Interaction of Hydrogen with Supported Ru Catalysts: High Pressure *in Situ* NMR Studies

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An *in situ* ^{1}H nuclear magnetic resonance (NMR) technique has been employed to study the interaction of hydrogen with silica-supported ruthenium catalysts in the temperature range 300–473 K and at pressures of 10^{-5}–760 Torr. In addition to an upfield NMR peak (called α) occurring at ~-60 ppm and observed at low pressures ($P < 100$ Torr), we have noted the emergence of a second peak (called β) occurring at ~-30 ppm at elevated pressures ($P > 100$ Torr). These two hydrogen populations represent adsorbed hydrogen interacting with Ru metal particles, as indicated by the observed Knight shifts. The α hydrogen species exists in the form of less mobile hydrogen species α_l, or a mobile hydrogen species α_M with heats of adsorption determined by microcalorimetry to be about 70 kJ/mol and 40 kJ/mol, respectively. The heat of adsorption of the β species was determined to be approximately 10 kJ/mol. Hydrogen adsorption isotherms were obtained from the NMR peak intensities calibrated by a gadolinium-doped lanthanum hydride internal reference. A higher dispersion of metal particles correlated with a larger amount of the weakly adsorbed β hydrogen species. The H/Ru$_{surface}$ ratio was observed to be in excess of 5 at elevated pressures (>500 Torr). The high H/Ru$_{surface}$ was due to the adsorption of large amounts of β hydrogen. © 1994 Academic Press, Inc.

INTRODUCTION

Considerable effort has been directed toward understanding the interaction of hydrogen with metals because of intense scientific interest in these systems and their practical applications in catalytic processes. Hydrogen plays a dual role in catalysis. It is a reactant or product molecule in many catalytic reactions, and it can be a powerful probe to investigate the nature of active sites. Several of the reactions involving hydrogen, such as hydrogenation/dehydrogenation, hydrogenolysis, and skeletal rearrangement reactions, are of particular importance in the catalytic reforming of petroleum feedstocks. Other important reactions include the synthesis of ammonia, of hydrocarbons or alcohols by means of the Fischer–Tropsch reaction, and solidification of unsaturated fatty acids.

In the studies of hydrogen adsorption on supported metals, a surface hydrogen-to-metal (H/M) stoichiometry of 1 has commonly been used, and this assumption has been justified by single crystal investigations using XRD and TEM (1–3). The stoichiometry of H/M = 1 has been assumed because the metal particles larger than 2 nm consist largely of [111]-like faces. A maximum of one chemisorbed hydrogen atom per metal atom was observed on Pt[111] by Christmann *et al.* (4). However, several studies have indicated stoichiometries exceeding one. The H/Pt ratios have been found to be in the range 1.5–1.65 for Pt/Al$_2$O$_3$ catalysts (5, 6) and 1.3–1.6 for silica-supported platinum catalysts (7, 8). Wanke and Dougharty (9) have reported the adsorption of more than one hydrogen atom per structure rhodium atom for Rh/Al$_2$O$_3$ catalysts. Kip *et al.* (10) have reported H/M ratios exceeding 1 for Pt, Rh, and Ir catalysts supported on Al$_2$O$_3$, SiO$_2$, and TiO$_2$. Sanz and Rojo (11) used NMR spectroscopy to study hydrogen adsorption on Rh/TiO$_2$ at room temperature. They reported the ratio of hydrogen-to-rhodium surface atoms (H/Rh$_{surface}$) to be 3 at a pressure of 400 Torr. In a study of unsupported transition metal clusters, Kaldor and Cox (12) have found the very high H/M ratios of 3, 5, 5, and 8 for Pd, Ni, Pt, and Rh, respectively. These H/M ratios were found to increase with decreasing cluster size. All of these studies demonstrate that hydrogen can adsorb on various metals in amounts exceeding a one-to-one stoichiometry.

In order to better understand the hydrogen–metal interactions at the atomic scale, hydrogen adsorption over well-defined single crystal Ru surfaces has been studied. The various methods employed include temperature programmed desorption (TPD) (13, 14), vibrational spectroscopy (15, 16), angle-resolved photoemission spectroscopy (17), low-energy electron diffraction (LEED) (13, 18–21), and measurements of the surface diffusion of hydrogen atoms (22–24). An interesting behavior was found when work function variations during adsorption were corre-

lated with temperature programmed desorption results (13). The nonmonotonic change of the work function with hydrogen dosage suggested the existence of two distinct states with negative (N) and positive (P) outward dipole moments, respectively. These two states were well correlated with the two desorption peaks in the temperature programmed desorption spectra and exhibited different sticking probabilities, with the P state having a smaller sticking coefficient. Initially, the desorption involved mainly the N state, which was adsorbed directly with a sticking coefficient proportional to $1 - \Theta_N$ (where Θ_N is the relative coverage of the N state) and was responsible for the initial rise of the work function. With higher hydrogen exposure, the population of the P state increased and the work function asymptotically decreased to a constant value. These results were explained in two ways. One explanation was based on the assumption that lateral interactions between hydrogen atoms adsorbed on the same site gave the appearance of two binding states (16). The other explanation associated the two binding states with two different sites (13).

