

Kinetic Study of Ethylene Hydrogenation

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Turnover frequencies and kinetic reaction orders were determined for ethylene hydrogenation over platinum catalysts at temperatures from 223 to 336 K, hydrogen pressures between 50 and 650 Torr, and ethylene pressures from 5 to 600 Torr. The hydrogen kinetic order was observed to decrease continuously from first order at 336 K to half order at 248 K. Zero-order ethylene kinetics were found at ethylene pressures above 75 Torr, and the ethylene order became negative at lower ethylene pressures. The half-order hydrogen kinetics at low temperatures and the observed zero-order ethylene kinetics at higher ethylene pressures can be explained by a Horiuti-Polanyi mechanism in which hydrogen is adsorbed noncompetitively on a surface essentially covered with adsorbed hydrocarbon species. Hydrogen competes with ethylene adsorption at higher temperatures and lower ethylene pressures. A combination of the noncompetitive and competitive pathways explains the steady-state kinetics over the entire range of temperatures and pressures studied. © 1991 Academic Press, Inc.

INTRODUCTION

Ethylene hydrogenation has been used extensively in heterogeneous catalysis as a probe reaction for metal catalysts. This catalytic reaction involves simple reactant molecules and proceeds at ambient temperature, producing only ethane. Numerous investigators have employed steady-state kinetics measurements and deuterium tracing studies to investigate the elementary steps important in ethylene hydrogenation over platinum catalysts (1-10). In recent years, various investigations have examined platinum metal surfaces with spectroscopic methods and identified adsorbed species that are believed to be important in ethylene hydrogenation. For example, adsorbed ethylene species have been observed by HREELS (11) and LEED (12) at temperatures between 150 K and ambient. *In situ* infrared spectroscopic studies (13-15) have observed the reaction of adsorbed ethylene species with hydrogen between 180 and 273 K. Temperature program desorption studies

(16-18) show that most of the adsorbates desorb below room temperature.

The simplicity of ethylene hydrogenation and the advanced degree to which reactant interactions with platinum metal surfaces have been studied create a unique situation for developing a quantitative understanding of the surface chemistry for this reaction. For example, temperature program desorption studies provide information about rate constants for the adsorption and desorption of hydrogen and ethylene. Steady-state kinetic data such as turnover frequencies, activation energy, and reactant kinetic orders provide information on kinetically significant elementary steps. Deuterium tracing studies provide information about the reversibilities of hydrogen transfer reactions. It is our goal to combine steady-state kinetics, deuterium tracing studies, and surface science results to extract kinetic parameters for ethylene hydrogenation on platinum metal over a wide range of temperatures and pressures.

The literature provides some of the necessary information for this kinetic analysis; however, there is a lack of desired steady-state kinetic data at temperatures below 273

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TABLE I
Survey of Previous Ethylene Hydrogenation Kinetic Studies

Investigator	Catalyst	Kinetic orders		Activation energy (kcal/mol)	Temperature range (K)
		Ethylene	Hydrogen		
Bond (2)	1.0% Pt/alumina	-0.5	1.2	9.9	273
Kazanskii and Strunin (4)	Wire	-0.5	1.2	10.0	357-655
Dorling <i>et al.</i> (6)	3.0% Pt/alumina	—	—	8.8	170-206
Schlatter and Boudart (7)	0.05% Pt/silica	—	—	9.1	273-348
Schlatter and Boudart (7)	0.5% Pt/silica	0	—	8.9	213-273
Zaera and Somorjai (5)	Pt(111)	-0.6	1.3	10.8	300-333

K. Table 1 shows the results of previous kinetic studies for ethylene hydrogenation over a variety of platinum catalysts. This table shows that Bond (2, 3), Kazanskii and Strunin (4), and Zaera and Somorjai (5) observed first-order hydrogen kinetics and slightly negative ethylene kinetic orders for temperatures above 273 K. Below 273 K, Dorling *et al.* (6) and Schlatter and Boudart (7) determined kinetic activities but did not determine the kinetic orders.

This present study was undertaken to determine the catalytic activities and kinetic orders for ethylene hydrogenation over a wide range of temperatures and pressures which would encompass the conditions of previous catalytic and surface science studies of this reaction. Accordingly, turnover frequencies and reaction orders with respect to hydrogen and ethylene were determined at temperatures from 223 to 336 K, at hydrogen pressures from 50 to 650 Torr, and at ethylene pressures from 5 to 600 Torr. In addition, these kinetic studies were conducted over platinum catalysts with different dispersions to study possible structure sensitivity over a wide range of conditions.

