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Studies of Supported Metal Catalysts

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The influence of nickel crystallites on the temperature-programmed exchange between deuterium and silica hydroxyl groups has been studied. Cab-O-Sil hydroxyl groups exhibited exchange with gaseous deuterium at 540°C. In the presence of nickel crystallites (2% nickel-Cab-O-Sil) two types of hydrogen participated in the exchange reaction at 280 and 525°C, respectively.

INTRODUCTION

Several investigators (*1–4*) have reported an enhanced reactivity for silica and alumina hydroxyl groups in the presence of metals. This increased reactivity was usually determined by following the rate at which deuterium exchanges with surface hydroxyl groups, and comparing these rates with those for the support. Ravi and Shepard (*2*) using infrared spectroscopy have shown that a silica–iridium catalyst is active in promoting deuterium exchange with surface hydroxyl groups. In their work the exchange is enhanced by the presence of a variety of preadsorbed promoters such as acetaldehyde and acetonitrile. Eischens and Pliskin (*1*) have reported similar results for a silica–platinum catalyst while Yates (*3*) has shown that there is a measurable exchange between deuterium and hydroxyl groups on a gold–silica catalyst at room temperature.

Carter and co-workers (*4*) have shown that the impregnation of alumina with platinum enhances the rate of deuterium–hydroxyl exchange. When the impregnation is performed using chloroplatinic acid the exchange increases for a platinum concentration of 0.001%, but a further increase in platinum results in a decrease in the exchangeable rate until a concentration of 0.6% platinum is reached at which point the exchange rate is comparable to that for the support. Impregnation using Pt $(NH_3)_2(NO_2)_2$ on the other hand shows an increase in the exchange rate even at platinum concentrations up to 0.6%. These promotional effects reported by Carter and co-workers are in agreement with results reported by Hall and Lutinski (*5*) on nonreduced platinum–alumina samples; they point out that the reaction of deuterium with oxygen leads to the formation of D_2O providing another mechanism for the exchange. For reduced catalysts this enhancement was not observed and for samples prepared from chlorine containing salts the exchange was actually depressed.

Recently Dorling, Eastlake and Moss (*6*) studied the effect of variables in the preparation of supported metal catalysts on ultimate crystallite size. They found that adsorption type catalysts prepared using platinum amine show little variation in crystallite size with increasing platinum content, whereas catalysts prepared by impregnation with chloroplatinic acid show a marked increase in crystallite size with increasing platinum content.

We had prepared a series of supported nickel catalysts to study the effect of dispersion on methane–deuterium exchange, and preliminary experiments showed deuterium–hydroxyl exchange at temperatures as low as 280°C. This is well below the

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deuterium–hydroxyl exchange temperature for silica as reported earlier by Hall and co-workers (*7*). In view of the results reported by Carter and co-workers (*4*), and Dorling, Eastlake, and Moss (*6*), we thought it might be instructive to examine the rate of deuterium–hydroxyl exchange as a function of crystallite size.

Anticipating the possibility of more than one type of hydroxyl groups exchanging with deuterium as suggested by Carter and co-workers (*4*), we felt that use of the rising temperature technique as adapted and used by Hall and co-workers (*5*, *7–9*), and Cvetanovic and co-workers (*10–14*), was, indeed, the best way to perform this investigation. If more than one type of hydroxyl groups is involved in the exchange, data collected in this manner should clearly indicate it.

Knowledge of possible deuterium–hydroxyl exchange was necessary in order to conduct our investigation of the methane–deuterium exchange reaction. Our preliminary investigations led us to believe that such an interference was present; if, in fact, different hydroxyl groups were involved in the exchange, the problem would prove to be more interesting.

METHODS

Apparatus and technique. In this study a vacuum system of conventional design and capable of an ultimate pressure of 1×10^{-6} Torr was used. A quartz reaction vessel was connected to a Pyrex-glass circulating loop which was equipped with a noncontaminating circulation pump. The reaction loop was directly connected to a conventional BET system enabling accurate volumetric measurements of reaction gases and *in situ* surface area measurements by physical adsorption of nitrogen.