Several attempts have been made to identify surface sites responsible for the adsorption of hydrogen on single crystals. The two fundamental frequencies observed in high-resolution electron energy loss spectroscopy (HREELS) were assigned to the symmetric (perpendicular to the surface) and to the asymmetric (parallel to the surface) vibrational frequencies of a hydrogen atom occupying threefold hollow sites (15, 16). LEED data (13, 20) revealed a 1×1 pattern at all coverages at a temperature above 80 K, suggesting that the ordered phase experienced no surface reconstruction. Similarly, recent studies using very low energy electron diffraction (VLEED) revealed hydrogen occupied the threefold hollow sites on the surface (21).

The occupation of subsurface sites on open surfaces such as Pd[110] (25) and Cu[110] (26) has been established and is associated with surface reconstruction. The existence of subsurface hydrogen has not been confirmed for close-packed surfaces. Yates et al. (14) have studied hydrogen adsorption on Ru[0001] by an isotope TPD method. They attributed the difference in the high temperature tail of the desorption spectra for H_2, HD, and D_2 to the desorption of subsurface hydrogen (14). Theoretical studies (22, 28) based on a pseudopotential method and local density functional approximation suggested that the Ru[0001] surface threefold hollow sites are of lowest energy for up to one monolayer of hydrogen. The subsurface octahedral sites are also energetically favorable, but they have an energy barrier to occupation. According to these calculations, when all threefold hollow sites are occupied, this barrier is reduced and the octahedral sites become accessible.

The results from UHV studies cannot always be directly extended to high-pressure conditions such as those ex-

isting in most industrial processes. At elevated pressures, steady-state concentrations of "weakly" bonded species can exist, and these species cannot be easily studied under high vacuum conditions. IR studies have attempted to identify the different hydrogen species interacting with Rh (29) and Pt (30–34) in supported catalysts at elevated pressures. On alumina-supported platinum catalysts three different modes of IR absorption have been reported. A mode at 950 cm^{-1} has been associated with strongly bound hydrogen and a mode at 2120 cm^{-1} has been associated with a weakly adsorbed hydrogen species. There is, however, some controversy regarding a mode observed at 2060 cm^{-1}, which appeared as a shoulder to the 2120 cm^{-1} mode at a pressure of 100 Torr. Dixon et al. (31) have assigned this shoulder to a weakly adsorbed hydrogen species, while other researchers (32–34) have indicated that it is due to a CO contamination of the sample. In another IR study of alumina-supported rhodium catalysts, only weakly adsorbed dissociated hydrogen was observed at 2013 cm^{-1} for pressures of 100 Torr and greater (29). It was concluded that any adsorbed hydrogen species at lower pressure were infrared inactive. It is expected that the presence of such "weakly" chemisorbed states may open new pathways for reaction mechanisms.

In this study, an in situ NMR technique was employed to investigate the various hydrogen species interacting with the silica-supported ruthenium metal catalysts at hydrogen pressures up to 760 Torr and temperatures up to 473 K. In contrast to the standard volumetric adsorption technique commonly used to characterize active metal sites (35), in situ NMR allows for quantitative measurements of hydrogen adsorbed on the metal at elevated pressures and temperatures, independently from the silanol protons and spillover hydrogen species associated with the silica support. The technique is not limited to low pressure and/or temperatures and can be used to examine the nature of hydrogen adsorption under typical reaction conditions. In addition to the identification and quantification of the strongly and weakly adsorbed hydrogen on the metal, we also explored the energetics of hydrogen adsorption via microcalorimetery.

EXPERIMENTAL

Catalyst Preparation and Reduction

Catalysts composed of ruthenium supported on Cab–O–Sil HS5 silica were prepared by incipient wetness impregnation as described previously (35). The catalyst dispersions were determined from strongly bound hydrogen chemisorption measured via volumetric uptake measurements and found to be 29 and 19% within a relative error of ±3%. The catalyst samples were reduced at 450°C for 2 h in flowing H_2 and re-reduced in the NMR probe

at 225°C for 2 h in 760 Torr of H_2 with the hydrogen evacuated and replaced every 30 min.

NMR Experiments

^{1}H NMR measurements were performed at 250 MHz on a home-built spectrometer. An in situ NMR probe was attached to a volumetric adsorption apparatus for studying the effect of adsorbate pressure (10^{-5}–10^3 Torr) and adsorption temperature (300–473 K). In the construction of the in situ probe, we followed the design by Haddix et al. (36). The probe was placed in a CF1200 Oxford cryostat controlled by an Oxford 3120 temperature regulator. The proton background signal of the probe was found to be negligibly small. For suppression of baseline artifacts in the spectra, a standard spin–temperature inversion pulse sequence was used. The T_1 measurements were made using the inversion recovery method (see Results and Table 1). Typically 2000 scans were averaged for each spectrum, using a recycle time of 0.3 s between scans to avoid saturation of the peaks corresponding to hydrogen-on-metal. The ^{1}H NMR shifts are referenced to tetramethylsilane (TMS) using the δ scale, with negative values being upfield. The reported shifts are within an error of ± 1 ppm.

