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Reversible Chemisorption on Highly Dispersed Ru Catalysts

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Hydrogen and carbon monoxide adsorptions have been studied by static gas volumetric measurement on a range of highly dispersed Y-zeolite-supported ruthenium catalysts prepared by ion exchange. At ambient temperature, the adsorption isotherms indicated two distinct types of adsorption—reversible (composed of both physisorption and weak chemisorption) and irreversible (strongly chemisorbed). The catalysts were highly dispersed and had average particle diameters ranging from 0.9 to 1.6 nm. Reversible hydrogen chemisorption was found to be a function of average particle diameter and dispersion. On the other hand, reversible carbon monoxide chemisorption seemed to be mainly due to interaction with the support.

INTRODUCTION

The recent interest in the hydrogenation of CO has encouraged particular interest in Ru since it is catalytically very active for this reaction (*1–3*). In general, zeolites offer great possibilities as supports because of their ion-exchange capabilities, shape selectivity, and catalytic properties. Obviously, in order to benefit from all these properties, the metal must be retained in large part within the zeolite and thus remain highly dispersed. Nijs *et al.* (*4*) have found Ru to be the only Fischer–Tropsch active metal that can be easily kept in the zeolite supercages.

In most cases, maintaining supported metal catalysts in a highly dispersed form (60–100% dispersion, $d_{ave} < 2$ nm) necessitates good characterization since the distribution of sites on small crystallites varies greatly with size and shape. Goodwin and Naccache (*5*) have found that highly dispersed Y-zeolite-supported Ru catalysts contain several different types of identifiable active Ru sites—probably existing on atomically dispersed Ru atoms, Ru clusters, and Ru particles greater than 1 nm in diameter. In addition, at high dispersions, there is an enhanced possibility that support–metal interactions may be significant. For the most part, these interactions can make surface characterization more difficult.

Chemisorption measurements can be used to determine adsorptive properties, metal surface area, dispersion, and average particle size for supported metal catalysts. Other techniques, such as electron microscopy (E.M.), SAXS, STEM, etc., are tricky, expensive, and time consuming, and give only physical characterizations. The standard chemisorption technique, while giving both chemical and physical characteristics of a catalyst, does not distinguish between catalysts at 100% dispersion and having various types of surface sites.

In characterizing by chemisorption RuY catalysts known by E.M. to have dispersions of 100%, Goodwin (*6*) found significant quantities of reversible (weak) hydrogen chemisorption at room temperature. McVicker *et al.* (*7*) have found that, on 100% dispersed iridium catalysts, reversible chemisorbed hydrogen is a linear function of the weight percentage of Ir suggesting that reversible H_2 chemisorption results from interaction with the metal surface.

The objective of the present study was to investigate reversible chemisorption at room temperature, its validity for surface characterization, and the factors which

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might affect its quantities for RuY catalysts having a range of metal loadings and various dispersions.

EXPERIMENTAL

RuY catalysts containing 0.19 to 3 wt% Ru were prepared by ion exchange of hexamine ruthenium (III) chloride. The $Ru(NH_3)_6Cl_3$, obtained from Strem Chemical Company, was dissolved in an acidic hydrochloride solution (pH = 4.5). This solution was then mixed with NaY-zeolite and stirred continuously for 50 h at room temperature. Excess solution was used for this purpose to maintain approximately a constant pH during ion exchange.

After the exchange reaction, the catalysts were filtered and washed several times in deionized water and dried in air for 18 h at 40°C. Ru metal loading was determined by atomic absorption spectrometry.

Prior to chemisorption measurements in a conventional gas volumetric apparatus, approximately 1 g of the supported complex was decomposed slowly under vacuum (10^{-6} Torr) by heating (at approximately 1°C/min) to 420°C and holding at that temperature for 2 h. A Stanton Redcroft 3077 programmable linear rate temperature controller was used. The catalyst was reduced in pure H_2 (p = 20 kPa) at 420°C for 2 h and then heated at the same temperature to desorb the hydrogen.

Air Products UPC-grade hydrogen and helium were passed through a liquid nitrogen trap before being admitted to the gas reservoirs. Helium was used for dead-volume determination. Carbon monoxide of 99.99% purity was used as received for adsorption measurements.

