

Investigation of alcohol dehydration by a cobalt(II) sulfate-promoted γ -alumina catalyst inside a gas chromatograph injection port

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Abstract

A catalyst consisting of a sulfated cobalt promoter on γ -Al₂O₃ was prepared and utilized in a gas chromatograph (GC) injector liner to investigate the dehydration of alcohols. The activation energy barrier for the dehydration of the test compound, 2-butanol, was determined to be 83 kJ/mol (under the given experimental conditions), the process obeying pseudo-first order kinetics. The chromatographic retention behavior of dichloromethane was used as a means of probing the catalyst surface. Changes in the retention of the molecule, as a function of the injection port temperature, were found to correlate with differences in the catalyst surface hydration.

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1. Introduction

Volatile components in the reaction mixtures of catalytic processes are often analyzed by gas chromatography (GC). The use of microreactors attached directly to the inlet of GC columns for the study of heterogeneously catalyzed reactions was pioneered by Kokes, Emmett and Hall [1–4]. The convenience and operational simplicity of the technique have led to its growth in popularity. Recent examples include a flow-through design [5] and a pulse-reactor configuration [6]. A microreactor for the study of methanol dehydration on γ -alumina was described

by Schiffino and Merrill [7]. In the work presented here, an injector liner (a commercially available, small diameter glass tube) containing catalyst is used as the reaction vessel for the dehydration of alcohols.

The conversion of commercial GC instrumentation for the reactor kinetic studies of catalysts in the injection port was described over 30 years ago [8]. The injection port of a GC is amenable to the reactions of small, labile molecules due to the elevated temperatures (up to ~ 350 °C) routinely used to facilitate sample vaporization. The injector liner (typically inert) represents the first contact surface in the GC with which volatilized compounds may interact and/or react. As such, the injector liner has been used to house reagent for the on-line chemical modification of analytes to facilitate their detection [9].

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The catalytic dehydration of alcohols is of interest for the selective, economically viable synthesis of alkenes or ethers on the industrial scale. Of the two types of products formed, lower temperatures typically favor alkenes while higher temperatures favor the formation of ethers [10]. Many types of catalysts for the dehydration of alcohols have been described in the literature [10–13]. A common such catalyst is γ -alumina, which is used in this work. Of the five polymorphs of alumina, γ - or η -alumina (obtained through calcination around 350 °C) is most often used in catalytic applications [14,15]. Dehydration above 750 °C yields δ - and θ -alumina, which is of much higher crystallinity but lower activity. In turn, these species can eventually be transformed into α -alumina, which contains mainly octahedrally coordinated Al atoms, at temperatures in excess of 1200 °C [14]. While the acidity of alumina originates mainly from octahedrally or tetrahedrally coordinated surface Al^{3+} sites [16], the latter sites, found predominantly in the transitional aluminas (e.g. γ -alumina), are believed to be responsible for the higher catalytic activity of these polymorphs.

In addition to the crystal structure, the hydration state of the alumina may be of interest in catalytic studies. Water adsorbs to γ -alumina following calcination at 600 °C upon exposure to moist air at room temperature [17]. The water may exist either physisorbed to the surface or as surface hydroxyl groups. Recent NMR studies have shown that heating alumina in the temperature region of 110–300 °C causes desorption of the physisorbed water, whereas temperatures between 350 and 550 °C result in the condensation of adjacent Al–OH groups [18]. Experiments have shown that the removal of the hydroxyls as water from the alumina surface is essential for catalytic activity [19]. However, Swecker and Datye [12] observed no change in activation energy or reaction product distribution for transitional aluminas activated at substantially different temperatures (400–600 °C). This was attributed to the fact that water, a product of dehydration reactions, can rehydroxylate the alumina surface regardless of its initial state of dehydration. Surface water is believed to play a key role in some of the observations reported in this work.

Metal sulfates have been established as catalytic promoters for use with silica supports [11]. Sulfates are useful in catalytic applications due, in part, to their

thermal stability and the low nucleophilicity of the sulfate ion. The type of metal used can greatly impact the catalytic activity: in general, the greater its Lewis acidity, the greater the catalytic activity. Cobalt(II) sulfate was selected as the promoter for γ -alumina to yield the alcohol dehydration catalyst used in the studies described here. In the case of alumina, a potential secondary benefit to using a transition metal dopant may be to reduce the catalyst-deactivating coke build-up on the surface with continued use [20].

