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Structure sensitivity of cyclopropane hydrogenolysis on carbon-supported platinum

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ABSTRACT

There has been debate in the past as to whether or not cyclopropane hydrogenolysis is a structure sensitive reaction. This paper addresses the structure sensitivity of cyclopropane hydrogenolysis on Pt using K^+ addition to Pt/C and compares the results to those for CO hydrogenation, a classic structure insensitive reaction. Kinetic parameters determined for both reactions show the effect of K^+ on Pt to be limited to simple site blockage at the reaction conditions used. Determination of the site ensemble size (number of contiguous surface metal atoms) required for reaction using Martin's model suggests that cyclopropane hydrogenolysis requires a site ensemble size of ca. 7, whereas the structure insensitive CO hydrogenation reaction requires only an ensemble size of ca. 1. In addition, evidence suggests that K^+ decorates Pt non-uniformly.

1. Introduction

The reaction of cyclopropane with hydrogen has been studied extensively on a wide variety of metal catalysts [1–8], and in particularly Pt [1,3,9–13]. This hydrogenolysis reaction, termed so due to the characteristic ring opening of cyclopropane, has been observed to yield three different sets of products depending on the metal and conditions used:

$$cC_3H_6 + H_2 \rightarrow C_3H_8 \quad (1)$$

$$cC_3H_6 + 2H_2 \rightarrow CH_4 + C_2H_6 \quad (2)$$

$$cC_3H_6 + 3H_2 \rightarrow 3CH_4 \quad (3)$$

Reactions (2) and (3), termed "selective" and "non-selective hydrocracking", respectively, have been observed to occur on metals such as Fe, Os, and Ru with a shift toward the latter reaction as temperature increases [3,5,7,8]. However, on metals such as Pt, Pd, Ir, and Rh, only reaction (1) has been observed [3,4,11,13].

The structure sensitivity of the three cyclopropane reactions has been widely debated in the literature; and within this debate, the structure sensitivity of reaction (1) on Pt has particularly been discussed. Early works by Boudart et al. [9] and Kahn et al. [12] comparing the specific activity of the hydrogenolysis reaction as a function of metal surface area and dispersion showed the turnover frequency (TOF) to vary by a factor of only 2 for various loadings of Pt on alumina/silica and for certain Pt single crystal planes investigated. Based on the hypothetical vast difference in surface structural characteristics of the metal between supported and single crystals of Pt, the authors concluded that the reaction was structure insensitive to particle size, nature of support, or method of preparation. Later, work by Gallaher et al. [4] on La_2O_3-supported Rh, which, like Pt, is only active for reaction (1), showed the reaction rate to increase linearly with an increase in Rh dispersion and suggested that the activity vs. dispersion on a TOF basis is constant and similar in behavior to that of other structure insensitive reactions.

On the other hand, Oteroschipper et al. [13] confirmed the factor of 2 difference in TOF observed by Boudart et al. [9] but found it to be beyond experimental uncertainty for a wide range of dispersed Pt/SiO_2 catalysts. They concluded that, for this difference to be real, the reaction must be at least moderately structure sensitive. Similar conclusions have been suggested in more recent works by Jackson et al. [11] and Sajkowski et al. [6], in which the activity of cyclopropane hydrogenolysis appeared to depend on the particle size of the various supported Pt and Ru catalysts investigated. It should be noted that, while Ru is active for reactions (1) and (2), both reactions appear to have the same rate determining step, which is the ring opening of cyclopropane and formation of a common intermediate [6].

It should be pointed out that the "structure sensitivity" of a particular reaction entails not just (a) an effect of particle size related to crystal planes exposed on the observed rate or TOF of the reaction. Parameters that can also affect the rate of a structure sensitive reaction are as follows: (b) coordination numbers of the active metal surface atoms in the active sites and (c) the number of contiguous metal surface atoms or ensemble size required for reaction. A general

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change in particle size and/or dispersion can potentially change the characteristics of all three parameters above and, depending on how "structure sensitive" the specific reaction is, the effect on the resulting reaction kinetics can be moderate to significant. In addition to particle size, the shape of a metal particle may also be an issue. However, a more specific investigation of structure sensitivity of a reaction on a metal catalyst can be made without varying metal particle size but by decoration of the metal surfaces using an additive or poison that effectively blocks surface metal atoms.

This paper reports, for the first time, the results of an investigation into the structure sensitivity of cyclopropane hydrogenolysis on Pt using a series of K^+-doped Pt/C catalysts prepared via sequential impregnation of the pre-reduced supported metal catalyst to prevent modification of the particle size distribution. Potassium was chosen due to evidence suggesting the promoter-metal interactions to be limited to simple site blocking on Pt and other noble metals if impregnated sequentially [14,15]. The methodology of this investigation is similar to that of Hoost and Goodwin [15] and utilizes the statistical dependence of the rate of structure sensitive reactions on simple site blockage originally established and reviewed in detail by Martin [16] in determining the approximate ensemble size required for reaction. In addition, results for the hydrogenation of CO, a classic structure insensitive reaction, on the K^+-modified Pt/C catalysts are also presented to contrast to those for cyclopropane hydrogenolysis. Due to the low temperature required for cyclopropane hydrogenolysis, if this reaction were shown to be structure sensitive, it could be used to characterize Pt catalyst surfaces in catalysts not stable at higher temperatures, such as Nafion-Pt/C, which is used as the anode catalyst in proton exchange membrane fuel cells (PEMFCs).