Location of a liquid nitrogen cold trap in the circulation loop immediately "down stream" from the catalyst removed water from the gas stream thereby reducing the possibility of it, being a co-catalyst for the hydrogen–deuterium exchange on the catalyst surface. The nearby BET system provided for the volumetric determination of the collected water to enable us to cross check the exchangeable hydroxyl content of the Cabosil surface.

The "blank" Cabosil and the nickel–Cab-O-Sil catalysts received identical pretreatment prior to being subjected to the TPE investigation. Once sealed in the quartz reaction vessel the Cab-O-Sil specimen was briefly degassed at room temperature, then heated to 400°C in flowing hydrogen (325 ml/min). Treatment in flowing hydrogen at 400°C continued for 5 hr after which the sample was degassed. As a matter of convenience the catalyst was usually degassed overnight; no detectable difference was observed when compared to samples degassed for a shorter period of time.

Following this pretreatment, the Cab-O-Sil was contacted with a known amount of deuterium at a reaction vessel temperature of 100°C. The gas phase was then circulated over the Cab-O-Sil as the temperature was increased at the rate of 2°C/min. Applying corrections for naturally occurring contaminants, the composition of the gas phase was sampled every 10 min and analyzed on a CEC (Du Pont) model 21–104 mass spectrometer. These data (% H vs time, and temp vs time) were converted into a plot of dH/dt, rate of hydrogen appearance vs reaction temperature. Different hydroxyl species yielding hydrogen will have different activation energies and form separate peaks on the latter plot. The experiments were usually concluded at 800°C. The number of Cab-O-Sil hydroxyl groups was determined from the equilibrium composition of the gas phase; this was compared with the amount of water collected in the liquid nitrogen cold trap of the circulating loop.

The metal surface area of the nickel–Cab-O-Sil catalysts was determined via hydrogen–deuterium exchange. The catalyst was cooled from the reduction temperature, 400°C, to room temperature in a hydrogen atmosphere, then quenched to −195°C, and degassed to 10^{-6} Torr. At this reaction vessel temperature, 100 Torr deuterium was admitted, and circulated over the catalyst. The reaction vessel was then warmed to −80°C at which temperature the gas phase was monitored to determine hydrogen–deuterium equilibration for the calculation of nickel surface areas. The catalyst was briefly degassed at room temperature, then prepared for TPE as previously described for Cab-O-Sil.

Crystallite sizes were varied by changing nickel concentrations rather than by the more conventional method of controlled sintering. We decided to use this approach in order to minimize irreversible dehydroxylations which occur at temperatures in excess of 500°C (*16*). We realize that concentration effects might create additional variables to be contended with, however, a more reproducible hydroxyl metal interaction could be obtained if heat treatments did not exceed 500°C.

Materials. CP grade deuterium (98% atom purity) was obtained from the Matheson Co. and passed through a liquid nitrogen cold trap prior to storing in the vacuum system; before use it was examined for purity with a mass spectrometer. A locally procured commercial grade hydrogen used for catalyst reduction was purified by passing it sequentially through a Deoxo unit containing a palladium catalyst to remove trace amounts of oxygen, and then a liquid nitrogen cold trap to remove water. To prepare the 2% nickel–Cab-O-Sil catalyst 19.48 g Cab-O-Sil (Grade M-5), a high purity amorphous silica, was impregnated with 1.98 g Baker and Adamson reagent grade $NiNO_3 \cdot 6H_2O$ previously dissolved in 100 ml distilled, deionized water. A spark spectra of the Cab-O-Sil which was furnished by the Cabot Corp., Boston, MA, indicated a total metallic impurity of less than 100 ppm (including less than 2 ppm aluminum).

While drying at 110°C the Cab-O-Sil–nickel nitrate mixture was stirred regularly to retain a uniform consistency. The Cab-O-Sil samples which were examined were wetted with an equal amount of distilled deionized water and also oven dried at 110°C.

The resultant dried catalysts were ground and/or pelleted, as necessary, and screened; the 35/60 mesh fraction was retained for examination.