Hydrogen-on-ruthenium peak intensities were measured to quantitatively determine the amount of hydrogen adsorbed on the metal. In this work, we have used lanthanium hydride ($LaH_{2.6}$) doped with 25 ppm gadolinium as an internal reference standard for the quantification of the amounts of adsorbed hydrogen. This method allowed us to avoid calibration problems associated with the Q factor of the NMR probe and Boltzmann distribution variations with temperature. $LaH_{2.6}$ is stable below 1000 K and exhibits a single motionally averaged peak at 3 ppm which could be well distinguished from the other features in a ^{1}H NMR spectrum of a catalyst. The reference sample was weighed and sealed in a capillary tube and placed in situ with the catalyst in an NMR tube. The amounts of adsorbed hydrogen were determined by comparing the integrated peak areas with that of the $LaH_{2.6}$ standard.

Microcalorimetric Experiments

The differential heats of hydrogen adsorption were measured in an isothermal Tian–Calvet-type heat flow microcalorimeter (Setaram C80) connected to a standard gas volumetric system. These measurements were taken in the Chemical Engineering Laboratory at the University of Wisconsin. The microcalorimeter consisted of a sample cell and a reference cell connected to a dosing volume. An MKS capacitance manometer was used to monitor gas phase adsorbate pressures. A typical experiment consisted of dosing micromolar quantities of hydrogen and monitoring the resulting differential heat flux. The integrated area under the calorimeter response curve divided by the quantity of gas adsorbed during the dose corresponded to the differential heat of adsorption. The details of the apparatus and the experimental procedure are given elsewhere (37). All calorimetric measuremens were carried out isothermally at 403 K.

RESULTS

The ^{1}H NMR spectra of a silica-supported Ru catalyst with a dispersion of 29% taken at 400 K and under various hydrogen pressures are given in Figs. 1 and 2. In spectrum (A) of Fig. 1, two distinct peaks were observed: a resonance at ~3 ppm due to hydrogen associated with the silica support (38) and the peak at ~−60 ppm, labeled α, attributed to hydrogen dissociatively adsorbed on ruthenium particles (35, 39). Spectrum (B) of Fig. 1 was obtained after the same sample was dosed with 50 Torr of hydrogen and subsequently evacuated to 5×10^{-6} Torr for 2 min to remove the relatively weakly adsorbed hydrogen species. In both evacuated and nonevacuated samples, the α peak represents strongly adsorbed hydrogen. As follows from the linewidths measured in this work and
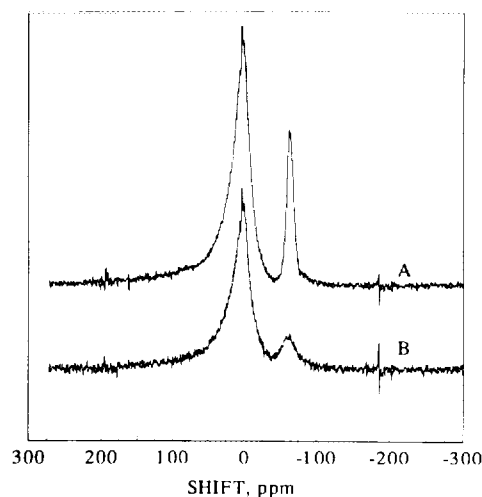
TABLE 1

Spin-Lattice Relaxation Times, T_1 (ms), of α and β Hydrogen at Various Temperatures

Temperature (K)	T_1 (α)	T_1 (β)
300	17.5	13.5
400	17	13
473	16.6	12.8

FIG. 1. NMR spectra of 29% dispersed ruthenium catalyst: (A) 50 Torr, (B) dosed with H_2 and evacuated to 5×10^{-6} Torr for 2 min.
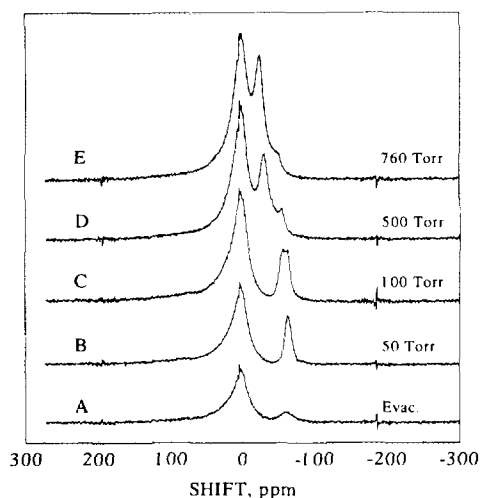
FIG. 2. NMR spectra of 29% dispersed ruthenium catalyst: (A) dosed with H_2 and evacuated to 5×10^{-6} Torr for 2 min, (B) 50, (C) 100, (D) 500, and (E) 760 Torr of hydrogen.

the results of a detailed 2D NMR study reported elsewhere (40), this hydrogen exhibits restricted mobility in evacuated samples (α_I) and becomes very mobile (α_M) in non-evacuated samples with an increase in pressure. The integrated intensity of α_I at room temperature is a measure of the dispersion of the catalyst and is in good agreement with the dispersion obtained from volumetric uptake measurements of strongly bound hydrogen, as noted in a previous study (35).

At pressures greater than 100 Torr, a third distinct peak, β, was noted between -30 and -50 ppm (see Fig. 2, spectra (C)–(E)). The two distinct upfield peaks, α and β, were present over the entire temperature range (300–473 K) investigated in this study. The presence of separate resonance lines reveals that the hydrogen populations α and β are different, and not in fast exchange with each other on the NMR time scale (i.e., on the order of $(\Delta\omega_{\alpha\beta})^{-1} \approx 0.05$ ms, where $\Delta\omega_{\alpha\beta}/2\pi$ is the difference of resonance frequencies of α and β). Clearly, the two distinct hydrogen populations must be interacting with the ruthenium metal, as is evidenced by the upfield Knight shifts (41). The variations in the spin-lattice relaxation times, T_1, of α and β with temperature are given in Table 1. The intensity of the α peak remains approximately constant above 100 Torr. The β hydrogen intensity increased continuously and the resonance peak moved downfield with increasing pressure (see Table 2).