2. Experimental

2.1. Catalyst preparation

A commercial carbon-supported Pt (Pt/C) with a nominal Pt loading of 20 wt.% was purchased from BASF and used as received. It was confirmed by BASF that the carbon black support (Vulcan XC-72) was purchased in-bulk from Cabot Co. and used directly for the synthesis of the Pt/C catalyst.

A portion of the purchased Pt/C catalyst were impregnated sequentially via incipient wetness with aqueous KNO_3 solutions of varying concentrations to prepare a series of K^+-doped catalysts with theoretical $(K/Pt_T)_{atom}$ ratios of 0, 0.1, 0.2, 0.4, and 0.8, where Pt_T stands for the total amount of Pt available. In order to obtain a more uniform distribution of the potassium for each batch, the KNO_3 (Sigma Aldrich, 99.999% purity) was dissolved in 30 mL of distilled water and added drop-wise to the catalyst until incipient wetness was achieved. The wet catalyst was then placed in a static oven at 90 °C for ca. 20 min to dry and the process was repeated until the entire solution has been used. The K^+-free Pt/C catalyst was treated with only distilled water to check for possible effects from the impregnation process. After impregnation, the material was dried at 90 °C overnight in a static air oven, then crushed, and sieved to obtain a catalyst particle size distribution of 60–180 μm. Nominal Pt and K compositions were confirmed via elemental analysis (performed by Galbraith Laboratories) for all catalysts. The K^+-modified Pt/C catalysts are designated as *xx*K/Pt to indicate $(K/Pt_T)_{atom} = xx/100$. It should be noted that the $(K/Pt_T)_{atom}$ ratio is based on the total amount of Pt in the catalyst.

2.2. Characterization methods

2.2.1. BET

Physical characteristics of the catalysts such as BET surface area, pore size, and pore volume measurements were performed in a Micromeritics ASAP 2020 unit. Samples of as-received Pt/C and K^+-promoted Pt/C catalysts were degassed under vacuum (10^{-3} mm Hg) at 110 °C for 4 h prior to analysis. Results were obtained from N_2 adsorption isotherms at -196 °C.

2.2.2. Static H_2 chemisorption

Static chemisorption experiments using H_2 were performed at 35 °C in a Micromeritics ASAP 2010 equipped with a chemisorption controller station. Catalysts were first reduced in H_2 at 80 °C for 3 h followed by an evacuation at 80 °C (10^{-5} mm Hg) for another 3 h prior to the start of the analysis. A low reduction temperature of 80 °C was chosen in order to be able to apply the results of this study to an investigation of temperature sensitive catalysts such as Nafion® supported on Pt/C. Nafion® polymer is an integral part of PEMFC Pt/C catalysts but is structurally unstable at higher temperatures. While no Nafion® was present on the Pt/C catalyst investigated here, the low reduction temperature was used to adhere to conditions employed for fuel cell catalysts. Temperature-programmed reduction (TPR) results has shown Pt/C catalysts to be fully reduced at these conditions [17]. After evacuation, the temperature was adjusted to 35 °C and the H_2 isotherms were obtained from 50 to 450 mm Hg at increments of 50 mm Hg. Volumetric uptakes of CO or H_2 on the catalysts were determined from the total adsorption isotherm of the specified gas by extrapolating the linear portion of the isotherm in the higher pressure region to zero pressure. These values were then used in determining total available Pt surface atom concentration (Pt_S) and metal dispersion by assuming stoichiometric ratios of 1:1 for H/Pt_S. Calculation of average Pt particle size was carried out using the metal dispersion approximated from the chemisorption results and has been shown to correlate very well with the average Pt particle size results obtained from TEM images [17].

2.2.3. TEM and XRD

Transmission electron microscopy (TEM) images of Pt/C and K^+-promoted catalysts were obtained using a TEM-Hitachi 9500, which offers 300 kV high magnification TEM and is designed for atomic resolution. Preparation of copper sample grids is explained in detail elsewhere [17]. Approximate Pt particle sizes of the catalysts were obtained by averaging diameters of 100+ particles from the TEM images. The results were further confirmed via X-ray Diffraction (XRD) (Scintag XDS 2000 powder diffractometer equipped with Cu Kα radiation) with a scanning range from 20° to 85° and a step-size of 0.02°/min.