RESULTS AND DISCUSSION

Activation energies for deuterium–hydroxyl exchange were determined using the rising temperature technique described by Cheselske, Wallace, and Hall (*8*), and dubbed temperature-programmed exchange (TPE) by us. In reviewing this technique, one has:

$$V_g\left(\frac{dx}{dt}\right) = A(x_\infty - x)e^{-E_a/RT}, \qquad (1)$$

where E_a is the apparent activation energy, dx/dt the rate of hydrogen appearance in the gas phase, x the concentration of hydrogen in the gas phase, and x_∞ the equilibrium value of x. Measurement of the appearance of hydrogen in the gas phase as a function of time for an experiment in which temperature rises linearly with time yields a sigmoid curve for each type of hydroxyl group exchanging with deuterium. At the inflection points the second derivatives are zero enabling the calculation of apparent activation energies. Setting the second derivative equal to zero, one has:

$$E_a = \frac{RT_i^2(dx/dt)_i}{(x_\infty - x)_i(dT/dt)_i}, \qquad (2)$$

where the subscript i indicates that the values for these variables must be taken at the inflection point. In a typical "TPE" chromatogram a plot of dx/dt vs T will yield peaks which should be proportional to the number of hydroxyl groups of each type.

A preliminary TPE experiment was conducted with "blank" Cab-O-Sil without the liquid nitrogen cold trap in the circulating loop, and approximately 20 Torr water was added to the circulation loop prior to the start of the experiment. The hydrogen–deuterium exchange proceeded rapidly at the initial temperature of 100°C demonstrating that water is a co-catalyst for the exchange reaction and/or participates directly in the exchange.

A composite of several TPE chromatograms for "blank" Cab-O-Sil is shown in Fig. 1. Maximum exchange on Cab-O-Sil occurred at 540 ± 10°C. Our data indicated the existence of 3×10^{14} exchange-

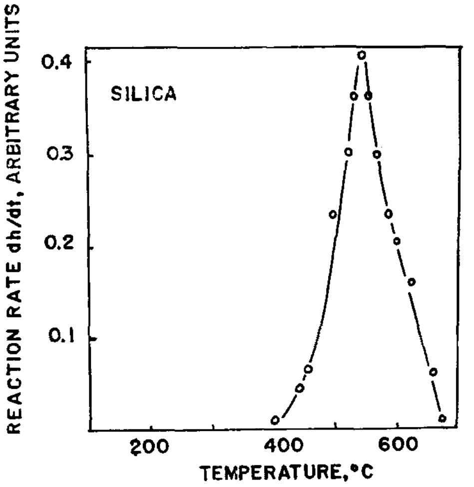

FIG. 1. TPE chromatogram for hydrogen-deuterium exchange conducted on a 2 g sample of silica (Cab-O-Sil).

able hydroxyl groups/cm^2 Cab-O-Sil surface area.

The Cab-O-Sil was "sintered" and partially regenerated by exposing to steam at 800°C for 2 hr. TPE results on sintered, regenerated Cab-O-Sil showed a slight shift in the maximum exchange temperature to 560 ± 10°C and a decrease in the number of exchangeable groups to $2.3 \times 10^{14}/\mathrm{cm}^2$. Our results on Cab-O-Sil compare favorably with those of Chien (*15*). It should also be mentioned that Cab-O-Sil exhibited stability at elevated temperatures in as much as the BET surface area, measured by nitrogen adsorption, decreased by less than 5% due to sintering. This shows that even at 800°C only partial rehydroxylation of the surface is possible. This may, in part, be due to the annealing of the siloxane bridges at these elevated temperatures. Similar observations on the irreversibility of the dehydroxylation of silica have been made by Gonzalez and Lee (*16*).

TABLE 1
CHARACTERISTICS OF NICKEL–CAB-O-SIL CATALYSTS

Wt % Ni	m^2 Ni/g cat	m^2 Ni/g Ni	Av crys size (Å)
2	6	293	19
10	17.2	190	30
23	30	130	44
50	20	40	140

Characteristics of the nickel–Cab-O-Sil catalysts used in our study are summarized in Table 1. The TPE results of our investigation of the hydrogen-deuterium exchange are summarized in Table 2.