The NMR spectra of hydrogen adsorbed on the silica-supported ruthenium catalyst with a dispersion of 19% are given in Fig. 3. As with the 29% dispersed catalyst, two hydrogen-on-ruthenium peaks can be seen clearly at elevated pressures. The increase in the β peak intensity relative to the α intensity was less for this catalyst than for the catalyst with a dispersion of 29%, as noted in Table

TABLE 2

NMR Shifts (± 1 ppm) of Hydrogen Adsorbed on 29% Dispersed Supported Ruthenium Catalyst at 323 K

Pressure (Torr)	NMR shifts (ppm)	
	α	β
10	-65	
100	-62	-55
200	-60	-45
300	-58	-40
400	-57	-35
500	-55	-30
600	-51	-26
760	-44	-23

3. The narrow resonance at 3 ppm results from the $LaH_{2.6}$ calibration reference.

The coverage of hydrogen on the metal surface determined from the integrated intensities was used to plot adsorption isotherms. The hydrogen adsorption isotherm at 323 K for the 29% dispersed Ru catalyst and the deconvoluted intensities of α and β are given in Fig. 4. The coverages reported as hydrogen-to-metal ratios are within a relative error of $\pm 20\%$. Note that a hydrogen to total ruthenium ratio, H/Ru_{total}, of up to about 1.25 was observed. The hydrogen to surface ruthenium ratio, $H/Ru_{surface}$, was in excess of 5 at pressures greater than 500 Torr. The number of surface ruthenium atoms, or dispersion, was determined from the sample that had been dosed and then evacuated for a short period of time (as noted above). This standard method assumes a one-to-one stoichiometry of strongly bound hydrogen to surface
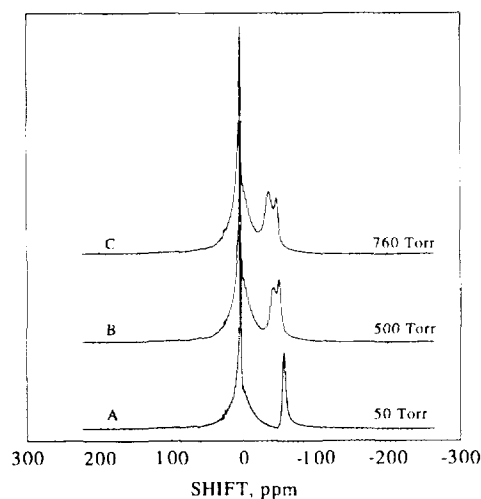

FIG. 3. NMR spectra of 19% dispersed ruthenium catalyst (with internal standard) under (A) 50, (B) 500, and (C) 760 Torr of hydrogen.

TABLE 3

H/Ru$_{surface}$ Ratios for Hydrogen Adsorbed on 29% and 19% Dispersed Supported Ruthenium Catalyst at 323 K

Pressure (Torr)	29% dispersed catalyst		19% dispersed catalyst	
	α	β	α	β
100	1.4	0.3		
150	1.3	0.4		
200	1.3	0.7		
250	1.2	1.1		
300	1.2	1.3	2.3	0.2
350	1.1	1.6	2.3	0.2
400	1.3	2.1	2.3	0.4
500	1.3	3.3	2.1	0.6
550	1.3	3.3	2.1	0.8
600	1.3	3.7	2.1	0.9
650	1.2	4.2	2.2	1.1
760	1.2	4.4	2.1	1.2

FIG. 5. Hydrogen adsorption isotherms at 323 (●), 400 (O), and 473 K (■) for 29% dispersed catalyst.

ruthenium. The α hydrogen population saturated at a pressure below 100 Torr, while the β hydrogen population became observable at 100 Torr and continued to increase for the entire pressure range studied (up to 760 Torr).

A set of isotherms for the 29% dispersed catalyst at 323, 400, and 473 K is given in Fig. 5. As the temperature was increased from 323 to 473 K, an appreciable decrease of the β population was observed. No significant desorption from the α hydrogen population was observed in this temperature range.

The hydrogen adsorption isotherm at 323 K for the catalyst with a dispersion of 19% is given in Fig. 6. Also given are the populations of the α and β states as a function of pressure. The amounts of hydrogen in each state normalized to the number of surface Ru atoms are listed in Table 3. Note that the lower dispersion catalyst had less hydrogen in the β state at a given pressure, whereas the population of hydrogen in the α state was higher.