2.3. Cyclopropane hydrogenolysis

Cyclopropane hydrogenolysis reaction rate results were obtained at 30 °C and 1 atm utilizing a conventional plug flow, micro-reactor system similar to the one described in Ref. [17] with a tubular quartz reactor with an internal diameter of ca. 5 mm. Due to the high activity of Pt for this reaction [3], low amounts of catalysts and a low partial pressure of C_3H_6 (American Gas Group, UHP) in the feed stream were required in order to achieve differential conditions for adequate kinetic analysis. To this end, 1.5–5 mg of the *xx*K/Pt catalysts (depending on activity) were diluted uniformly with 38.5–35 mg of XC-72, respectively, to achieve a catalyst bed of ca. 1 cm in thickness. Prior to reaction, the catalysts were reduced in 100 sccm of H_2:Ar (50:50) (National Specialty Gases, UHP) for 3 h at 80 °C and 1 atm. After reduction, the temperature was decreased from 80 °C to 30 °C and stabilized. Reaction was initiated by flowing a gas mixture of C_3H_6:H_2:Ar (1:50:149) (total flow = 200 sccm) through the catalyst bed and allowing the reaction to stabilize for 5 min before sampling the gas effluent with a Varian 3800 GC equipped with FID and a Restek RT-QPLOT column (30 m, 0.53 mm ID). It is meaningful to note again that high space velocity and low partial pressure of C_3H_6 were required to achieve differential conditions due to the high activity Pt has for this reaction. All reaction rates reported were those for initial reaction (TOS = 5 min) to avoid possible complications from catalyst deactivation due to carbon deposition [18]. The measured apparent activation energy of 12 kcal mol^{-1} for Pt/C, obtained by variation of reaction temperature from 30 to 50 °C in increments of 5 °C and from an Arrhenius plot of the data, is within the 8–12 kcal mol^{-1} range observed for this reaction on Pt-based catalysts in the literature [12]. This agreement in the value of E_{app} and the linearity of the Arrhenius plot confirm the absence of mass and heat transfer effects.

2.4. CO hydrogenation

The hydrogenation of CO on Pt was done to contrast to cyclopropane hydrogenolysis. Rate measurements of methanation on the Pt/C catalysts were taken at 392 °C due to evidence indicating the dominant role of K^+ on Pt for this reaction to be simple site blockage in this higher temperature range [14]. The reaction temperature of 392 °C was also required due to the low activity of Pt for this reaction. The reaction rate measurements were made using 100 mg of catalyst loaded in a fixed-bed differential reactor (316 stainless steel) with a length of ca. 300 mm and an internal diameter of ca. 5 mm.

The catalyst, placed in between quartz wool plugs, was positioned in the middle of the reactor with a thermocouple close by to allow accurate temperature control. Prior to reaction, the catalyst was first reduced in 22 sccm H_2 for 3 h at 80 °C and 1.8 atm. After reduction, the temperature was ramped at 5 °C/min from 80 °C to 392 °C, still in the flow of H_2. Once the temperature was stabilized, reaction was initiated by flowing a H_2:CO (12:1) mixture with a total flow rate of 22 sccm through the catalyst bed to achieve the same partial pressures of H_2 and CO used by Bajusz et al. [14]. The high relative partial pressure of H_2 to CO was employed to produce primarily methane as the product to simplify analysis.

Initial reaction data were collected after 5 min of reaction using a Varian 3800 GC equipped with both a flame ionization detector (FID) and thermal conductivity detector (TCD). The FID was connected to a Restek RT-QPLOT column (30 m, 0.53 mm ID), capable of separating C_1–C_7 hydrocarbons, while the TCD was connected to a Restek Hayesep® Q column (1.83 m, 3.18 mm ID) used to separate CO and other inorganic gases. At these conditions, the reaction conversion was kept low (less than 0.5% in all cases) and differential behavior could be assumed. Specific activities were determined and are reported in terms of the rate of CH_4 formation per gram of catalyst. The formation of higher hydrocarbons was minimal and was excluded from our analysis.

Apparent activation energy (E_{app}) of CO hydrogenation on Pt/C was obtained by varying the reaction temperature from 380 to 410 °C at increments of 10 °C and determined to be 26 kcal mol^{-1}. Based on the linearity of the Arrhenius plot, the agreement of E_{app} with literature values [14], and the lack of an effect of space velocity in this range on rate, it could be concluded that there were no mass or heat transfer effects on the rate of reaction.