This paper presents the results of this steady-state kinetic study and provides a qualitative description of the surface chemistry. The results of this kinetic study show a continuous decrease of the hydrogen kinetic

order from unity at 336 K to half-order hydrogen kinetics at temperatures below 248 K. An ethylene kinetic order of zero was observed at ethylene pressures above 75 Torr, whereas the ethylene kinetic order was negative below this pressure. The half-order hydrogen kinetics at low temperatures and the observed zero-order ethylene kinetics at higher ethylene pressures suggest a mechanism in which hydrogen is adsorbed noncompetitively on a surface essentially covered with adsorbed hydrocarbon species. The hydrogen and ethylene compete for the same adsorption sites as the temperature increases and the ethylene pressure decreases. At higher temperatures and lower ethylene pressures, this competitive adsorption supplements the noncompetitive pathway and accounts for the observed catalytic activity.

In the future these steady-state kinetics will be combined with deuterium tracing experiments currently being conducted in our laboratory over the same range of conditions to produce a more quantitative understanding of the surface chemistry.

EXPERIMENTAL

Apparatus

Ethylene hydrogenation kinetics were measured in a glass reactor system that could be operated as a flow-through or recirculating batch reactor (see Fig. 1). The flow-

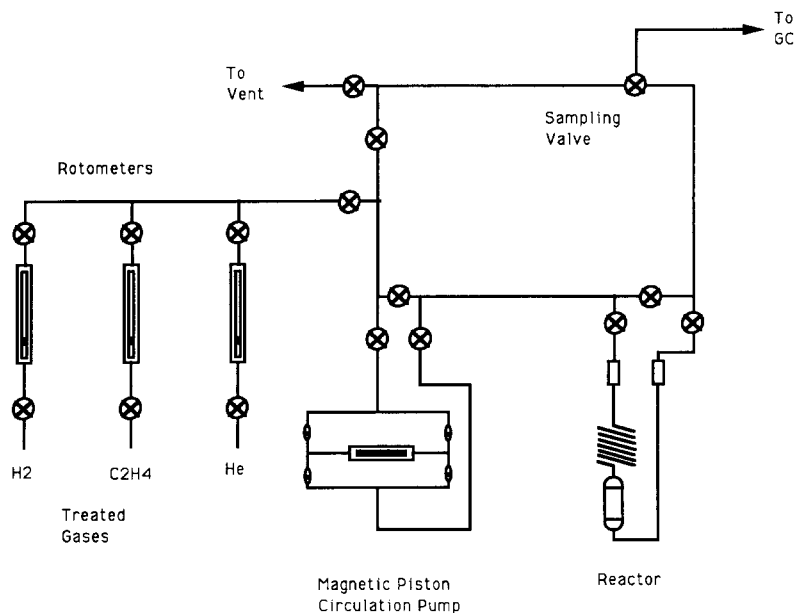


FIG. 1. Experimental apparatus for ethylene hydrogenation kinetic studies

through configuration allowed operating conditions to be varied over a wide range, and the majority of the kinetic studies were carried out in this mode at atmospheric pressure. The recirculating batch configuration allowed the effects of total pressure on the reaction to be determined.

All reactant gases were treated to remove oxygen and water impurities, which were found to cause catalyst deactivation. Hydrogen was purified by a Deoxo unit (Englehard) followed by passage through molecular sieves (13X) at 77 K. Ethylene was treated by passage through a bed of reduced Oxytrap (Aldridge) followed by molecular sieves at 190 K. Helium was used as a diluent gas, and it was purified by passing it through a bed of reduced Oxytrap and a subsequent bed of molecular sieves at 77 K.

In flow-through kinetic studies, the individual gas streams of helium, hydrogen, and ethylene were mixed in a glass manifold and then routed to the catalytic reactor. Total flow rates between 100 and 1000 cm³ (STP)/min were employed. The reactant gas stream could be directed either to flow

through the reactor or to bypass the reactor, allowing analysis of the reactor outlet or inlet gases, respectively.

For recirculating batch reactor experiments, gas circulation was accomplished with a recirculation pump consisting of a magnetic piston fitted in a glass cylinder. Machined Teflon plugs at both ends of the piston provided gas-tight seals within the glass cylinder, and the piston was driven with solenoid coils positioned outside of the glass cylinder. At atmospheric pressure, a circulation rate of 750 cm³/min was achieved for this system.

For both reactor configurations, reaction temperatures from 223 to 336 K were obtained by immersing the reactor in a well-stirred 65% ethylene glycol/water bath. A Flexi-Cool two-stage cooling system in conjunction with an immersion heater controlled by a rheostat allowed regulation of the bath temperature.

Supported catalysts were loaded into a 10-mm-diameter glass reactor, equipped with a glass coil upstream of the catalyst chamber to facilitate temperature equilibration of the

inlet gas stream. Kinetic studies over platinum wire were conducted using a glass U-tube reactor, in which the desired length of wire was loosely wound around a glass rod sized large enough to fill the majority of the cross-sectional area of the U-tube. This arrangement provided good contact of the flowing reactant gases with the wire.