The heats of adsorption of hydrogen on the 29% dispersed catalyst were determined by two methods: by microcalorimetric measurements and by applying the Clausius–Clapeyron equation (42) to the series of adsorption isotherms derived from *in situ* NMR experiments. The
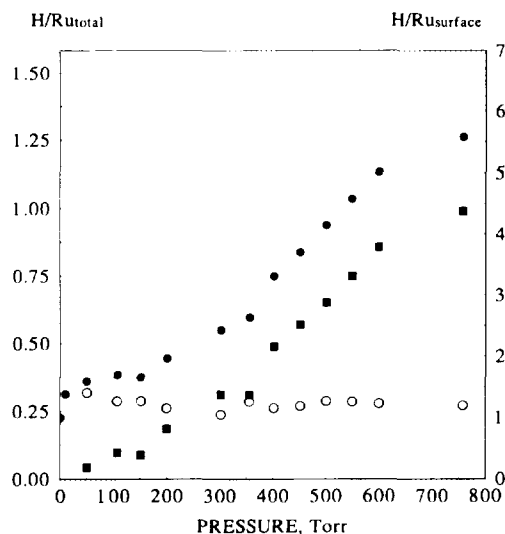

FIG. 4. Hydrogen adsorption isotherm at 323 K for 29% dispersed Ru catalyst: (●) total hydrogen adsorption on the metal, (O) α state only,and (■) β state only.
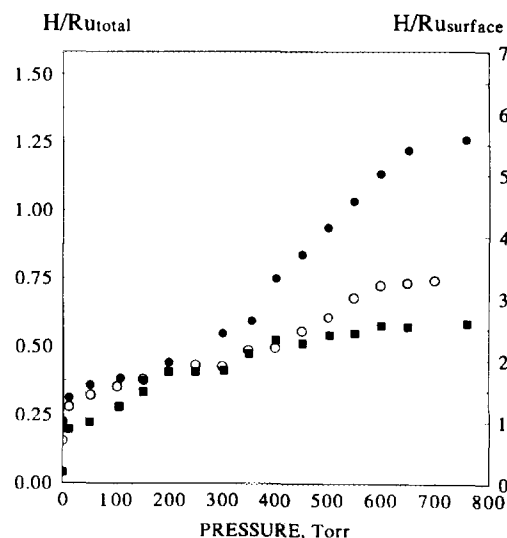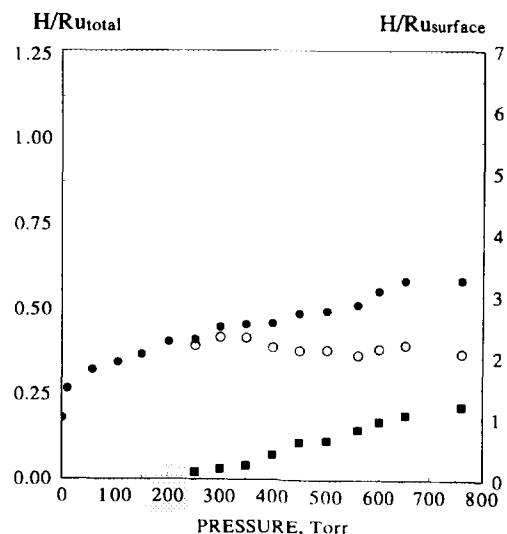

FIG. 6. Hydrogen adsorption isotherm for 19% dispersed Ru catalyst: total hydrogen adsorption on the metal (●), α state only (O), and β state only (■) at 323 K.

differential heats of adsorption determined from microcalorimetric measurements, within an error of ±5 kJ/mol, are plotted versus pressure in Fig. 7. The initial (or zero coverage) heat of adsorption was found to be about 80 kJ/mol. In the low pressure range (10^{-2} Torr $< P < 10^{-1}$ Torr), the heat of adsorption was 60–70 kJ/mol. With increasing pressure, the heat of adsorption dropped, reaching a value of approximately 40 kJ/mol at ~10 Torr and finally a constant value of about 10 kJ/mol at 100 Torr. The Clausius–Clapeyron equation was applied at the coverage of H/Ru_{total} = 0.75 (the region where the β state is partially saturated, see Fig. 5) to obtain the isosteric heat of adsorption of about 7 kJ/mol.

To investigate the catalytic properties of the α and β populations, a 1 : 3 mixture of ethene/hydrogen (300 Torr) was dosed on to the 29% dispersed catalyst. The hydrogen was monitored via in situ NMR as a function of time (Fig. 8). The two sharp peaks at 0 and 6 ppm are due to the hydrogen associated with the hydrocarbon species. At the conclusion of the reaction, an upfield peak at about −40 ppm became observable. The sample was then evacuated to remove all weakly adsorbed species, and the hydrogen was dosed at 10 Torr. In Fig. 9, hydrogen interacting with the metal surface can be seen resonating at −48 ppm (compared to −60 ppm on a clean catalyst noted earlier). At a pressure of 300 Torr, the β peak was observed at −32 ppm. The upfield resonance of −60 ppm noted for hydrogen on the clean catalyst was not observed here.

DISCUSSION

In this study, various hydrogen populations interacting with the ruthenium metal were observed by NMR. The

FIG. 8.　NMR spectra of 29% dispersed catalyst dosed with a 1 : 3 mixture of ethene/hydrogen after (A) 1 min, (B) 30 min, (C) 1 h, and (D) 5 h.

population of α hydrogen saturated at a pressure below 100 Torr, while the β hydrogen population appeared at a pressure of 100 Torr and continued to increase up to 760 Torr in the temperature range 300–473 K.