In addition to the measurement of reaction rate data, steady-state isotopic transient kinetic analysis (SSITKA) was employed to understand the effect of K^+-loading on surface kinetic parameters such as average surface residence times and surface concentrations of intermediates for the formation of CH_4. The reaction conditions utilized for these measurements were the same as above. These parameters were determined from isotopic transient curves, obtained by switching between (95% ^{12}CO + 5% Ar) and (^{13}CO), using SSITKA data analysis [19]. The switch was made with a Valco four-port valve with an electric actuator to minimize turbulence effects and variation of flow rates, while two back-pressure regulators were also employed to minimize pressure disturbance effects. The 5% Ar present in ^{12}CO was used as an inert tracer to determine the gas hold-up time of the entire reaction system. The isotopic concentrations were followed by an online mass spectrometer (MS, Pfeiffer Vacuum) capable of high-speed data acquisition. An example of the normalized transients for CO and CH_4 obtained by switching from ^{12}CO to ^{13}CO during the reaction can be observed in Fig. 1. The average residence time of CH_4 (τ_{CH_4}) was obtained from the area between the normalized transient curves for CH_4 and the inert tracer (Ar). The concentrations of reversibly adsorbed CO (N_{CO}) and of the active surface intermediates leading to the formation of CH_4 (N_{CH_4}) were calculated by Eqs. (4) and (5) below, respectively:

$$N_{CO} = \text{Rate}_{CO} \times \tau_{CO} = F_{0,CO}(1 - x)\tau_{CO} \tag{4}$$

$$N_{CH_4} = \text{Rate}_{CH_4} \times \tau_{CH_4} = F_{0,CO}(x)\tau_{CH_4} \tag{5}$$

where x is the reaction conversion and $F_{0,CO}$ is the initial flow rate of CO.

3. Results and discussion

3.1. Catalyst characterization

The effects of the impregnation process on the physical characteristics of the catalyst were minimal as the BET surface area, average pore size, and pore volume measured for 00K/Pt were the same as those for the as-received Pt/C (Table 1). However, with the addition of K^+, a noticeable decrease in BET surface area with increasing K^+ concentration was evident. The loss of such a large amount of surface area (up to ca. 37%) is most likely due to blockage of some of the smaller pore structures in the support by K^+ species. This is substantiated by the increase in the average pore size from ca. 16 to 19 nm. The effect of K^+-loading on the total pore volume of the catalysts appears to have been minimal, but this parameter is mainly a function of the larger pores.

Results from TEM and XRD spectra of the as-received Pt/C, 00K/Pt, 40K/Pt, and 80K/Pt catalysts showed no differences in the average Pt particle size (2.6 ± 0.4 nm, 2.6 ± 0.4 nm, 2.7 ± 0.3 nm, and 2.7 ± 0.4 nm, respectively) determined for these catalysts. This was expected as the mild conditions used during the sequential impregnation process should not alter the metal particle size or dispersion of the Pt.

Elemental analysis results from Galbraith Laboratories showed an actual Pt loading of ca. 18 wt.% for all catalysts, compared to

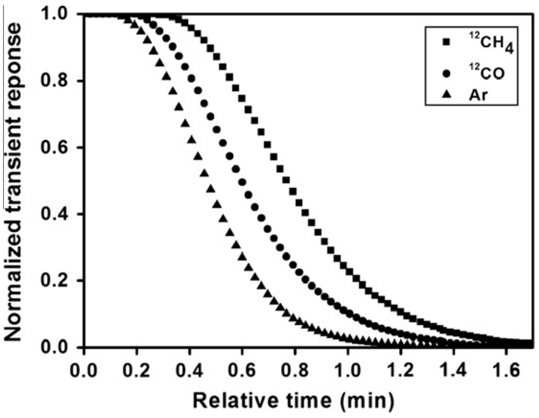

Fig. 1. Typical normalized transients for ^{12}CO, $^{12}CH_4$, and Ar resulting from an isotopic switch, during CO hydrogenation at 392 °C on 40K/Pt.

Table 1
BET surface area, average pore size, and pore volume of K$^+$-doped Pt/C.

Catalyst	BET SA[a] (m^2/g cat)	Pore size[a] (nm)	Pore volume[a] (cm^3/g cat)
Pt/C	170	15.9	0.44
00K/Pt	171	16.4	0.45
10K/Pt	159	16.2	0.44
20K/Pt	151	17.2	0.43
80K/Pt	107	19.1	0.48

[a] Experimental error was less than ±6%.

the nominal loading of 20 wt.%. The amount of K measured was 0.0, 0.24, 0.54, 1.02, and 1.82 wt.% for the 00–80K/Pt catalysts, respectively. Based on these Pt and K loadings, consequent calculation of the actual $(K/Pt_T)_{atom}$ ratios for the K$^+$-doped catalysts resulted in ratios of 0.07, 0.15, 0.29, and 0.53 for the 10–80K/Pt catalysts, respectively (Table 2). Even though subsequent rinsing with distilled water of the KNO_3 solution containers were done to impregnate as much of the K$^+$ as possible, it appears that a portion of the K$^+$ was inevitably lost during the impregnation process.