Gas composition analysis was carried out chromatographically. The sampling system consisted of a Valco six-port valve with a 100- μ l sample loop. Gas samples were analyzed with a H-P 5890A GC equipped with a thermoconductivity detector and a 6-ft Poropak Q-column operated at 343 K. Under these conditions, gas sampling was possible every 3 min.

Catalyst Preparation

Four catalysts were studied in this investigation: platinum wire and three silica-supported platinum catalysts with loadings of 0.04, 0.13, and 1.2 wt% Pt as determined by Galbraith Laboratories, Inc.

Silica-supported Pt catalysts were prepared by ion-exchange as described by Benesi *et al.* (19). The silica support was Cab-O-Sil (Cabot Corp. EH-5), which was mixed with a dilute aqueous solution of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ to achieve ion exchange. The pH of the slurry was adjusted to control the amount of platinum exchanged onto the surface. After ion exchange, the slurry was filtered, washed with deionized water, and then dried in air at 403 K for 8 to 12 h. The resulting catalyst cake was ground to 100–200 mesh.

The Pt dispersions of the supported catalysts were determined by hydrogen chemisorption at 300 K. Prior to measurement, the supported catalyst was pretreated for 1 h in flowing oxygen at 723 K, followed by treatment for 1 h in flowing hydrogen at 673 K and then evacuation at this temperature for 1 h. The catalyst was then cooled under vacuum to 300 K, at which temperature the extent of hydrogen chemisorption was measured by collection of the adsorption isotherm and extrapolation of the hy-

drogen uptake to zero pressure. This technique showed a dispersion of 0.7 for the 1.2 wt% Pt catalyst and a dispersion of unity for the other two catalysts. After measurement, the supported catalyst was stored under air at ambient conditions prior to use in the kinetic studies.

The 0.127-mm-diameter platinum wire employed in the kinetic studies of this investigation was obtained from Materials Research Corp; it had a state purity of 99.99%. The number of Pt surface sites for this material was estimated from the smooth geometric surface area of the wire.

Transport Criteria

Ethylene hydrogenation is an exothermic reaction with a high turnover frequency at ambient temperature. These properties suggest that care must be taken to collect kinetic data that are not limited by heat and mass transport phenomena.

For packed bed catalytic systems, Mears (20, 21) has discussed various dimensionless transport criteria for determining whether heat and mass transport limitations exist in the intraparticle, interphase, and interparticle regions of a catalyst bed. These criteria predicted no heat or mass transport limitations in the present study for either the intraparticle or interphase regions. However, an interparticle heat transport limitation was suggested to be important for the 0.13 and 1.2% Pt/Cab-O-Sil catalysts. Dilution of these catalysts with silica avoided this heat transport limitation. Therefore, in all experiments with these catalysts, 25 to 50 mg of the supported catalyst was diluted to a total solids weight of 500 mg using acid washed Cab-O-Sil EH-5 silica. Analysis of dimensionless transport criteria suggested that dilution of the 0.04% Pt/Cab-O-Sil catalyst was not necessary at temperatures from 223 to 336 K.

Catalyst Pretreatment

The stored supported catalysts which had undergone hydrogen chemisorption were used for the kinetic runs. Consistent catalyst

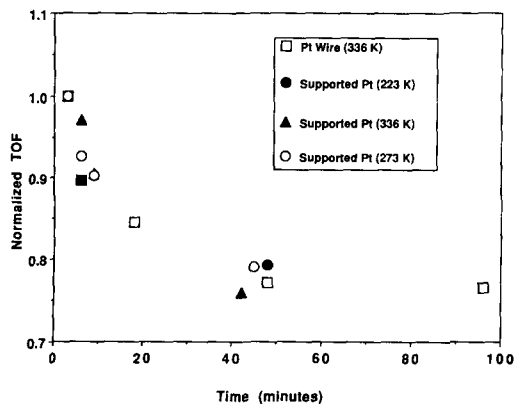


FIG. 2. Initial deactivation for ethylene hydrogenation on various Pt catalysts for flow-through kinetics. Catalytic activities are normalized to the initial activity observed for all runs. Reaction conditions are the standard conditions for this work.

activities were obtained for these supported catalysts after a further pretreatment with flowing hydrogen at 573 K for 45 min. The platinum wire was initially washed with solvents (toluene, acetone, and methanol) and pretreated for 1 h in flowing oxygen at 723 K. Prior to the kinetic runs, the wire was pretreated with hydrogen at 573 K for 45 min. The amount of catalyst used was adjusted to maintain the ethylene conversion less than 5% for all flow-through kinetic experiments.

After hydrogen pretreatment, the catalyst was cooled under flowing hydrogen to the desired reaction temperature. The reactor was then isolated, and the reactant gases were introduced to the system. Following analysis of the gas composition, the reactor was opened to the system. The initial composition of the reactor effluent was then determined, followed by subsequent analyses every 3 min during the kinetic experiment.