The hydrogen adsorption measurements were made at 25°C and isotherms of total H_2 adsorption on the fresh catalyst were determined from 50 to 400 Torr. The time for the equilibration at each pressure was about 4 h. The catalysts were then evacuated for 10 min at the same temperature and a second adsorption was carried out in the same manner. However, there was no significant difference in the quantity of adsorbed species removed for evacuation times ranging between 2 and 20 min.

Carbon monoxide uptakes at 25°C on the same samples were made after desorption of H_2 at 420°C for 2 h under vacuum. The same procedure as in H_2 adsorption was used. However, 12 h was required for each measurement. Studies indicated that adsorption and desorption of H_2 did not cause sintering of the Ru provided no prior exposure of the catalyst to O_2 or CO had occurred.

RESULTS AND DISCUSSION

A typical set of hydrogen adsorption isotherms is shown in Fig. 1 for the RuY catalyst. Two separate isotherms, designated as a and b, indicate the total and reversible adsorptions, respectively. The linear region of isotherm a above 120 Torr indicates complete coverage of the ruthenium surface by hydrogen. Following evacuation for 10 min, isotherm b was obtained. The two isotherms were parallel, as expected. The observed increasing amount of adsorbed hydrogen with increasing pressure above the point of complete coverage of the ruthenium surface was due to physical adsorption on the catalyst.

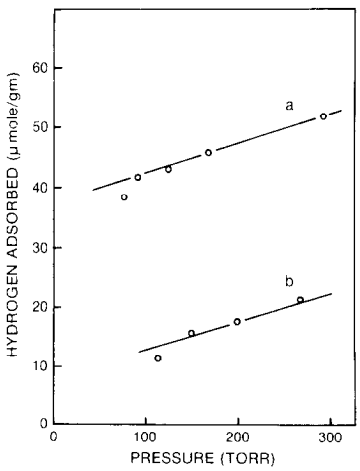

FIG. 1. Hydrogen adsorption isotherms on 0.76 wt% RuY at 25°C: (a) total adsorption; (b) reversible adsorption.

Extrapolation of the hydrogen adsorption isotherms to zero pressure gives the amount of total and reversible chemisorbed hydrogen, namely, $H_{2(T)}$ and $H_{2(r)}$. The net irreversible hydrogen uptake, $H_{2(ir)}$, at zero pressure was obtained by subtracting the reversible contribution from the initial uptake.

$$H_{2(ir)} = H_{2(T)} - H_{2(r)}.$$

It is evident that on ruthenium two distinct types of hydrogen chemisorption occur at room temperature: a rather strong, activated chemisorption (designated here as "irreversible") and a weak, nonactivated chemisorption (designated as "reversible") which is rapidly removed under vacuum.

Earlier work (*6*) on highly dispersed NaY-supported Ru utilizing both chemisorption and transmission electron microscopy (TEM) has shown that such catalysts can be accurately characterized using H_2 chemisorption by assuming a stoichiometry of $H_{(ir)}/Ru_{(s)} = 1$. Characteristics of the Ru catalysts studied here were thus determined from the irreversible hydrogen chemisorption and are shown in Table 1. The ruthenium surface area per gram of metal, S, was calculated from hydrogen adsorption assuming an average Ru area of 8.17 Å^2/Ru atom. Dispersion, D, is defined according to the following:

$$D = \frac{\text{number of surface metal atoms}}{\text{number of total metal atoms}} \times 100\%.$$

Average particle size, d, was calculated from the surface area data employing the relation $d = 5/(S \cdot \rho)$, assuming the particle to be cubic with five sides exposed to the gas phase and where ρ is the density of bulk ruthenium. It should be noted that the particle size thus obtained represents a good estimation of the average Ru size range since zeolites usually provide a rather uniform distribution for metal particles due to their crystalline cage structure, although some larger particles tend to exist on the external surfaces of the zeolite. Thus, Ru particles having diameters less than 16 Å, are sufficiently small to remain in the zeolite cages (*4, 8*). The catalysts in this range, therefore, are designated as highly dispersed.

TABLE 1

Catalyst Characteristics[a]

Weight percentage Ru	S.A.[b] (m^2 Ru/g cat.)	d_{ave}[c] (nm)	D[d] (%)
0.19	0.89	0.87	95.8
0.38	0.95	1.59	52.0
0.76	2.86	1.07	77.4
1.5	4.03	1.50	55.3
3.0	9.56	1.27	65.5

[a] Based on atomic absorption spectrometry and gas volumetry.
[b] 8.17 Å^2/Ru surface atom, $H_{(ir)}/Ru_{(s)} = 1$.
[c] $d_{ave} = 5/(S \cdot \rho)$, S = m^2/g Ru.
[d] $D = (\#\ Ru_{(s)}/\#\ Ru_{(T)}) \times 100\%$.