In samples which were dosed with hydrogen and subsequently evacuated, the hydrogen population consisted of a species with restricted mobility, α_I. Upon increase of hydrogen pressure, a more mobile species, α_M, was observed on the ruthenium surface (40). In previous studies (35, 43, 44), the α_I and the α_M hydrogen populations have been termed the "strongly" adsorbed hydrogen and the "weakly" adsorbed hydrogen, respectively. Weakly adsorbed hydrogen has been defined as that hydrogen adsorbed on the surface which can be removed via short
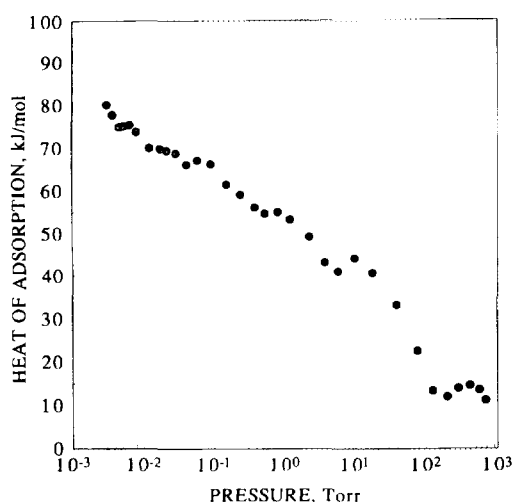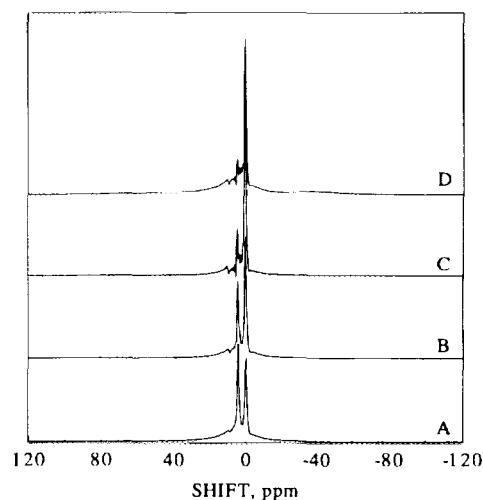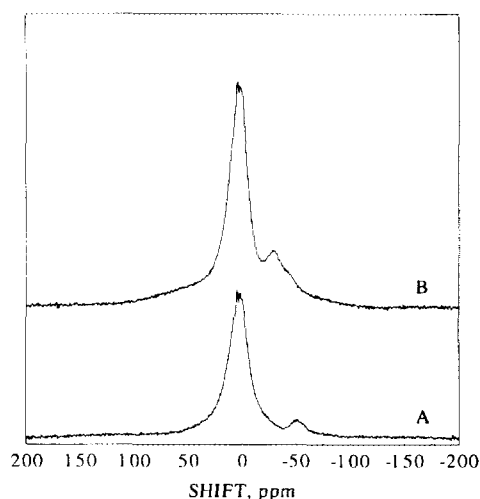

FIG. 7.　Heats of hydrogen adsorption isotherms at 403 K versus adsorbate pressure for 29% dispersed Ru catalyst.

FIG. 9.　NMR spectra of 29% dispersed catalyst dosed with a 1 : 3 mixture of ethene/hydrogen, evacuated, and dosed with (A) 10 Torr and (B) 300 Torr of hydrogen.

evacuation (2–10 min) at room temperature (35, 43, 44). The adsorbed hydrogen that cannot be pumped out in that short interval of time has been termed the strongly adsorbed hydrogen. Evacuating for long time intervals (e.g., overnight) eventually removes all adsorbed hydrogen. The two species, α_1 and α_M, have been distinguished by a volumetric chemisorption technique (35, 43, 44), NMR (35), 2D NMR (40), and on the basis of their heats of adsorption. However, no evidence was found to suggest that at any given pressure, the α_1 and α_M species coexist at the ruthenium surface. The possibility cannot be excluded that the entire α hydrogen population has the properties of either α_1 or α_M, depending on the hydrogen pressure.

The initial heat of adsorption was measured via microcalorimetry to be about 80 kJ/mol for the 29% dispersed catalyst. In comparison, the value of the initial heat of adsorption on Ru[0001] single crystals was reported to be 80 (13) and 120 kJ/mol (18). In the low pressure regime ($10^{-2} < P < 10$ Torr), the heat of adsorption varied between 70 and 40 kJ/mol in the work reported here. This range corresponds closely with the hydrogen species α_1 and α_M. The constant value of approximately 10 kJ/mol (in the pressure range >100 Torr) correlates well with the β hydrogen population observed by NMR. The heats of adsorption of the α_1 and the α_M states were observed to decrease with increasing hydrogen coverage, which can be due to (i) repulsive adsorbate–adsorbate interactions (1) and/or (ii) the presence of a distribution of adsorption sites, as proposed by Langmuir (45).

The β hydrogen is a weakly adsorbed hydrogen species, considerably more weakly bound than the α_M hydrogen. The low value of the heat of adsorption of the β hydrogen raises the question of whether it is chemically or physically adsorbed. Physical adsorption is defined to be due to weak van der Waal interactions or dispersion forces. The highest possible temperature at which true physical adsorption of hydrogen can occur is considered to be 20 K (46). The temperature and pressure of the experiments reported here suggest that physical adsorption of hydrogen is unlikely in this case. Reports in the past, in which it was claimed that physically adsorbed molecular hydrogen had been detected on single crystal metal surfaces between 100 and 300 K, have turned out mostly to suffer from water impurities, thermal gradients, and spurious desorption in temperature programmed thermal desorption spectroscopy (46). The large Knight shift of the β peak shows interaction of this species with the conduction electrons of ruthenium and suggests that it does not reside primarily on the silica support. Also, the β population, as distinguished in this study, is not the hydrogen in the gas phase. The hydrogen gas by itself cannot account for all the observed hydrogen, which was in excess of

5 monolayer equivalents, and the Knight shift of the β hydrogen indicated that it is interacting with the metal. However, a fast exchange between the weakly bound hydrogen and the gas phase cannot be excluded here.