RESULTS

Catalytic Activity

Standard reaction conditions are defined in this study as 25 Torr of ethylene and 150 Torr of hydrogen. Helium composed the balance of the reactor gas for the flow-

through experiments at atmospheric pressure. Similar conditions were employed by Schlatter and Boudart (7) in their studies of ethylene hydrogenation.

All fresh or regenerated catalysts initially exhibited deactivation during ethylene hydrogenation, as shown in Fig. 2. Catalytic activities are expressed in this study in terms of turnover frequencies, i.e., the number of ethane molecules produced per surface platinum atom per second. In Fig. 2, the turnover frequencies (TOF) are normalized with respect to the fresh catalyst TOF at the standard conditions. After the initial deactivation, reproducible steady-state activities were observed at approximately 75% of initial catalyst activity. Fresh catalyst activity was regained after treatment with hydrogen for 1 h at 573 K. After 20 such regeneration cycles, original activity could still be achieved. The rate of catalyst deactivation was observed to be independent of catalyst and temperature.

A comparison of steady-state turnover frequencies at standard conditions for the four investigated catalysts shows ethylene hydrogenation over platinum to be a structure-insensitive reaction, as reported by Schlatter and Boudart (7). Specifically, it can be seen in Fig. 3 that the turnover frequency changes little when the catalyst dis-

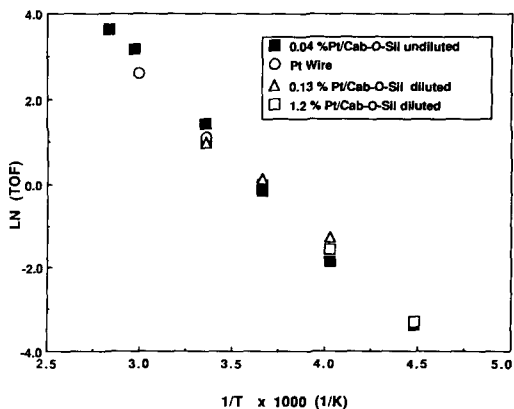


FIG. 3. Catalytic activities for the catalysts investigated in this work at standard conditions determined from flow-through kinetics.

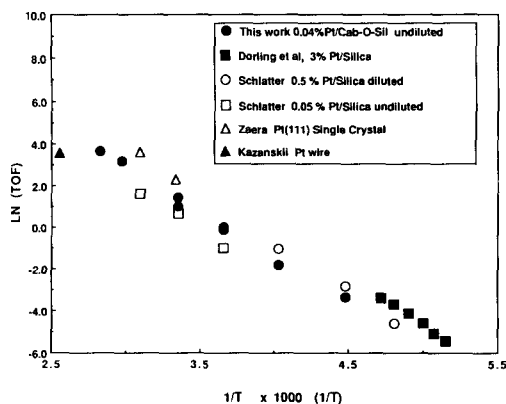


FIG. 4. Comparison of results from the present study to those from earlier investigations. All activities are at the standard conditions of this work.

person is varied essentially from unity on the 0.04% Pt/Cab-O-Sil catalyst to the low dispersion characteristic of the platinum wire.

The turnover frequencies observed in this investigation compare well with the values reported in the literature, as shown in Fig. 4. These turnover frequencies are compared at the standard conditions of this study. Extrapolation of the literature values was done whenever possible, by using the rate expression reported by that investigator. However, in cases where the rate expression was not reported, the rate expression determined in this investigation was employed.

Figure 4 shows that the turnover frequencies of this investigation compare well with those observed by Schlatter and Boudart over similar catalyst systems. These reported results are also in agreement with the results of Dorling *et al.* (6) on Pt/alumina and Kazanskii and Strunin (4) over Pt wire.

It should be noted that regeneration with flowing oxygen at 673 K followed by flowing hydrogen at 573 K produced inconsistent catalyst activities. For example, order of magnitude changes in activity could be achieved after this treatment. Schlatter and Boudart (7) also noted increases in catalytic activity after treatment of a supported Pt catalyst with air at 573 K followed by hydro-

gen treatment. Variations in catalytic activity were also noted for the Pt wire after treatment with oxygen. Therefore, oxygen treatment was not employed for regenerations in the present study.

Ethylene and Hydrogen Kinetic Orders

The majority of the ethylene and hydrogen kinetic orders discussed below were determined from steady-state activities by adjusting to a new pressure after two consistent activity measurements were made at a given pressure. The ethylene kinetic orders were observed to be slightly negative at low partial pressures of ethylene, as seen in Fig. 5. This figure shows the effect of ethylene pressure at 223 K on the 1.2 wt% Pt/Cab-O-Sil catalyst and at 336 K over the Pt wire at 150 Torr hydrogen pressure. The turnover frequencies have been normalized with respect to the activity at the standard conditions. Figure 5 shows that as the ethylene pressure increases from 5 Torr, the ethylene kinetic order became less negative and approached zero order at approximately 75 Torr of ethylene. Similar effects of ethylene pressure were observed for 0.04 and 0.13 wt% Pt/Cab-O-Sil.