In this work, alcohols in dichloromethane solution are introduced into a GC injection port housing a CoSO_4 -promoted $\gamma\text{-Al}_2\text{O}_3$ catalyst, using splitless injection. The dehydration products are subsequently chromatographed under isothermal and isobaric conditions. The dehydration kinetics of a test compound, 2-butanol, are examined using this technique and the interactions of dichloromethane with the catalyst surface investigated by monitoring changes imparted to the chromatographic retention as a function of the injector temperature.

2. Experimental

2.1. Preparation of the CoSO_4 -promoted $\gamma\text{-Al}_2\text{O}_3$ catalyst

Approximately 5.0 ml of Type I water (Picotech, Hydro Systems and Supplies, Garfield, NJ) was added to 1.1 g of aluminum oxide (Type T (neutral), E. Merck, Darnstadt, Germany) and 1.0 g of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma–Aldrich, Milwaukee, WI). The pink suspension was sonicated for 15 min and evaporated to dryness under atmospheric pressure at a temperature of ~ 90 °C. The pink solid obtained was ground lightly with a mortar and pestle and the powder calcined inside a platinum crucible at a temperature of 600 °C for 1 h. Following calcination, the powder became mauve in color. The resulting catalyst was stored in a desiccator at room temperature prior to introduction to the GC injector liner.

2.2. Preparation of the catalyst-containing injector liner

A portion (ca. 50%) of the deactivated glass wool contained inside a split/splitless HP#5183-4711 liner

(Agilent Technologies, Wilmington, DE) was removed with tweezers. Approximately 80 mg of the CoSO₄-promoted γ -Al₂O₃ catalyst was deposited into the liner, to a depth of \sim 1 cm. After installation of the injector liner into the GC, the catalyst was conditioned by heating the injection port at 350 °C for 60 min. The catalyst surface was then primed (prior to initiating experimental work), using 10 injections of dichloromethane followed by 15 injections of a solution of 2% (v/v) 2-butanol in dichloromethane and, finally, five additional injections of neat dichloromethane (all injections made using an injection port temperature of 250 °C).

2.3. GC experiments

All chromatograms were obtained under isothermal and isobaric conditions on a Hewlett-Packard HP6890 (Agilent Technologies) GC system equipped with an autoinjector, a flame ionization detector (FID) and dual split/splitless injection port. Data points were acquired at a rate of 10 points per second and the resulting chromatograms analyzed using TurbochromTM (Perkin-Elmer, San Jose, CA) software. A Stabilwax[®] (Restek, Bellefonte, PA) open-tubular capillary column, 30 m in length with a 0.32 mm i.d. and 1 μ m film (poly(ethylene glycol), PEG), was used for all experiments. The column pressure of He carrier gas was held constant at 6.3 psi for all experiments. For sample injections, the injection port was operated in splitless mode, either with or without catalyst in the liner, with a 0.5 μ l injection volume, hold time of 21 s and purge flow of 75.0 ml/min. Six syringe flushes in the wash solvent (dichloromethane) and six sample flushes were made prior to each injection. A ThermogreenTM LB-2 injection port septum (Supelco, Bellefonte, PA) was used for all sample injections.

The GC oven temperature was maintained at 50 or 100 °C (isothermal) for dehydration studies involving the following alcohol solutions: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, *tert*-butanol, 1-hexanol and 2-ethyl-1-hexanol in dichloromethane (\sim 2% (v/v), all compounds purchased from Sigma–Aldrich). The injection port temperature was held at 250 °C. For the investigation of the dehydration kinetics of 2-butanol, the column temperature was maintained at 50 °C while

the temperature of the injection port (containing catalyst) was varied from 100 to 300 °C, using 50 °C increments. The retention times of all alcohols were obtained without catalyst in the injector liner, with a column temperature of 50 or 100 °C and injection port temperature of 250 °C.

Chromatographic retention time measurements were also performed for dichloromethane peaks, both with and without catalyst in the liner. Injections of the neat solvent were made with the detector signal attenuation increased to ensure the peaks were on-scale. For all cases, the oven temperature was maintained at 50 °C while the temperature of the injection port was varied from 100 to 300 °C.

2.4. Differential scanning calorimetry (DSC)

Heat flow was measured as a function of temperature for a sample of the catalyst (exposed for a short period of time to open atmosphere), using a TA Instruments (New Castle, DE) DSC 2910. Approximately 7 mg of the catalyst was accurately weighed into an open aluminum pan and heated under nitrogen atmosphere at a rate of 10 °C/min, from 40 to 350 °C. A second, empty pan served as a reference.