The large population of adsorbed hydrogen (H/Ru$_{surface}$ ratios greater than 5) observed in this study may play an important role in catalysis. In order to understand this phenomenon and gauge its importance to catalysis, we must first address several important questions, namely: how does the identification of a new species, β, distinct from the α species, compare with the previous studies on similar adsorption systems? Is the large amount of hydrogen observed in this study a general phenomenon? Where does all the observed hydrogen exist in the catalyst?

Infrared (IR) spectroscopic studies of hydrogen on alumina-supported platinum catalysts report three different IR modes. Two of the modes have been associated with a strongly adsorbed and a weakly adsorbed hydrogen species (31–34). However, the third mode has not been conclusively shown to be due to hydrogen. Dixon et al. (31) assigned the third mode observed at 100 Torr to a weakly adsorbed hydrogen species, while other researchers (32–34) have indicated it was due to CO contamination of the sample. IR studies of hydrogen on an alumina-supported rhodium catalyst revealed only a weakly adsorbed, dissociated hydrogen species at pressures above 100 Torr (29). However, in our NMR study, the β hydrogen on ruthenium particles was identified and quantified, distinct from the α hydrogen.

Hydrogen to metal stoichiometries of greater than one have been reported for supported metal catalysts (10, 11) and unsupported metal clusters (12). In the present work, we found the high H/Ru$_{surface}$ stoichiometric ratios to be due to adsorption of large amounts of β hydrogen on the metal particles. While the β hydrogen population reached a H/Ru$_{surface}$ ratio of about 4 at elevated pressures on the catalyst with a dispersion of 29%, the α hydrogen population saturated at a H/Ru$_{surface}$ ratio of around 1.2 (Fig. 4). For the 19% dispersed catalyst, the β hydrogen population reached a H/Ru$_{surface}$ ratio of only about 1 at elevated pressures, while the α hydrogen population saturated at a H/Ru$_{surface}$ ratio of around 2. This variation will be discussed later.

Surface science studies at submonolayer hydrogen coverages of hydrogen adsorption on Ru[0001] suggest that hydrogen is adsorbed on the threefold hollow sites (15, 16). Although small particles in supported catalysts contain different crystallographic surfaces, edges, and corner atoms, it has been assumed that the surface species, α_1 (which corresponds to a surface coverage of up to one monolayer), is adsorbed in the threefold hollow sites (1–3). However, the location of the weakly adsorbed hy-

drogen species cannot be inferred from the surface science studies. Below, we consider the following hypotheses regarding the nature of the large β hydrogen population: it could be associated with (i) subsurface species, (ii) multiple adsorption on some or all of the *surface* metal atoms, or (iii) adsorption on alternate sites such as bridge and atop sites or in the overlayers of a saturated layer of hydrogen atoms covering the surface.

(*i*) *Subsurface hydrogen.* The existence of subsurface H on Ru[0001] is an interesting possibility discussed in the theoretical studies of Chou and Chelikowsky (27, 28). They report that the possible locations for subsurface hydrogen adsorption are the tetrahedral sites and the octahedral sites. They conclude that tetrahedral sites are energetically unfavorable for hydrogen adsorption. The octahedral sites are favorable for adsorption *if* the surface threefold hollow sites are already occupied by hydrogen and there is still hydrogen available for adsorption. The hydrogen can reach the octahedral sites by passing through the fcc site. TPD investigations by Yates *et al.* (14) suggest the presence of subsurface hydrogen on Ru[0001]. They attribute the difference in the high temperature tail of the TPD spectra for H_2, HD, and D_2 to the desorption of subsurface hydrogen (14).

However, if the β hydrogen were a subsurface species, its population could be expected to increase with increasing particle size. In contrast, the β population was observed to decrease with an increase in particle size. That is, as the volume of subsurface sites increased relative to the surface, the population of the β state decreased. Furthermore, because of its closer proximity to Ru atoms, we expect the Knight shift of subsurface hydrogen to be larger than that for the hydrogen adsorbed on the surface. Again, this is in contrast to our experimental result; the Knight shift of the β peak was observed to be less than that of α. Thus, we conclude that the β hydrogen is not a subsurface species, although the possibility of the existence of undetected subsurface hydrogen in this system cannot be excluded. A higher ratio of defect-like corner and edge atoms was correlated with a higher ratio of β hydrogen, whereas a higher ratio of atoms in the basal planes resulted in a larger α population.