In addition to Pt and K, elemental analysis (performed by Galbraith) and EDX confirmed the existence of large amounts of sulfur present in the bulk (ca. 0.5 wt.% or 5000 ppm) and on the surface (ca. 0.2 wt.% or 2000 ppm) of the Pt/C catalyst, respectively. Similar concentrations of sulfur were detected for the carbon support itself and are due to the vulcanization process (treatment with sulfur) used to produce a better dispersion of the Pt particles [20], especially at such high metal loadings. While most of the sulfur appears to be in the interior rather than on the surface of the carbon support (total S concentration = 0.5 wt.% with ca. 0.2 wt.% being the equivalent relative concentration on the surface), exposure of the catalyst to high temperatures could potentially cause the sulfur in the interior to migrate to the surface of the support and onto the Pt surface, thereby poisoning the reaction. In fact, results from EDX analysis of a similar but different batch of Pt/C catalysts after 48 h at 450 °C in the presence of H_2 showed relative surface concentration of sulfur to double from ca. 0.1 to 0.24 wt.%. However, based on the relatively minor loss of hydrogen uptake capability of the catalyst (static chemisorption) from the prolonged thermal treatments (no treatment: 288 μmol/g cat, compared to 252 μmol/g cat after heating at 450 °C for 50 h in H_2:) and taking into account sintering effects, the presence and increase in surface sulfur did not appear to affect significantly or poison many Pt surface sites. Thus, because of the low reduction temperature used (80 °C), the low reaction temperature used for cyclopropane hydrogenolysis, and fast ramp rate (5 °C/min) to 392 °C from 80 °C used in our study of CO hydrogenation, the migration/poisoning effect of the sulfur on the initial reaction rates should be minimal. Even so, only initial rate data, collected after 5 min of reaction, will be used in the discussion of structure sensitivity for both CO hydrogenation and cyclopropane hydrogenolysis on the Pt/C catalysts.

Table 2
Surface coverage of Pt by K$^+$.

Catalyst	K/Pt_T[a] (atomic)	K^+_{impreg}[a] (μmol/g cat)	Pt_S[b,c] (μmol/g cat)	θ_{Pt}[d]
Pt/C	0.00	0	286	–
00K/Pt	0.00	0	278	1.0
10K/Pt	0.07	63	270	0.97
20K/Pt	0.15	135	264	0.95
40K/Pt	0.29	260	252	0.90
80K/Pt	0.53	475	177	0.64

[a] Based on elemental analysis results from Galbraith Laboratories.
[b] From static H_2 chemisorption at 35 °C using the total adsorption isotherm and assuming (1:1) H:Pt_S.
[c] Experimental error was less than ±5%.
[d] Based on Pt_S of the 00K/Pt catalyst determined from static H_2 chemisorption at 35 °C.

While more than enough K$^+$ was added to completely block all Pt surface atoms available, results from static hydrogen chemisorption (Table 2) and a plot of available surface Pt vs. the amount of K$^+$ added (Fig. 2) clearly show that only a small portion (ca. 12%) of the K$^+$ impregnated on the Pt/C to be associated with surface Pt (i.e., blocking it) for the 10–40K/Pt catalysts. This increased to ca. 21% for 80K/Pt. Repeat analyses of specific samples show the experimental error to be well below ±5%, suggesting the K$^+$ to be more or less well distributed throughout each sample of catalyst.

3.2. Cyclopropane hydrogenolysis

Due to the high activity of Pt for cyclopropane hydrogenolysis and the high weight loading of Pt in the catalysts, low amounts of catalyst and a low partial pressure of cyclopropane were required to keep the conversion below 15%. While this conversion is a little high for perfect differential reactor behavior, it has been found that the rate of this reaction on Pt increased linearly up to 50% conversion [9]. As expected, propane was the only product observed from this reaction on Pt. Table 3 shows the initial (5 min) reaction rate data obtained for cyclopropane hydrogenolysis on the various K$^+$-doped Pt/C catalysts and Fig. 3 shows a plot of initial rate of this reaction as a function of K$^+$-coverage on Pt $(1 - \theta_{Pt})$.

Initial reaction rate results for cyclopropane hydrogenolysis on the as-received Pt/C and 00K/Pt catalysts were the same, within experimental error. For the *xx*K/Pt catalysts, rate decreased with increasing K$^+$-loading. As can be seen from Fig. 3, most of the significant reduction in initial reaction rate data was before a K$^+$-coverage of 0.15, with rate leveling off as K$^+$-coverage increased further. Calculation of the TOF for cyclopropane hydrogenolysis based on the amount of exposed Pt surface atoms (Pt_S) obtained from static H_2 chemisorption showed an overall decrease of ca. a factor of 6 (0.34–0.06 s^{-1}) for the range of K$^+$-coverage investigated. Comparison of TOF of Pt/C with those of other supported Pt catalysts reported in literature (Pt/Al_2O_3 [9] and Pt/SiO_2 [9,13]) shows the values to be in very good agreement within the same order of magnitude, considering all the differences in catalyst preparation, composition, and reaction conditions.