2.5. Fourier transform infrared (FT-IR) spectroscopy

Infrared spectra were recorded of self-supporting disks of the catalyst (material compacted using a KBr press) using a Nexus 670 spectrometer (Thermo Nicolet, Madison, WI) equipped with a DTGS detector. Each spectrum consisted of 32 co-added scans acquired at 4 cm⁻¹ resolution in the 4000–600 cm⁻¹ range. A PC running Omnic E.S.P. software (version 5.1) was used to capture the spectra. A dry nitrogen purge was employed during data acquisition.

2.6. X-ray powder diffraction (XRPD)

XRPD was performed using a Philips (Bothell, WA) APD XRG 3100 X-ray generator (producing Cu K α radiation) and a Philips PW 3710 MPD controller. The analyses used an accelerating potential of 45 kV and a current of 40 mA. Samples of the catalyst were scanned from 2 to 40° (2 θ) with a continuous scan of 475 s duration.

3. Results and discussion

In the studies performed here, it was observed that alkenes were the major products of the alcohol dehydration reactions on the CoSO_4 -promoted $\gamma\text{-Al}_2\text{O}_3$ catalyst surface. The chromatographic peaks of these compounds were found to be unretained on the PEG stationary phase. Void elution for the alkene dehydration products of the lower molecular weight alcohols (methanol to butanol, all structural isomers considered) was confirmed by the injection of a sample mixture containing hexenes, which were found to be minimally retained under identical experimental conditions. The formation of predominantly alkene products at the injection port temperatures of these studies is consistent with the observations of others [10]. For instance, Macho et al. [21] found that *cis*-2-butene was the major dehydration/isomerization product of 2-butanol on γ -aluminas under atmospheric pressure at temperatures ranging from 300 to 470 °C. A recent theoretical study of the dehydration of alcohols on metal oxide surfaces showed that the reaction proceeds by cleavage of the C–O bond following an attack on the oxygen atom by a surface electrophile [22]. Subsequently, the reaction continues by the abstraction of a β -hydrogen atom by the oxygen atom (in a unimolecular fashion) to yield the alkene and water.

The higher-boiling ether products for the lower molecular weight (≤ 74 amu) alcohols were not observed at levels above 5% of the corresponding alkene product peak areas, in any of the chromatograms. In addition, unreacted alcohols were found to be poorly transmitted through the catalyst-containing injector liner (at all injector temperatures), as indicated by the absence of the corresponding peaks in the chromatograms. (Without catalyst in the liner, retention time markers for each alcohol, as well as some of the likely ether products, were established under identical experimental conditions.) These observations may imply that the unreacted alcohols (and possibly ether products, if formed in appreciable quantities), or their degradation products (discussed more later), are irreversibly adsorbed on the catalyst surface.

Significantly less alkene dehydration products were obtained over the same injector temperature range for the higher molecular weight, primary alcohols (such as 1-hexanol) than for the smaller, secondary or tertiary alcohols. This observation may reflect more sluggish

reaction kinetics for the former species, which could be a result of either the size or geometry (or both) of the compounds. It has been reported previously that the order of reactivity in the dehydration of alcohols is typically tertiary > secondary > primary [11]. However, based on comparisons of the dehydration data obtained for the larger and smaller primary alcohols, it was found that the size of the compound may also play a role in its reactivity. Interestingly, Ballantine et al. [23] found that the dehydration of 1-hexanol (using a different catalyst and experimental conditions) generated predominantly ether product while the corresponding secondary alcohol produced mainly alkene. Here, minimal levels of ether product were observed for the dehydration of 1-hexanol.

3.1. Kinetics of 2-butanol dehydration using the CoSO_4 -modified $\gamma\text{-Al}_2\text{O}_3$ catalyst

The test compound, 2-butanol, was selected to investigate the kinetics of alcohol dehydration on the CoSO_4 -modified $\gamma\text{-Al}_2\text{O}_3$ catalyst surface. The relative chromatographic peak areas of the butene dehydration products (where all isomers are considered collectively), plotted as a function of the injection port temperature for serial injections of a solution of the alcohol (see Fig. 1), show that as the temperature increases the formation of butene also increases. Accurate quantitation of the void-eluted alkenes was possible because there were no co-eluting species in the void volume. Also shown in Fig. 1 is the effect of the injection port temperature on the ‘transmission efficiency’ of inert dichloromethane through the injector liner, as indicated by the respective peak areas for the compound obtained at the various temperatures. Without catalyst in the liner, the thermal expansion of the sample inside the injection port results in less dichloromethane being deposited on the column, over the fixed duration of the injection hold time, at higher injection port temperatures. However, with catalyst present, more of the compound is transferred to the column at the higher injection port temperatures, despite the thermal expansion. In the latter case, the catalyst powder inside the liner acts as a restrictor, increasing the pressure. This limits, to some degree, the thermal expansion of the sample. However, molecular interactions of dichloromethane with the catalyst surface may be responsible for the actual increase in

