the simultaneously promoted catalyst at an identical Cs-promotion level indicates that roughly one-third of the dose adsorbs on Cs oxide and the remaining CO_2 adsorbs on the Ag/AlOOH. Therefore, sequentially prepared catalysts appear to have a higher level of external surface promotion than simultaneously prepared catalysts at this identical loading of Cs, indicating that the simultaneous preparation procedure does not effectively disperse Cs on the active silver surface, thus explaining the similar epoxidation activity observed for the simultaneously prepared catalysts investigated herein. Our results confirm the DFT calculations of Linic and Barteau showing that surface Cs is necessary for the promotion to have the greatest effect on reactivity [18].

At higher Cs loadings (∼0.80 wt% Cs and greater), the initial heat of CO_2 adsorption remained around 120 kJ/mol for both preparation methods, indicating that some breakthrough Cs-promotion level is reached between 0.35 and 0.80 wt% Cs, where an adequate amount of Cs is present at the catalyst surface from the simultaneous preparation procedure to measure via adsorption microcalorimetry of CO_2. At higher Cs-promotion levels (which includes the experimentally determined optimum epoxidation catalyst), total CO_2 uptake is comparable between the two preparation methods as measured using adsorption microcalorimetry, indicating that most of the Cs species are located at the catalyst surface when either preparation method is followed to promote with higher amounts of Cs. The higher initial heats of adsorption observed for these Cs-promoted catalysts clearly indicate that basic sites exist on the surface of the most active catalysts and that these sites help enhance the stability of the Ag-based epoxidation catalyst and do not solely neutralize surface acidity, as has been suggested [24].

This is not to say that Cs has no role in neutralizing surface acidity when producing an effective silver-based epoxidation catalyst. Although the role of Cs as a promoter can easily be seen from adsorption microcalorimetry of CO_2, the effect of Cs loading on surface acidity can be better understood by using adsorption microcalorimetry of NH_3, a basic molecule, to probe surface acidity. Fig. 6 illustrates the effect of Cs loading on NH_3 uptake for epoxidation catalysts prepared by the sequential preparation procedure. The figure clearly shows a reduction in the total uptake of NH_3 adsorption sites with the incorporation of Cs on the catalyst surface. A loading of 1.6 wt% Cs reduces the total uptake of NH_3 by roughly 25%, but does not reduce the strong initial heat of adsorption of 90 kJ mol^{-1} observed on the as-received boehmite. Only after we reach the Cs loading that corresponds to the optimum epoxidation catalyst (3.1 wt%) do we see a reduction in the initial heat of adsorption to a value of 75 kJ mol^{-1}. Clearly, the Cs promoter has a neutralizing effect on the surface that is important for the production of an optimum silver-based epoxidation catalyst. The 3.1 wt% loading also corresponds to the lowest total uptake for NH_3, for (as Fig. 6 clearly shows) a higher Cs loading of 4.7 wt% produced an increase in the total amount of NH_3 adsorbed compared to the 3.1 wt% Cs catalyst.

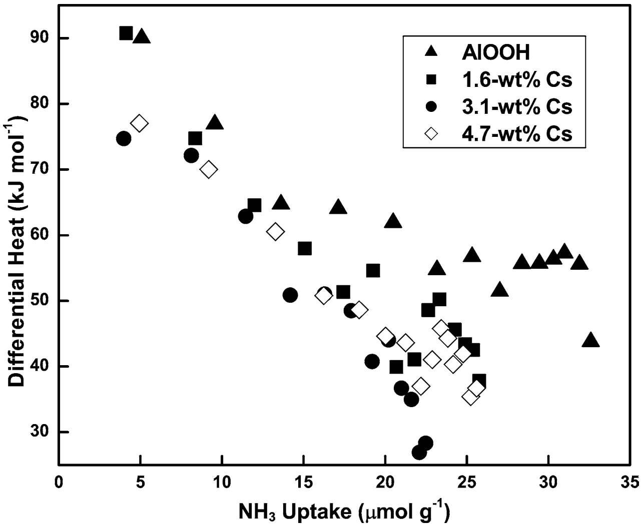

Fig. 6. Effect of Cs-promotion on the differential heat of adsorption as a function of NH_3 uptake at 25 °C for Cs/Ag/AlOOH catalysts.