The apparent activation energy (E_{app}) of 11.9 kcal/mol measured for the non-modified Pt/C catalyst is in agreement with what has been reported in the literature [12] for Pt catalysts. The relatively constant E_{app}, within experimental error, with the addition of K$^+$ suggests the lack of electronic and/or promotion effects between the Pt and K$^+$ species for cyclopropane hydrogenolysis, such that the reaction mechanism and heats of adsorption remain

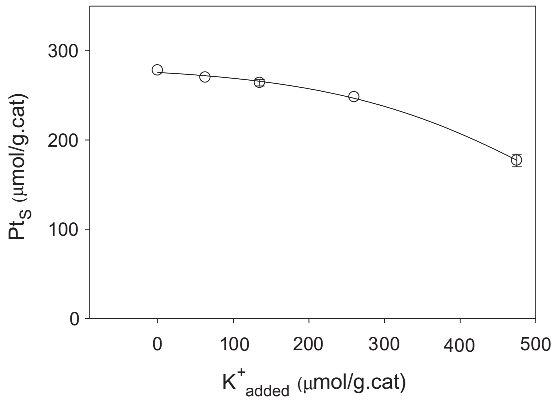

Fig. 2. Relationship of amount of K$^+$ impregnated to the amount of surface Pt (based on static H_2 chemisorption, 35 °C).

Table 3
Initial reaction results[a] of cyclopropane hydrogenolysis on K^+-modified Pt/C catalysts.

Catalyst	Initial R_P[b] (μmol/g cat-s)	TOF[c] (s^{-1})	E_{app}[d] (kcal/mol)
00K/Pt	96	0.34	11.9
10K/Pt	81	0.30	11.7
20K/Pt	69	0.26	10.9
40K/Pt	41	0.16	10.1
80K/Pt	10	0.06	10.4

[a] 30 °C, 1 atm, $H_2/C_3H_5/Ar$ = 50/1/149 sccm.
[b] Initial reaction rate for the formation of propane: Error < ±7%.
[c] Based on Pt_S from static H_2 chemisorption.
[d] Apparent activation energy: Error < ±10%.

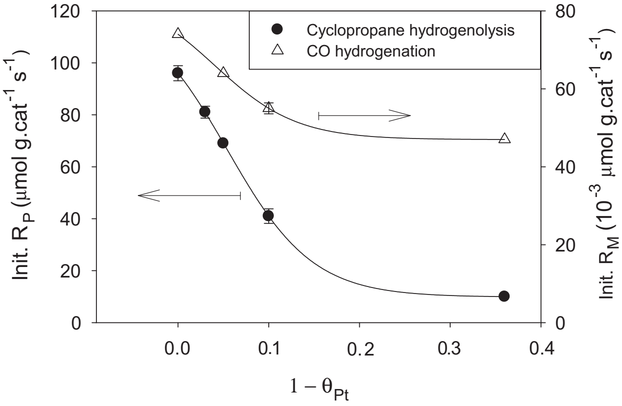

Fig. 3. Initial rates of cyclopropane hydrogenolysis and CO hydrogenation as a function of K^+-coverage on Pt surface.

relatively essentially the same. Thus, K^+ appears to act only as a blocking agent for this reaction.

3.3. CO hydrogenation

The reaction of CO and hydrogen on Pt was performed to provide a comparison with the rate data for cyclopropane hydrogenolysis. Even at the high reaction temperature of 392 °C utilized, required due to the low intrinsic activity of Pt for this reaction, the reaction conversion on the 18 wt.% Pt/C (100 mg) was less than 0.5%, compared to 1.5% reaction conversion for 4.5 wt.% Pt/SiO_2 (25–35 mg) at the same reaction temperature [14]. This difference in catalytic activity between the two catalysts may be due to differences in metal-support interactions and the fact that the carbon support used had been vulcanized. As mentioned previously, the main reason for choosing 392 °C was due to evidence for K^+-modified Pt/SiO_2 indicating that, at this high temperature range, the dominant role of K^+ on Pt for methanation was simple site blockage [14]. Table 4 lists the initial reaction rate data and surface kinetic parameters, as determined by SSITKA, for CO hydrogenation on the various K^+-doped Pt/C catalysts. Fig. 3 gives a plot of the initial rate of CO hydrogenation as a function of K^+-coverage on Pt $(1 - \theta_{Pt})$.