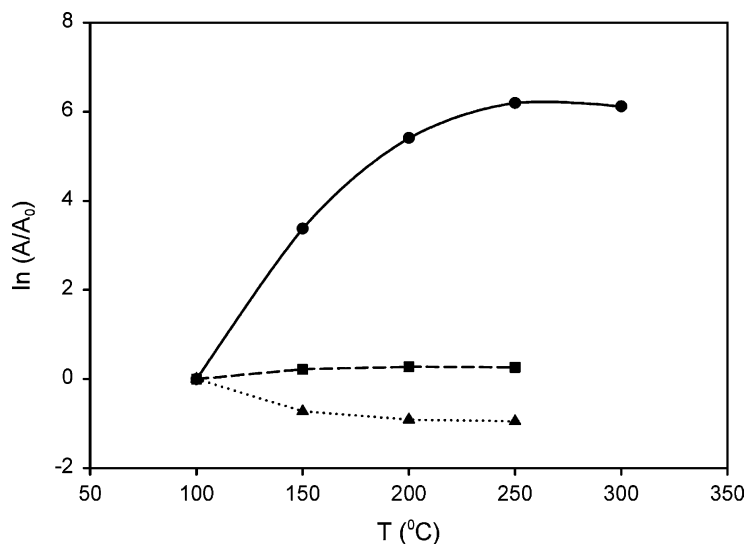


Fig. 1. Plots of the natural logarithm of the ratios of the chromatographic peak areas (A) obtained as a function of injection port temperature (T), relative to the corresponding peak areas (A_0) obtained at the lowest injector temperature (100 °C) studied, for butene product ((●) catalyst present in the injector liner) and for dichloromethane solvent (either with (■) or without (▲) catalyst in the injector liner). Note that the effective injector liner volumes are different for cases in which catalyst is present relative to those in which it is absent. Each data point represents the average of duplicate measurements (error bars too small to plot).

the injection port transmission efficiency observed as a function of the temperature (discussed more later).

Fig. 2 shows the sigmoidal dependence of butene formation on the injection port temperature. Generally, as the temperature is increased, more 2-butanol is converted into alkene on the catalyst surface (1:1 stoichiometry) as seen previously in Fig. 1. Assuming a (pseudo-) first order reaction rate law (Eq. (1)), the combination of Eq. (1) and the Arrhenius equation (Eq. (2)) provides an expression which allows the activation energy (ΔG^\ddagger) for the alcohol dehydration process to be estimated (Eq. (3)) [24]:

$$1 - X = \exp[-kt] \quad (1)$$

$$k = A \exp\left[-\frac{\Delta G^\ddagger}{RT}\right] \quad (2)$$

$$\frac{1}{T} = -\frac{R}{\Delta G^\ddagger} \ln\left[\ln\left(\frac{1}{1-X}\right)\right] + \frac{R}{\Delta G^\ddagger} \ln(At) \quad (3)$$

In Eqs. (1)–(3), k is the rate constant for the dehydration, T the injection port temperature, R the gas constant and X the mole fraction of alkene product (assuming 100% conversion at 300 °C, see Fig. 2)

obtained at temperature T after hold time t (fixed) in the injection port. The Arrhenius constant, A , relates the number of collisions between alcohol molecules and surface catalytic sites, independent of their energy.

Fig. 3 shows a plot of the kinetic data presented in Fig. 2, constructed using Eq. (3). The slope of the line is $-R/\Delta G^\ddagger$ and the y-intercept is the product of $R/\Delta G^\ddagger$ and $\ln(At)$. A linear regression fit of the data returned a value of $R^2 = 0.992$. From the slope, the activation energy for the process was calculated to be 83 kJ/mol (note: this value is less than the activation energy of 114 kJ/mol reported for the dehydration of the analogous compound, *tert*-butanol, on unpromoted γ -alumina (Kaiser A-201) [12]). The Arrhenius constant was found to have a value of approximately $4 \times 10^7 \text{ s}^{-1}$. The linearity of the plot demonstrates that pseudo-first order kinetics were maintained over the entire temperature range studied, consistent with the reaction model used by others [14].