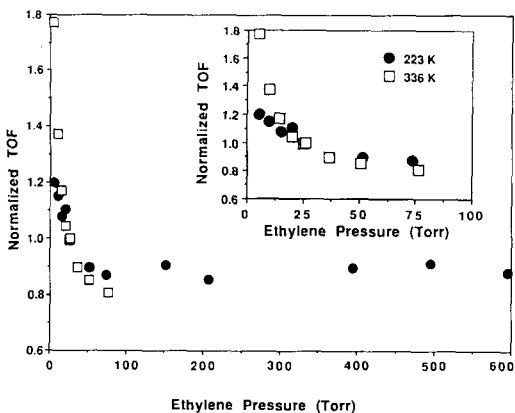


FIG. 5. Effects of ethylene pressure on ethylene hydrogenation catalytic activities for various Pt catalysts and temperatures at 150 Torr hydrogen. Catalytic activities are normalized to the catalytic activities observed at standard conditions. Insert shows catalytic activities at lower ethylene pressures. Temperatures and catalyst: 223 K, 1.2 wt% Pt/Cab-O-Sil; and 336 K, Pt wire.

TABLE 2

Summary of Ethylene Kinetic Orders from Flow-Through Kinetics for Ethylene Hydrogenation Over Supported Pt Catalysts and Pt Wire

Temperature (K)	0.04 wt% Catalyst:		Pt wire	1.2 wt% Pt/Cab-O-Sil	1.2 wt% Pt/Cab-O-Sil
	Pt/Cab-O-Sil		150	150	500
Hydrogen pressure (Torr)	150		150	150	500
223	-0.17			-0.13	-0.12
248	-0.17			-0.18	
273	-0.17				
298	-0.20				
336	-0.43		-0.33		

The ethylene kinetic orders in Table 2 were determined between 5 and 75 Torr ethylene pressure at various temperatures and catalysts. This ethylene order was found to be temperature dependent, changing from -0.41 at 336 K to -0.17 at and below 273 K for the 0.04% Pt/Cab-O-Sil catalyst.

Figure 6 shows that between 223 and 336 K, the hydrogen kinetic order is temperature dependent. Hydrogen kinetic orders in Figure 6 were determined from flow-through kinetics at an ethylene pressure of 25 Torr over 0.04 Pt/Cab-O-Sil catalyst at hydrogen

pressures from 50 to 650 Torr. At 336 K, heat transfer limitations were observed at hydrogen pressures above 350 Torr. Accordingly, data collected under these conditions were not used in our kinetic analyses. Figure 6 shows that the hydrogen kinetic order continuously decreases from first order at 336 K to half order at and below 248 K.

The hydrogen kinetic order was observed to be independent of catalyst dispersion and ethylene pressure. Table 3 shows no difference in hydrogen orders between the high-dispersion 0.04% Pt/Cab-O-Sil catalyst and the low-dispersion Pt wire. Hydrogen orders determined for the 1.2 and 0.13 wt% Pt/Cab-O-Sil were similar to those in Table 3. Table 3 also shows that the hydrogen kinetic orders for the 0.04% Pt/Cab-O-Sil catalyst vary little between regions of negative ethylene order (5 Torr) and regions of zero ethylene order (75 Torr).

No difference between kinetic orders determined at initial and steady-state catalytic activities was observed. Reaction orders were determined from initial catalyst activities by regenerating the catalyst with flowing hydrogen at 573 K for 1 h between each measurement.

Recirculating batch reactor kinetic experiments showed the hydrogen kinetic order to be independent of total pressure. These experiments showed no change in the hy-

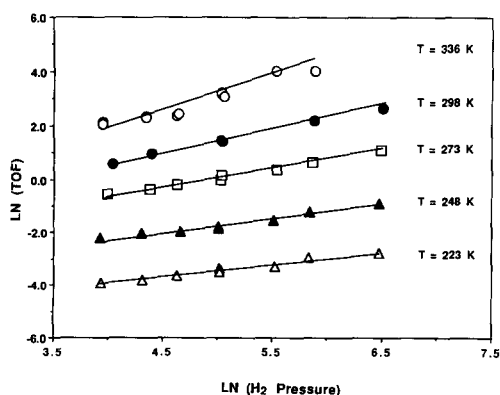


FIG. 6. Effects of hydrogen pressure on ethylene hydrogenation catalytic activities for 0.04 wt% Pt/Cab-O-Sil catalyst at various temperatures and at 25 Torr ethylene pressure. Hydrogen kinetic orders: 1.10 (336 K), 0.77 (298 K), 0.66 (273 K), 0.53 (248 K), and 0.48 (223 K).