In contrast to the single peak observed for pure Cab-O-Sil, a TPE chromatogram for a 1.9 g sample of 2% nickel–Cab-O-Sil catalyst shows a more complex structure

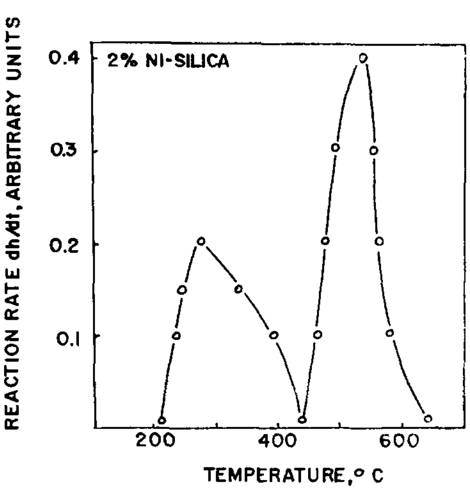

FIG. 2. TPE chromatogram for hydrogen-deuterium exchange conducted on a 1.9 g sample of 2% nickel-silica (Cab-O-Sil).

TABLE 2
SUMMARY OF TPE RESULTS OF HYDROGEN–DEUTERIUM EXCHANGE

Catalyst	Max exch temp	E_a (kcal/mole)	OH $\times 10^{-14}/\mathrm{cm}^2$
Cab-O-Sil, original	540	20 ± 3	3.
sintered	560	16 ± 3	2.3
2% Ni-Cab-O-Sil	280/525	9.5 ± 3/22 ± 3	5.2
10% Ni-Cab-O-Sil	(330)/(410)/515	—/—/24 ± 5	3.8

(Fig. 2). The high temperature peak is still dominant but has shifted to a slightly lower temperature, 525 ± 10°C, and another peak centered at about 280 ± 10°C has appeared. The appearance of this multiplet structure for supported nickel is evidence that deuterium is exchanging with, at least, two different kinds of hydroxyl groups having different activation energies. The activation energies obtained for the 280 and 540°C peaks are 7.5 ± 1 and 22 ± 3 kcal/mole, respectively. The number of exchangeable hydroxyl groups for the 2% nickel–Cab-O-Sil is 5.2×10^{14} OH groups/cm^2, a noticeable increase over that for Cab-O-Sil. Since we can safely assume that the 540°C peak corresponds to the deuterium exchanging with the bulk hydroxyls as in the pure Cab-O-Sil, it is interesting to speculate as to the origin of this second peak centered at 280°C. We feel that the 280°C peak might possibly be due to hydroxyl groups which are adjacent to nickel crystallites and might interact with nickel atoms in such a way that the activation energy for exchange would be lower (see Table 2). The increase in the density of exchangeable hydroxyl groups for the nickel–Cab-O-Sil compared to the pure Cab-O-Sil might be due to this added interaction with a consequent increase in the activity for exchange.

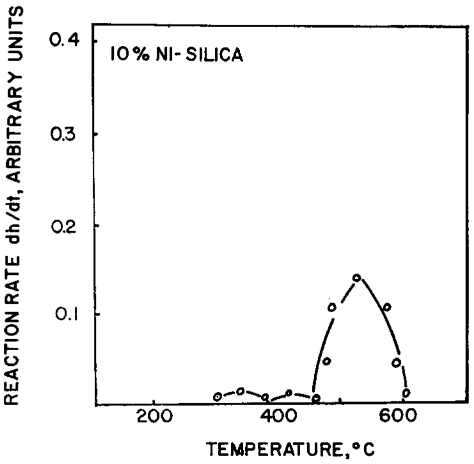

Fig. 3. TPE chromatogram for hydrogen-deuterium exchange on 0.75 g sample of 10% nickel–silica (Cab-O-Sil).

Chromatograms for 10, 23, and 50% nickel–Cab-O-Sil preparations were also obtained. The chromatogram for the 10% nickel–Cab-O-Sil is shown in Fig. 3. It is evident that the low temperature peak is not well defined and considerably less developed than the 2% nickel–Cab-O-Sil preparation. Presumably this is due to the lower number of hydroxyl groups interacting with the metal at higher nickel concentrations and greater particle sizes.

In conclusion, we feel that we have evidence for an interaction between the metal crystallites and the silica hydroxyl groups. In the literature several discussions (*17–19*) about hydrogen atom spillover involve the proposed existence of a transfer mechanism involving an intermediary, or bridge, such as water, by which the hydrogen can be transferred from the metal to the support. We feel that hydrogen is adsorbed too strongly to the metal surface to permit unlimited mobility across the support. However, the presence of a low energy transfer process between surface hydrogen atoms and support hydroxyl groups is quite possible.

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