3.2. Physical properties of the catalyst

The molar ratio of Al:Co in the catalyst used in this work was 6:1, as prepared. The preparation of

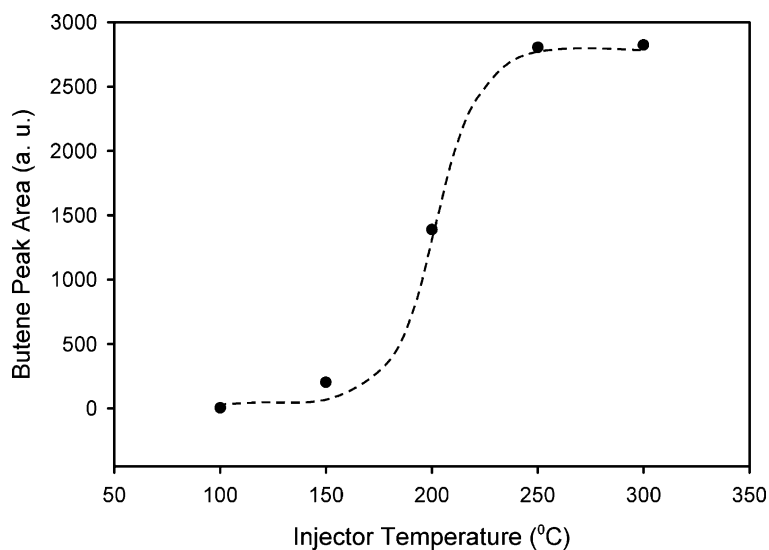


Fig. 2. Plot of the chromatographed butene peak area as a function of injection port temperature (with catalyst supported inside the injector liner). The injected sample is a 2% (v/v) solution of 2-butanol in CH_2Cl_2 . Each data point represents the average of duplicate measurements (error bars too small to plot). Broken line added to guide the reader.

similar catalysts by ion-exchange [10], impregnation [25] or precipitation [26] has been described. The cobalt may be present as supported Co_3O_4 crystallites, well-dispersed Co^{3+} , well-dispersed Co^{2+} or catalytically inactive CoAl_2O_4 [27]. An XRPD

spectrum (not shown) indicated that the catalyst was highly amorphous, consistent with high-surface area (typically $\sim 100 \text{ m}^2/\text{g}$) γ -alumina [12]. Transitional γ -alumina has been observed by others to form via calcination at 600°C [15].

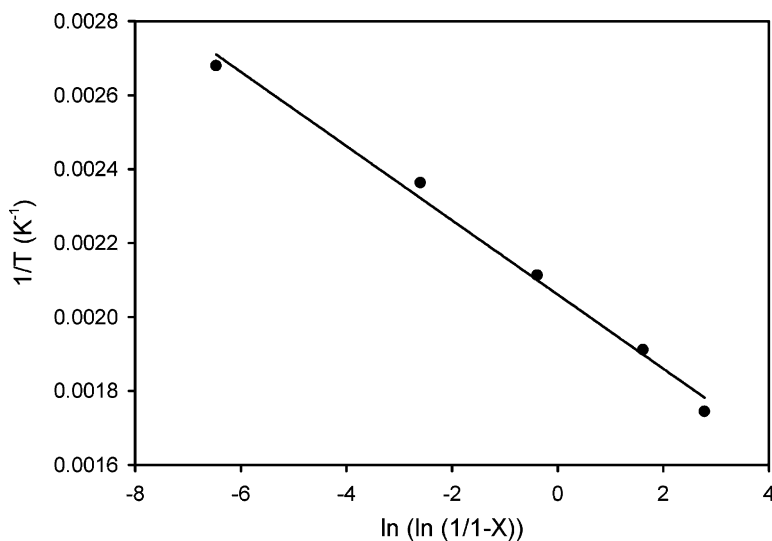


Fig. 3. Plot of $1/T$ vs. $\ln\{\ln[1/(1-X)]\}$ for data contained in Fig. 2 (see text for details). The slope has a value of $(-1.00 \pm 0.05) \times 10^{-4} \text{ K}^{-1}$, the intercept is $(2.06 \pm 0.02) \times 10^{-3} \text{ K}^{-1}$.

Over the finite set of experiments carried out in this work (including >40 injections of a 2% (v/v) solution of 2-butanol in dichloromethane at various injector temperatures), the CoSO_4 -modified $\gamma\text{-Al}_2\text{O}_3$ catalyst was observed to lose activity and become grey in appearance (versus the mauve color obtained following calcination, see Section 2), suggestive of carbonaceous deposits on the surface. However, infrared (IR) bands characteristic of coke species [28] were not observed in the transmission-mode spectra (not shown) of the catalyst, likely indicating a relatively small amount (<0.1 wt.%) of these materials was present [29]. The kinetics of catalyst deactivation by surface deposition of highly saturated carbon species has been investigated, and possible solutions to the problem noted [30]. Interestingly, in the case of hydrogenation and isomerization reactions of various hydrocarbon species on metal–metal oxide surfaces, the reactants themselves have been observed to promote catalytic activity by modifying the surface [31]. In this work, the catalyst surface was primed with injections of alcohol solution (see Section 2) to ensure reproducible dehydration behavior.