TABLE 3

Summary of Hydrogen Kinetic Orders from Flow-Through Kinetics for Ethylene Hydrogenation Over Highly Dispersed Supported Pt and Pt Wire

Temperature (K)	Catalyst: 0.04 wt% Pt/Cab-O-Sil			Pt wire	
	5	25	75	5	25
Ethylene Pressure (Torr)					
223	0.55	0.48	0.54		
248	0.58	0.53	0.54		
273	0.74	0.67	0.67		
300	0.77	0.77	0.75		0.70
336	1.04	1.10	0.91	0.95	1.03

drogen kinetic order at 298 K and total pressures from 100 to 800 Torr. However, slightly higher catalytic activities were noted at lower total pressures. These higher activities may be due to poor interphase heat transfer at low flow rates and low pressures.

Activation Energy

Apparent activation energies determined by other investigators are summarized in Table 1. These studies assumed that the kinetic orders were independent of temperature. If we make this same assumption for comparison, then we obtain an activation energy of 8.6 kcal/mol, and this compares well with the activation energy of 8.9–9.0 kcal/mol determined by Schlatter and Boudart.

DISCUSSION

At standard conditions, the turnover frequencies shown in Fig. 4 are in agreement with the kinetic activities observed by Schlatter and Boudart (7) between 223 and 336 K. The ethylene and hydrogen kinetic orders shown in Tables 2 and 3, respectively, supplement these catalytic activities.

The hydrogen kinetic order in Table 3 changes from half order at 248 K to first order at 336 K for Pt. Table 1 shows that earlier investigators did not observe a temperature dependence of the hydrogen kinetic order for Pt. The work of Zaera and

Somorjai at 333 K (5) and Kazanskii and Strunin (4) at higher temperatures agrees with our observation of first-order hydrogen kinetics at 336 K, as shown in Table 3. Below 330 K, these previous investigators did not observe hydrogen kinetic orders less than unity. Table 3 shows that the hydrogen kinetic order decreases to 0.77 at 300 K and 0.66 at 273 K, whereas Zaera and Somorjai at 300 K and Bond (2) at 273 K observed orders greater than unity.

Two previous investigations have observed hydrogen kinetic orders less than unity over platinum. Half-order hydrogen kinetics were observed by Sinfelt (8) at ambient temperature. However, the turnover frequencies of that study were considerably lower than those reported in the present work and by others in the literature. Schuit and Van Reijen (9) reported a hydrogen order of 0.77 at 233 K over a platinum film. They employed a batch reactor with the platinum film coated on the surface to prevent heat transfer limitations. However, in that work a positive order in ethylene of 0.25 was noted and an activation energy of 16 kcal/mol was found.

The temperature dependence of the hydrogen kinetic order for platinum observed in the present study has also been observed for nickel. With the results of several studies combined, the hydrogen kinetic order on nickel has been observed to increase with

temperature. Kemball (22) observed half-order hydrogen kinetics between 153 and 173 K over evaporated nickel films. Masuda (23) found a hydrogen kinetic order of 0.7 over nickel wire at temperatures between 228 and 273 K. Numerous investigators (1) have observed first-order hydrogen kinetics over nickel catalysts at or above ambient temperature.

Previous investigators observed negative ethylene kinetic orders similar to those shown in Table 2 and Fig. 5. Bond (2) and Sinfelt (8) both showed that the ethylene order became less negative with increasing ethylene pressure, with zero-order kinetics observed at higher ethylene pressures. Bond showed a transition to zero-order ethylene kinetics at ethylene pressures higher than 150 Torr compared to 75 Torr shown in Fig. 5. Zaera and Somorjai (5) reported an ethylene order of -0.6 at ethylene pressures between 10 and 20 Torr. A larger negative order would be expected at these lower ethylene pressures. Figure 5 and Table 2 indicate a higher negative order at higher temperatures and at lower ethylene partial pressures. At ethylene pressures between 10 and 25 Torr on 0.04% Pt/Cab-O-Sil at 336 K, an ethylene order of -0.52 was observed, in contrast to a value of -0.41 for ethylene pressures between 5 to 75 Torr.

Zero-order ethylene kinetics indicate a metal surface essentially covered with adsorbed hydrocarbon. Negative reaction orders suggest that the number of vacant surface sites decreases with increasing ethylene pressure. At lower ethylene partial pressures, more vacant sites for hydrogen adsorption become available. Accordingly, with a higher surface coverage by adsorbed hydrogen, a faster rate of hydrogenation of the dominant adsorbed hydrocarbon fragments is achieved. Figures 5 and 6 show that the highest rates are observed at the lowest ethylene pressures and highest hydrogen pressures. These conditions produce the lowest hydrocarbon and the highest hydrogen surface coverages.