3.4. DRIFTS investigation of hydroxyl stretches

The effect of Cs loading on the hydroxyl groups associated with boehmite is illustrated in Fig. 7. As this figure shows, the intensity of the hydroxyl stretches at 3313 and 3126 cm^{-1} decreases with increased Cs loading, indicating an interaction between the Cs and –OH groups [25]. The DRIFTS in the hydroxyl region for α-alumina, which is the ideal support for silver-based epoxidation catalysts, shows an insignificant amount of hydroxyl stretching compared with the boehmite-based epoxidation catalysts, indicating that minimizing the exposed hydroxyl groups plays an important role in producing an optimum silver-based epoxidation catalyst. Coupling the DRIFTS and microcalorimetric observations, it can be inferred that the Cs promoter functions both as a neutralizer for exposed surface –OH groups that exist as strong acid sites and as a promoter on the sup-

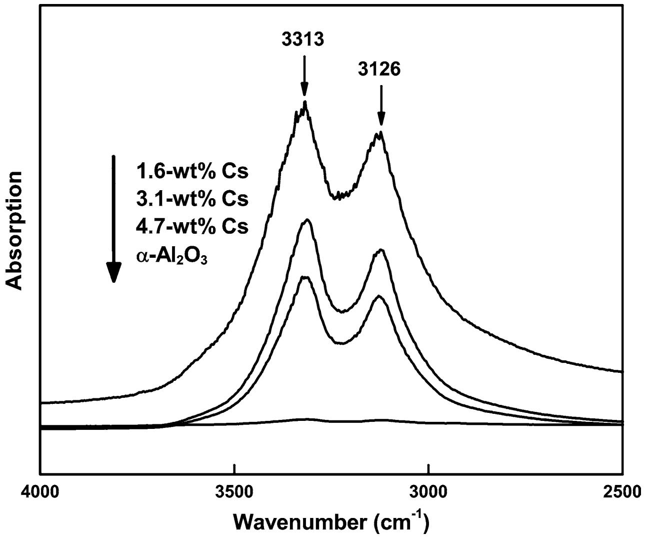

Fig. 7. Diffuse reflectance infrared spectra (DRIFTS) indicating the reduction in the number of hydroxyl groups due to increased Cs-promotion for Cs/Ag/AlOOH catalysts heated to 180 °C.

ported silver surface. The fact that more Cs is needed to produce a catalyst using a boehmite support with reduced deactivation than when using an α-alumina support can be clearly linked to the number of surface hydroxyl groups existing as acid sites on the support surface of choice. These exposed acid sites allow cracking and polymerization, significantly reducing the effectiveness of the epoxidation catalyst and causing catalyst deactivation.

4. Conclusion

We used two different preparation methods to prepare Cs-promoted Ag/AlOOH epoxidation catalysts: (1) loading the silver nitrate and Cs nitrate onto the support simultaneously and (2) loading the silver onto the support, then sequentially loading the Cs nitrate. The simultaneously promoted catalysts prepared in this study exhibited similar epoxidation behavior, indicating that the higher Cs levels in the higher promoted catalysts were not located near the surface, where the promoter would have the greatest impact on enhancing the rate of epoxidation. Conversely, Cs-promoted Ag/AlOOH catalysts prepared via the sequential method demonstrated enhanced epoxidation activity with increased Cs-promotion level, reaching an optimum in the steady-state rate of EpB formation at a Cs loading near 3.4 wt%. Above this loading, the EpB production rate decreased, and the catalyst eventually lost activity, most likely because of the large amount of Cs promoter blocking the silver active sites. Adsorption microcalorimetry of CO_2 as a probe for Cs oxide indicated that at low Cs-promotion levels, the initial heat of adsorption of CO_2 for both types of Cs-promoted Ag/AlOOH catalysts were similar to that of boehmite, indicating that CO_2 was not adsorbing on stronger Cs oxide sites. Furthermore, whenever the Cs loading for both types of promoted Ag/AlOOH catalysts approached 0.35 wt%, a higher initial heat of CO_2 adsorption was observed for the sequentially prepared catalyst compared with the simultaneously Cs-promoted Ag/AlOOH catalyst, indicating that the sequential preparation method more effectively disperses the Cs-promoter on the catalyst surface. Therefore, effective alkali promotion of Ag/AlOOH catalysts should be done using sequential promotion techniques to more efficiently disperse the promoter salt in the synthesis of epoxidation catalysts on the silver surface. Adsorption microcalorimetry of NH_3 and DRIFTS investigations of the hydroxyl region indicated that neutralization of surface acidity associated with the AlOOH structure is necessary to produce an effective catalyst with limited deactivation with respect to TOS. It appears that for silver-based epoxidation catalysts, Cs promotion plays a role in both the neutralization of the support surface and the promotion of the supported silver surface.

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