A DSC scan (Fig. 4) of the catalyst shows a very broad endotherm with $\Delta H = 64.2 \text{ J/g}$, onset temperature of 212°C and peak temperature of 275°C . The endotherm is due to the surface dehydration of

physisorbed water [18], the broadness of the peak reflects a wide distribution of surface adsorption sites. Note that since water is a byproduct of any dehydration reaction, elimination of all surface water is not possible at the injection port temperatures investigated in this work.

3.3. Thermodynamics of dichloromethane retention on the CoSO_4 -promoted $\gamma\text{-Al}_2\text{O}_3$ surface

In addition to the characterization of the catalyst physical properties by DSC and XRPD, changes in the retention time of dichloromethane with injector temperature were used to investigate the thermodynamics of interactions of the molecule with the catalyst surface. Without catalyst in the injector liner, the isothermal/isobaric retention time of dichloromethane was found to be constant ($\sim 12.0 \text{ min}$ at a column temperature of 50°C) and independent of the injector temperature. However, with the catalyst added, the retention time was observed to increase by almost one minute at an injector temperature of 250°C , relative to that obtained at 100°C (column temperature/pressure constant). It is believed that dichloromethane, an inert but polar molecule, may have sufficiently strong interactions with the catalyst surface to impart significant retention time differences to the chromatographed peaks

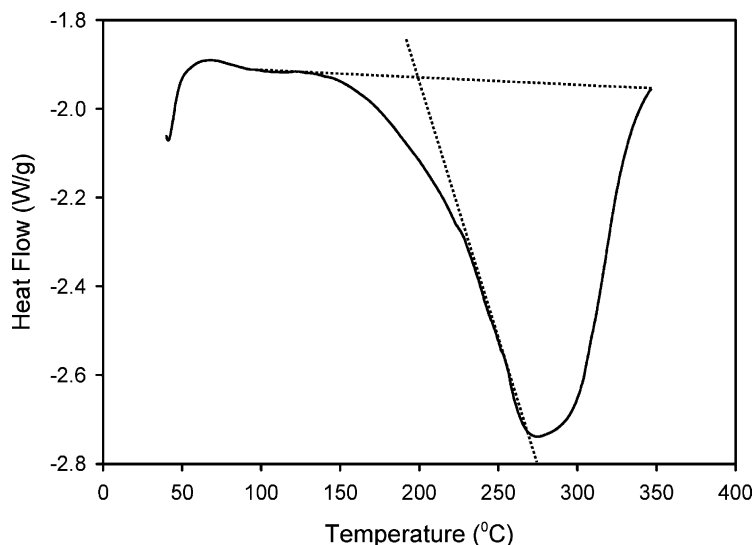


Fig. 4. DSC scan of the CoSO_4 -promoted $\gamma\text{-Al}_2\text{O}_3$ catalyst used in the experiments described in this work. The endotherm is produced by dehydration of physisorbed water (see text for details). Broken lines added to reflect computer integration.

at the various injector temperatures. (The period of time required for molecules to travel through the injection port of a GC not containing catalyst in the liner is typically much shorter than the column residence time. Thus molecular interactions with a catalyst placed inside the injection port must be relatively strong compared to the interactions with the column stationary phase in order to be detectable as a change in the retention time.) Since the interactions of dichloromethane with both the catalyst surface and the column stationary phase (PEG) impact the overall retention of the molecule, the catalyst surface itself can be considered to be a type of stationary phase, placed in-line (serially) with the column stationary phase. Considering this, the retention behavior of dichloromethane can be analyzed to provide thermodynamic information about the interactions between the molecule and the catalyst surface.

Typically van't Hoff plots ($\ln(k')$ versus $1/T$) of retention data are linear, allowing the change in enthalpy (ΔH) and change in entropy (ΔS) associated with the partitioning of an analyte molecule between the stationary and mobile phases of a chromatographic column to be ascertained with the aid of the following equation [32,33]:

$$\ln(k')_{P,T} = \frac{-\Delta H_{P,T}}{RT} + \frac{\Delta S_{P,T}}{R} + \ln \phi \quad (4)$$

where k' is the retention factor for a given analyte ($\equiv (t_R - t_0)/t_0$, where t_R is the retention time of the compound and t_0 is the column void time), ϕ is the ratio of the column stationary phase and mobile phase volumes, P is the column pressure, T is the column temperature and R is defined as before. The subscripts P and T indicate the dependence of the key thermodynamic parameters on both the pressure and temperature, hence these variables were maintained constant in all experiments (note, however, that the pressure drop down a capillary column may be considered negligible [34]).