Boudart and Djega-Mariadassou (24)

have discussed several structure-insensitive reactions. In the cases of hydrogenation of ethylene, propylene, and cyclohexane all reactions are essentially zero order in hydrocarbon and were observed to be structure insensitive. These authors suggest that structure insensitivity is observed because the reaction takes place on a "metal-alkyl" surface, where structural features have been essentially erased.

Zaera and Somorjai (5) proposed that ethylene hydrogenation occurs over a surface covered with ethylidyne (CCH_3). This species, as identified through LEED (12), is oriented perpendicular to the surface in a threefold hollow site. In this proposed mechanism, ethylidyne in the presence of adsorbed hydrogen is converted to ethylidene ($\text{CH}-\text{CH}_3$). This ethylidene species then serves as a hydrogen transfer agent to an ethylene molecule which is adsorbed weakly in the second layer. These authors argued that ethylidyne was formed rapidly from the first ethylene molecules to adsorb on the surface, and this explained the observation that the hydrogenation rate was the same whether the surface was initially clean or precovered with ethylidyne.

Beebe and Yates (13) showed that ethylidyne was not essential to ethylene hydrogenation. They used *in situ* IR spectroscopy to monitor the surface of a Pd/alumina catalyst during ethylene hydrogenation. They identified ethylidyne on the surface and showed that this species formed rapidly on the surface under ethylene-rich conditions. They did not detect ethylidyne formation under hydrogen-rich conditions, and they observed no difference in reaction rates with or without ethylidyne on the surface. Rekoske *et al.* (27) conducted similar *in situ* IR studies over supported Pt catalysts and they also found no ethylidyne formation at high ratios of hydrogen to ethylene at ambient temperatures.

Backman and Masel (25) suggested that ethylidyne occupies active sites and poisons the surface for ethylene hydrogenation. They studied ethylene hydrogenation over

Pt(111) and (5×20) Pt(100) single crystal surfaces. Employing a 1 : 1 ratio of hydrogen to ethylene in a recirculating batch reactor at 300 K, they observed initial catalyst deactivation followed by constant catalytic activity at steady state. X ray photoelectron spectroscopy detected an accumulation of carbon on the surface during deactivation, suggested to be due to ethylidyne species. Zaera and Somorjai (5) showed through ^{14}C radiotracer studies that ethylidyne hydrogenation is orders of magnitude slower than ethylene hydrogenation. However, at a regeneration temperature of 470 K the surface ethylidyne was rehydrogenated and removed from the surface in 5 min.

The deactivation observed in Fig. 2 may be due to a carbonaceous species blocking active sites; however, it is unlikely that this carbonaceous species is ethylidyne. At a hydrogen to ethylene ratio of 6 : 1, Fig. 2 shows deactivation from 223 to 336 K. The *in situ* IR studies discussed above showed that no ethylidyne was formed at low temperatures and high ratios of hydrogen to ethylene. Accordingly, these *in situ* IR studies suggest that ethylene hydrogenation occurs on the metal surface and the observed deactivation indicates that the metal surface is modified by a carbonaceous species blocking active sites.

The deactivated catalyst of Fig. 2 was regenerated successfully with hydrogen at 573 K for 1 h. Accordingly, the carbonaceous species blocking the active sites are reactive with hydrogen at higher temperatures, as evident from the successful regenerations.

The inconsistent activities noted after regenerating the catalyst with oxygen may be related to residual oxygen on the surface. Steininger *et al.* (11) used EELS to determine that ethylene adsorbed in only the di- σ -form on Pt(111) at low temperatures. These authors showed that upon warming, ethylidyne species are formed from the di- σ -adsorbed form of ethylene. They also noted that if the Pt(111) surface was first treated with oxygen, then π -adsorbed ethylene was the predominant surface species. Mohsin *et*

al. (14) employed transmission FTIR to investigate the adsorption of ethylene at low temperatures on Pt/alumina catalysts. These authors observed primarily di- σ - and π -adsorbed forms of ethylene, with evidence of ethylidyne formation. They suggested that the π -adsorbed species they observed was situated on a Pt/O site formed either by residual oxygen left on the surface after oxygen treatment or by an interaction of Pt with the oxygen atoms of the Al_2O_3 support.

Ethylene Hydrogenation Mechanistic Considerations

An ethylene hydrogenation mechanism should explain the observed temperature dependence of the hydrogen kinetic order, the ethylene pressure dependence on the ethylene kinetic order, and the catalytic activity. Previous investigators have employed the Horiuti–Polanyi mechanism to explain the observed first order in hydrogen and zero order in ethylene.

Horiuti and Polanyi (26) investigated the rate of exchange between ethylene and heavy water and ethylene and hydrogen. From this work they proposed a mechanism where ethylene is associatively adsorbed and hydrogen is dissociatively adsorbed on the surface. The adsorbed ethylene species then reacts with adsorbed hydrogen atoms in a highly reversible reaction to form a *half-hydrogenated state*. This state then reacts irreversibly with another adsorbed hydrogen atom to form ethane.