As seen in Fig. 3, decrease in the initial reaction rate was relatively proportional to the increase in K^+-coverage from 0 to 0.1 and began to level off as K^+-coverage increases to 0.36. Thus, the overall subtle decrease in rate with increasing fraction of Pt surface covered by K^+ suggests that this reaction is less sensitive to surface structure than cyclopropane hydrogenolysis. Surface parameters measured by SSITKA for CO hydrogenation show that, considering the large amount of surface Pt atoms available based on static H_2 chemisorption, only a small portion (ca. 10%) appeared to be occupied by reversibly adsorbed CO (N_{CO}) at 392 °C and even less (ca. 1%) for the formation of active intermediates (in terms of carbon atoms) that led to the production of CH_4 (N_M). The fact that the average residence time of the carbon-based intermediates leading to the formation of CH_4 (τ_M) remained constant with K^+-coverage suggests that the decrease in the activity of the catalyst was solely attributable to the blockage of the sites that were active for the formation of CH_4. The quantity, $1/\tau_M$, is a measure of the TOF of reaction based on the sites active for the formation of methane. The relatively constant value of $1/\tau_M$ for the various K^+-doped catalysts suggests either uniform poisoning or, more likely, the lack of variation in activity among the different sites available, which is what would be expected for a structure-insensitive reaction. The reason for the decrease in rate is clearly due to a loss in surface intermediates (sites), N_M, with increasing amounts of K^+, since $Rate = (1/\tau_M)N_M$. Similar to what was observed for cyclopropane hydrogenolysis, comparison of TOF ($1/\tau_M$) obtained for CO hydrogenation on Pt/C to that for Pt/SiO_2 [14] shows the values to be similar within the same order of magnitude.

The E_{app} of 26.3 kcal/mol measured for CO hydrogenation on the non-doped (bare) Pt/C is similar to the literature value of 27 kcal mol^{-1} [14]. Similar to cyclopropane hydrogenolysis results, the lack of variation (within experimental error) in E_{app} between the bare and K^+-doped Pt/C catalysts observed for this reaction also indicates the absence of any electronic or promotion effects caused by K^+. All results suggest that the effect of K^+ as a Pt modifier for both reactions appears to have been limited to simply blocking active sites.

3.4. Structure sensitivity analysis

While the variation in the TOF for cyclopropane hydrogenolysis is an indication of structure sensitivity that evidence alone is not enough as confirmation. Utilizing the simplified exponential expression relating the statistical dependence of rate on site blockage by a blocking agent presented by Hoost and Goodwin [15] and originally proposed by Martin [16], the ensemble size required for a specific reaction can be approximated by the following equation:

Table 4
Initial reaction rates and SSITKA results for CO hydrogenation on K^+-doped Pt/C catalysts.

Catalyst	R_M[a] (10^{-3} μmol/g cat-s)	τ_{CO}[b] (s)	N_{CO}[c] (μmol/g cat)	τ_M[b] (s)	N_M[d] (μmol/g cat)	$1/\tau_M$ (s^{-1})	E_{app} (kcal/mol)
00K/Pt	74	2.4	30	5.0	0.37	0.20	26.3
20K/Pt	64	2.3	29	4.8	0.31	0.21	28.5
40K/Pt	55	2.4	30	4.8	0.25	0.20	27.9
80K/Pt	47	2.5	32	4.8	0.20	0.21	28.2

[a] Rate of CH_4 formation: Error = ±2 × 10^{-3} μmol/g cat-s.
[b] Average surface residence time of rev. ads. CO: Error = ±0.2 s.
[c] Surface concentration of rev. ads. CO: Error = ±5%.
[d] Surface concentration of carbon-containing intermediates leading to CH_4: Error = ±4%.

$$\frac{R}{R_{P=0}} = (1-\theta_P)^{N_E} \tag{6}$$

where R is the reaction rate of the doped catalyst (K^+-doped Pt/C), $R_{P=0}$ is the rate of the non-doped (non-blocked) catalyst (Pt/C), N_E is the ensemble size required for the reaction, and θ_P is the fraction of the surface metal blocked by the blocking agent or poison P. This simplified expression is only valid when the number of available surface atoms on a particle is greater than the site ensemble size, which is usually the case for supported catalysts.

Fig. 4 shows the semi-logarithmic plot of the normalized initial rates of reaction ($R/R_{P=0}$) as a function of fraction of Pt surface exposed (θ_{Pt}) for both cyclopropane hydrogenolysis and CO hydrogenation. The slopes of the individual curves should yield the value for N_E or ensemble size required for reaction. As one would expect for a structure insensitive reaction, data points for CO hydrogenation on the semi-log plot follow the same trend as that of a uniformly poisoned reaction with an ensemble size requirement of ca. 1 (single-atom ensemble model). While there is some slight deviation from the theoretical line, the difference is minimal. Similarly, interpretation of the decrease in initial rate with K^+-coverage for $\theta_{Pt} = 1–0.8$ suggests the ensemble size required for cyclopropane hydrogenolysis to be ca. 7 (7-atom ensemble model). As the K^+-coverage increased to give $\theta_{Pt} < 0.8$, a deviation from the 7-atom ensemble theoretical line predicted by Martin's model can be observed. This variation, as clearly shown by the modeling results of Hoost and Goodwin [15], is indicative of preferential blockage of certain surface planes of the metal by the blocking agent (in this case K^+).