In situations where the predominant retention mechanism changes from being enthalpically-driven to entropically-driven (or vice versa) over a given temperature range, non-linearity in the van't Hoff plot may be observed. The non-linearity is due to a non-zero heat capacity term (ΔC_p) found in the mathematical description of the retention for the compound on a given stationary phase [35]. The quadratic

equation (the subscripts P and T are omitted in this and all subsequent equations):

$$\ln(k') = a_0 + \frac{a_1}{T} + \frac{a_2}{T^2} + \ln \phi \quad (5)$$

employs the constants a_0 , a_1 and a_2 which can be extracted from a plot of $\ln(k')$ versus $1/T$ and used to relate the thermodynamic parameters given below:

$$\Delta H = -R \left[\frac{a_1 + 2a_2}{T} \right] \quad (6)$$

$$\Delta S = R \left[\frac{a_0 - a_2}{T^2} \right] \quad (7)$$

$$\Delta C_p = \frac{2Ra_2}{T^2} \quad (8)$$

Eqs. (4)–(8) may be applied to the retention of dichloromethane in either the open-tubular capillary column or the ‘packed column’ of the injection port microreactor. Because the retention caused by multiple interactions and/or sources of interactions is additive, in order to examine only the interactions of dichloromethane with the catalyst surface the retention contributions from all other sources in the chromatographic system must be subtracted from the measured peak retention times.

The retention time of dichloromethane in the injection port, $t_{R,c}$, at a given injector temperature, is approximated here as:

$$t_{R,c} \approx t_{R,1} - t_{R,0} \quad (9)$$

where $t_{R,1}$ is the retention time of the compound after passing through both the catalyst-containing injection port and the column, and $t_{R,0}$ is its retention time under identical chromatographic conditions but without the catalyst present in the liner.

The retention factor for dichloromethane on the catalyst surface, k'_c , can be defined as:

$$k'_c = \frac{t_{R,c} - t_1}{t_1} \quad (10)$$

where t_1 is the ‘void time’ of the injection port microreactor (i.e. the average time required for completely unretained/non-interacting compounds to pass through the liner containing the catalyst particles). As t_1 is difficult to measure experimentally, for the purposes of this work it is estimated at 4.8 s, at 100 °C (using half the difference between values of $t_{R,1}$ and $t_{R,0}$ at this

temperature to arbitrarily yield a value of unity for k'_c) and assumed to be directly dependent on the injection port temperature (as for an ideal gas). The void time for the injection port without catalyst is assumed to be negligible (hence this term was omitted from Eq. (9)). To describe the retention of dichloromethane on the catalyst surface, Eq. (5) can be written as:

$$\ln(k'_c) = a_0 + \frac{a_1}{T} + \frac{a_2}{T^2} + \ln \phi \quad (11)$$

where T is the injection port temperature and ϕ is the ratio of the volume of packed catalyst particles to the volume of gas in the injector liner (estimated here to be ~ 0.4). Eqs. (6)–(8) can be used as before with this equation.

Fig. 5 shows that the data points in the van't Hoff plot of dichloromethane retention on the catalyst surface are better represented by a quadratic regression fit ($R^2 = 0.983$) than a linear fit ($R^2 = 0.688$). The approximate values for ΔH , ΔS and ΔC_p obtained by fitting the data are 180 kJ/mol, 220 J/(K mol) and -430 J/(K mol), respectively, at an injection port temperature of 150 °C (arbitrarily selected to be inside the temperature range studied). The large magnitudes of these values (relative to those obtained for

typical chromatographic stationary phases) exemplify the strong nature of the retention mechanisms of dichloromethane on the catalyst surface. The values suggest a predominantly entropic driving force for the retention of dichloromethane on the catalyst surface at 150 °C. In fact, this driving force dominates over the temperature range of 100–230 °C, as can be seen by the negative slope of a tangent to the curve drawn at any point in this range. Entropically-driven retention behavior is most commonly observed in size-exclusion chromatography (SEC) [36–38]. This behavior reflects the confinement of the dichloromethane molecules inside the catalyst pores: increasing the temperature increases the confinement. However, at higher temperatures (in excess of ~ 230 °C), the predominant mode of retention appears to become enthalpically-driven for this compound.