Sato and Miyahara (10), employing the Horiuti–Polanyi mechanism, concluded that the dissociative adsorption of hydrogen is irreversible and rate limiting for ethylene hydrogenation over Pt. This gave rise to first-order hydrogen kinetics. They investigated the hydrogenation of ethylene on evaporated Pt and Rh films at and above ambient temperature, using deuterium as a tracer. They further determined that the adsorption of ethylene was nearly irreversible, leading to zero-order ethylene kinetics.

We suggest that a noncompetitive Hori-

uti-Polanyi mechanism explains half-order hydrogen kinetics at low temperatures over Pt. This noncompetitive mechanism employs an *S*-site on which only hydrogen may adsorb, as discussed by Boudart and Djega-Mariadassou (24) for ethane hydrogenolysis. These *S*-sites are the result of the size difference between atomic hydrogen and adsorbed hydrocarbon species, according to which atomic hydrogen is able to adsorb on a surface saturated with carbeneous species. This formalism eliminates the competition between hydrocarbons and hydrogen for vacant surface sites.

This mechanism shows half-order hydrogen kinetics if the surface is covered with hydrocarbon species and the dissociation of hydrogen on the *S*-site is an equilibrated process. First-order hydrogen kinetics are obtained when the hydrogen dissociative adsorption step becomes irreversible. The temperature dependence of the hydrogen kinetic order is observed because the rate of hydrogenation of the half-hydrogenated species increases more quickly with temperature than the rates of hydrogen adsorption and desorption.

A microkinetic model of the above noncompetitive mechanism is discussed by Rekoske *et al.* (27). Using kinetic parameters derived from the temperature program desorption studies of Godbey *et al.* (16) and Berlowitz *et al.* (17) on Pt(111), this model shows the desired increase of hydrogen kinetic order with temperature. This noncompetitive model also predicts an ethylene kinetic order of zero at low ethylene pressures. Furthermore, the catalytic activities predicted by this model are in agreement with the values measured experimentally at temperatures below 273 K. However, above 273 K, this noncompetitive model predicts catalytic activities that are lower than experimental values.

The failure of the noncompetitive model to predict catalytic activities above 273 K and to predict negative ethylene orders suggests that the adsorption of hydrogen and ethylene becomes more competitive as the

total surface coverage decreases, as suggested by Rogers *et al.* (28) and Mezaki (29). Accordingly, at lower temperatures and higher ethylene pressures, the noncompetitive pathway predominates. As the temperature increases and the ethylene pressure decreases, hydrogen adsorption competes with ethylene adsorption for surface sites. This competitive mechanism, therefore, supplements the noncompetitive mechanism at higher temperatures and lower ethylene pressures.

A microkinetic model that incorporates both the noncompetitive and competitive adsorption of hydrogen shows the observed increase of hydrogen kinetic order with temperature, the observed ethylene kinetic orders with ethylene pressure, and the observed catalytic activities between 223 and 336 K. The details of this model will be presented elsewhere (27).

CONCLUSIONS

The hydrogen kinetic order was observed to be temperature dependent for ethylene hydrogenation on platinum catalysts. First-order hydrogen kinetics were observed at 336 K, and the order decreased continuously to half order at 248 K. This temperature dependence has not been observed in previous investigations for platinum, but there is experimental evidence for a similar temperature dependence over nickel catalysts. The hydrogen kinetic order was found to be independent of catalyst dispersion and ethylene pressure.

Zero-order ethylene kinetics were found at ethylene pressures above 75 Torr, and the ethylene order became negative at lower ethylene pressures. Ethylene hydrogenation was shown to be structure insensitive over platinum, with equivalent turnover frequencies observed over highly dispersed Pt supported on silica and on platinum wire. The observed turnover frequencies of this work are in good agreement with the results of previous investigations at similar conditions.

These observed steady-state catalytic ac-

tivities and kinetic reaction orders can be explained qualitatively by a Horiuti-Polanyi mechanism which accounts for both competitive and noncompetitive hydrogen adsorption on the platinum surface. The half-order hydrogen kinetics at low temperatures and the observed zero-order ethylene kinetics at higher ethylene pressures suggest a mechanism in which hydrogen is noncompetitively adsorbed on a surface essentially covered with adsorbed hydrocarbon species. The hydrogen and ethylene compete for the same adsorption sites as the temperature increases and the ethylene pressure decreases. At higher temperatures and lower ethylene pressures, this competitive adsorption supplements the noncompetitive pathway and accounts for the observed catalytic activity.

The initial catalyst deactivation observed in the flow-reactor experiments and subsequent successful hydrogen regeneration suggests that a carbonaceous species covers active sites and poisons the surface for ethylene hydrogenation.

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