Although a key assumption in Martin's ensemble model is uniform poisoning of the metal surfaces, the reality, however, is that this is rarely the case. Monte Carlo simulations performed by Strohl and King [21] on various supported bimetallic (but non-alloying) systems (Cu–Pt, Ag–Pt, and Au–Pt) showed non-uniform decoration of the Pt surface by the other metal. All three metals (Cu, Ag, and Au), based on the simulation, preferentially adsorb on surface sites of low coordination with varying degrees of filling. For example, Au completely filled lower coordinated Pt surfaces at lower fractions of the metal adsorbed than Ag, followed by Cu. Furthermore, the simulation also showed that, depending on the "bonding nature" of the species, the blocking behavior of the Cu atoms differed from that of Au and Ag. Such non-uniform decoration by K^+ of a metal surface has been shown for $K^+/Ru/SiO_2$ [15].

Thus, it would appear that K^+ preferentially blocks certain Pt planes on Pt particles such that the distribution of the alkali species is non-uniform. As a result, this non-uniform blocking behavior would, of course, have dramatic effects on the activities observed for structure sensitive reactions. In other words, if the K^+ were to preferentially adsorb on surface Pt sites with the lowest activity for the reaction, the resulting minor loss in overall activity with increasing coverage could result in the misinterpretation of the reaction as being structure insensitive. Conversely, if the opposite were true, then the complete loss in activity with only a fraction of the surface Pt covered would lead to the misinterpretation of the reaction to being extremely structure sensitive. Given the large decrease in rate with K^+-coverage and the existence of probable preferentially blockage of certain Pt surface structures with higher activities, it can be concluded that cyclopropane hydrogenolysis on Pt is definitely structure sensitive. The ensemble size required for cyclopropane hydrogenolysis of Pt is possibly less than 7, however, but likely greater than 2, the value found for cyclopropane hydrogenolysis on Ni–Cu/SiO_2 by Cale and Richardson [2]. A more precise estimation of ensemble size would be speculative at this time.

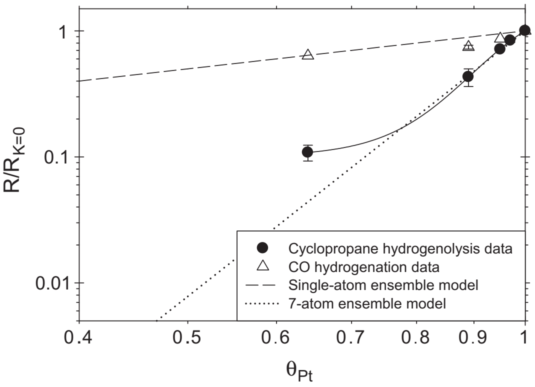

Fig. 4. Fraction of Pt surface exposed vs. normalized initial reaction rates for cyclopropane hydrogenolysis and CO hydrogenation.

4. Conclusions

The structure sensitivity of cyclopropane hydrogenolysis on Pt was investigated via a series of K^+-doped Pt/C catalysts. While the BET surface area and average pore diameter decreased with K^+-loading, sequential impregnation of the alkali species had no effect on the average Pt particle size as determined from TEM and XRD. Static H_2 chemisorption results confirm that, of the large amount of K^+ added, only a small portion (ca. 10–20%) was associated with surface Pt atoms. Sulfur poisoning of Pt due to sulfur contained in the carbon support from vulcanization was not evident.

Based on the surface parameters, as determined from SSITKA, and apparent activation energies, the effect of K^+ on the Pt for both reactions appear to be limited to simple site blockage. No evidence indicating promotion or true poisoning effects were observed at the reaction conditions employed. Initial reaction rate results for cyclopropane hydrogenolysis on the as-received Pt/C and 00K/Pt catalysts were the same, within experimental error, indicating also no effect due to aqueous impregnation.

The value for the site ensemble size required for cyclopropane hydrogenolysis on Pt, based on Martin's model [16], was estimated to be ca. 7, whereas, CO hydrogenation, a classic structure insensitive reaction appears to require a site ensemble size of ca. 1, as might be expected. In addition, calculation of TOF (based on H_2 chemisorption) for cyclopropane hydrogenolysis shows a decrease with increasing K^+-loading, while the TOF (based on $1/\tau_M$ from SSITKA) for CO hydrogenation remained essentially constant. Based on these results and the extremely high probability of non-uniform distribution of K^+ on specific Pt surfaces, as suggested by Monte Carlo simulations for bimetallic systems [21], reaction results for K^+-modified Ru/SiO_2 [15], and the deviation observed from the ensemble model at the higher K^+-coverages, it can be concluded that the significant loss of rate with increasing K^+-coverage for cyclopropane hydrogenolysis is dependent not only on the number of Pt surface atoms exposed but also on the Pt surface planes exposed and the availability of sites with higher numbers of contiguous atoms for reaction. The evidence clearly shows that cyclopropane hydrogenolysis on Pt is structure sensitive.

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