Relatively low temperature phase transitions have been observed for common HPLC chromatographic stationary phases, which can impact the retention characteristics of the phase [39]. Such phase changes have been characterized with the aid of DSC. By comparing Figs. 4 and 5, it is evident that the temperatures at which the most significant changes in heat

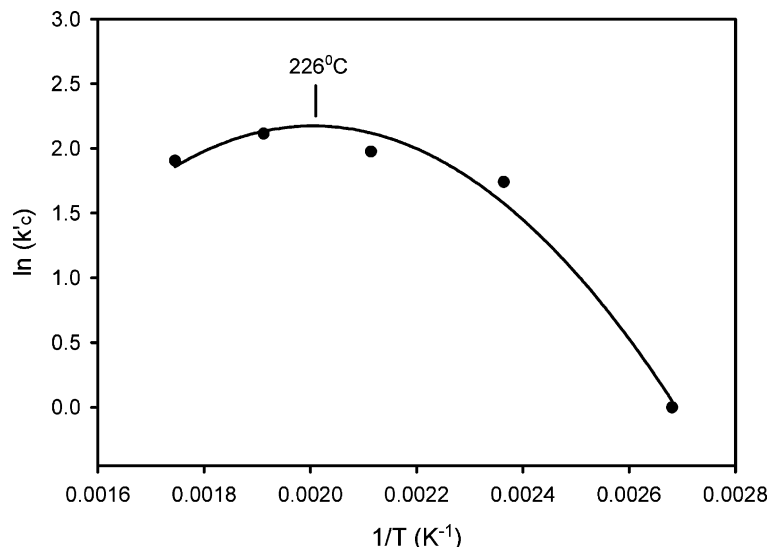


Fig. 5. The van't Hoff plot relating the temperature (T) dependence of dichloromethane retention on the catalyst surface (k'_c), inside the GC injection port (see text for details). The coefficients of the quadratic regression fit (see Eq. (11) in the text) are as follows: $a_0 + \ln \phi = (-1.7 \pm 0.4) \times 10^1$, $a_1 = (1.9 \pm 0.4) \times 10^4$ and $a_2 = (-4.7 \pm 0.8) \times 10^6$. The curve maximum (226 °C) is highlighted on the plot. Each data point represents the average of duplicate measurements (error bars too small to plot).

flow are found in the DSC scan of the catalyst mirror the temperature range in which the non-linear chromatographic retention behavior of dichloromethane is observed on the catalyst surface. In fact, even the endotherm peak in the DSC scan (at $\sim 275^\circ\text{C}$) appears to correlate reasonably well with the curve maximum in the van't Hoff plot (estimated to be $226 \pm 25^\circ\text{C}$, using the equation of the quadratic fit). It is believed that the level of catalyst surface hydration (mainly physisorbed water) at the various injection port temperatures affects the interactions of the dichloromethane molecules with the surface. As the temperature is increased, the material dehydrates and may be more able to interact with the hydrophobic dichloromethane molecules. Hence both size-exclusion and interaction mechanisms likely play a role in the retention of dichloromethane on the catalyst surface. The former mechanism dominates at temperatures below $\sim 230^\circ\text{C}$, based on the predominantly entropic nature of the retention. At higher injection port temperatures, the enthalpically-driven retention mechanism (i.e. Lewis acid–Lewis base interactions [40] of dichloromethane molecules with dehydrated surface alumina surface sites) dominates.

4. Conclusions

The dehydration of alcohols inside the injection port of a GC was studied using a CoSO_4 -promoted $\gamma\text{-Al}_2\text{O}_3$ catalyst. Using the injection port as a reactor for catalytic studies may circumvent the need for more specialized apparatus in certain situations. For example, the technique may allow different catalyst preparations to be rapidly evaluated, under similar experimental conditions, for their activity toward various test compounds.

The reaction rates of various alcohols were observed to be dependent on the injection port temperature, allowing the kinetics to be investigated. The dehydration of the test compound, 2-butanol, on the catalyst surface was found to obey pseudo-first order kinetics. An activation energy of 83 kJ/mol was obtained for the process under the experimental conditions used in the investigation. Chromatographic principles of retention were used to investigate the interactions of dichloromethane with the catalyst surface. Dichloromethane was observed to be predominantly retained in an entropic manner at temperatures below

$\sim 230^\circ\text{C}$, but increasingly enthalpically retained at higher temperatures. Correlating the retention data (in the form of a van't Hoff plot) with a DSC scan of the catalyst led to the observation that differences in water content on the catalyst surface, as a function of temperature, may be responsible for the change in the predominant retention mechanism.

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