(*ii*)   *Multiple   hydrogen   adsorption   on   surface atoms.* The defect-like edge and corner metal atoms have been speculated to be the sites where multiple hydrogen adsorption can occur (9, 10, 47, 48). This assumption is based on the fact that stepped sites are more active for hydrogen dissociation than the basal plane atoms (49). Specifically, a hydrogen-to-metal stoichiometry of 2 has been assumed for hydrogen atoms coordinated to the edge and corner metal atoms (9, 47, 48). Given a particle morphology and an assumed stoichiometry, one can calculate hydrogen adsorption amounts. For example, the edge and

corner atoms consist of 22% of the surface metal atoms for a perfect truncated cubo-octahedron with a dispersion of 30%. Even if a H/M stoichiometry of 2 is assumed for defect-like sites (with a H/M of 1 for the basal planes), only about 25% of all the adsorbed hydrogen detected in this study can be explained. H/M stoichiometric ratios of 18 : 1 and 20 : 1 must be assumed for the defect-like sites to account for all the hydrogen we observe on the 19 and 29% dispersed catalysts, respectively. If a H/M stoichiometry of 2 is assumed for the basal planes, then the stoichiometric ratios for the defect-like sites must be 12 : 1 and 16 : 1 for the 19 and 29% dispersed catalysts, respectively, to account for all the hydrogen we observed.

(*iii*) *Hydrogen in the overlayer.* The large populations of hydrogen can be accounted for if, in addition to multiple adsorption on defect sites, it is assumed that the β hydrogen can be adsorbed on bridge and atop sites. Also, it can be speculated that the β hydrogen exists in the overlayers or multiple layers. Mårtensson *et al.* (50) have studied hydrogen adsorption on stepped Ni[510] and Ni[100] surfaces at 100 K by EELS. They report molecular hydrogen chemisorbed at edge sites, over a dense layer of atomic hydrogen which covers the edge sites. No such state was observed on Ni[100] surfaces (50).

The proposal that hydrogen exists in overlayers has also been used to explain the mechanism of ethene hydrogenation reaction over metals. It has been proposed that a carbonaceous layer covers the surface and that the reaction takes place on top of the carbonaceous residues instead of on the metal surface (51). Hydrogen/deuterium exchange over the carbonaceous layer suggests that the hydrogen can interact with the metal and dissociate even when the surface is covered by carbonaceous species. It was proposed that the role of the metal is to dissociate hydrogen, which can then migrate to an overlayer where the reaction takes place (51). Similarly, ^{13}C NMR studies of ethene adsorption on silica-supported ruthenium catalysts have shown that the metal can be predominantly covered by a layer consisting of strongly bound, partly dehydrogenated carbonaceous species which were not consumed during the reaction (52).

We found that the β state could be populated but the α state suppressed simply by dosing the catalyst with ethene and hydrogen. The Knight shift of the observed hydrogen population suggests that the hydrogen present was interacting with the ruthenium d electrons even in the presence of a carbonaceous layer. It can be concluded that the adsorption of β hydrogen (on surface sites or in an overlayer) is not inhibited by the presence of the cabonaceous layer on the surface. However, the α hdyrogen adsorption sites were blocked by the presence of the carbonaceous residue. No evidence for the α state was observed even after evacuating the sample and introduc-

ing pure hydrogen for up to 5 h at 400 K. Thus, even when the surface sites are occupied by hydrocarbon fragments (52), β hydrogen can be observed, whereas the α hydrogen is suppressed.

The surface sites for β adsorption are not clearly understood, and attempts to rigidly fix the location of adsorbed hydrogen to specific adsorption sites may be futile. The β hydrogen population may best be described by terms such as "hydrogen cloud" or "hydrogen fog," similar to those proposed by Mate et al. (53). They used theoretical calculations and vibrational spectroscopy to study hydrogen adsorption at submonolayer coverages on single crystals under UHV conditions and on high-surface-area metals at atmospheric pressure. They concluded that hydrogen atoms on metal surfaces are a unique form of "delocalized hydrogen." This delocalized adsorption is more pronounced for hydrogen adatoms than for other adatoms because of hydrogen's low mass. The high mobility of the β hydrogen due to its weak interaction with the surface perhaps makes the binding site even harder to fix. If this view is correct, the adsorbed hydrogen atoms (or molecules) should not be thought of as having a well-defined bonding geometry but rather as resembling a "hydrogen cloud" or "hydrogen fog" that covers the surface.

The availability of such large amounts of weakly adsorbed, delocalized β hydrogen can have implications for the understanding of catalytic reactions involving hydrogen. Catalytic reactions are generally thought of as occurring between species adsorbed on different surface sites or between adsorbed species and gases. The possibility that hydrogen can populate the β state and interact with transition metals saturated with carbonaceous residues suggests that alternate route for catalytic reactions may be operable.

CONCLUSIONS

An in situ NMR technique was utilized in this study to observe hydrogen adsorbed on supported ruthenium catalysts under variable temperatures and pressure conditions. Two distinct adsorbed states, α and β, were found. The β hydrogen is a much more weakly adsorbed species with a heat of adsorption of about 10 kJ/mol and was found to exist only at pressures greater than 100 Torr. The equilibrium amounts of hydrogen on the suface were found to be structure sensitive. A higher ratio of defect-like corner and edge atoms correlated with a larger β population, while a larger α population was found on particles with a higher ratio of atoms in the basal planes. The availability of such large amounts of weakly adsorbed β hydrogen (greater than 4 monolayer equivalents) on the ruthenium particles can have implications for the understanding of catalytic reactions involving hydrogen. Also,

the structure sensitivity of the β state may play a role in structure sensitive reactions.

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