In order to determine the catalyst characteristics from H_2 chemisorption it was not possible to use the intersection of the extrapolated total adsorption isotherm at zero pressure. It has been reported earlier (*6*) that, on totally dispersed RuY catalysts (as determined by electron microscopy), employing the extrapolated total hydrogen adsorption isotherm produced a stoichiometry ratio, $H_{(T)}/Ru_{(s)}$, as high as 1.94. Since the stoichiometric ratio for irreversibly (strongly) chemisorbed hydrogen, $H_{(ir)}/Ru_{(s)}$, was found to be approximately unity, it was suggested that an assumption of $H_{(ir)}/Ru_{(s)} = 1$ would be a better approximation for the purpose of characterization. It is felt that this quantity is more constant with varying particle size than $H_{(T)}/Ru_{(s)}$. For a more complete discussion of the earlier work on the determination of values for $H_{(T)}/Ru_{(s)}$ using Ru powder and of the relationship of this ratio to the characteristics of highly dispersed NaY-supported Ru please refer to Goodwin (*6*).

Similar adsorption isotherms were obtained for carbon monoxide on RuY, such as those shown in Fig. 2. $CO_{(T)}$, $CO_{(r)}$ and

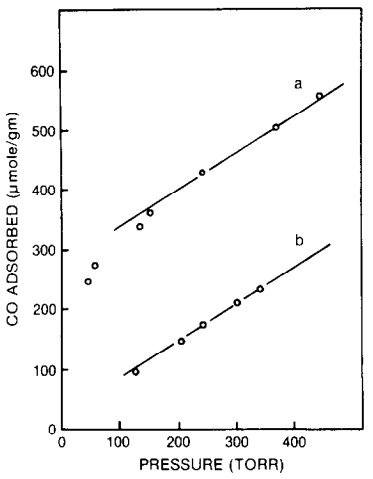

FIG. 2. CO adsorption isotherms on 0.76 wt% RuY at 25°C: (a) total adsorption; (b) reversible adsorption.

$CO_{(ir)}$, given in Table 2, were determined in a manner identical to that for values for H_2. The values found for $CO_{(ir)}/H_{(ir)}$ imply that CO molecules were multiply chemisorbed on the surface Ru atoms for all the samples investigated. These results for CO adsorption are in agreement with previous findings of multiple adsorption of CO on highly dispersed Ru (*1, 9, 10*).

Reversibly adsorbed hydrogen which desorbs upon evacuating at ambient was found to be significant. This reversibly adsorbed hydrogen includes the hydrogen molecules in the physisorbed state and the hydrogen species in the weakly chemisorbed state, either a transition state at total surface coverage or an adsorption state on low-energy sites. Taylor (*11*) has noted reversible chemisorption of H_2 on 1% Ru/Al_2O_3 following evacuation of the catalyst for 1 h. As much as 75% of the hydrogen initially adsorbed was found to be reversible at ambient. Kubicka and Kuźnika (*12*) have also observed 25% reversibly adsorbed hydrogen on Ru/Al_2O_3 at 25°C. While at 400°C, 80% of the total chemisorption became reversible.

Obviously, all chemisorption is reversible if one evacuates long enough or at high enough temperatures. Desorption occurs when the adsorbate–adsorbent bond acquires the activation energy for desorption in the form of vibrational energy. Temperature-programmed desorption (TPD) spectra of hydrogen and CO adsorption from 20 to 500°C indicate considerable nonhomogeneity of chemisorbed molecules or atoms on highly dispersed Ru surfaces (*13*). For certain metals, i.e., Co, chemisorption may be so weak that all can be removed fairly fast by evacuation at room temperature. For hydrogen adsorption on RuY surfaces, however, two distinct types of chemisorption coexist at room temperature: reversible and irreversible. Each type is associated with a specific average activation energy and kinetics. It is believed that, at total surface coverage and equilibrium, some factors which might influence the reversibility of hydrogen adsorption are metal

TABLE 2

Comparison of Hydrogen and Carbon Monoxide Chemisorption on RuY Catalysts

Sample (wt% Ru)	H_2 uptake (10^{-6} mole/g)			CO uptake (10^{-6} mole/g)			Ratio	
	$H_{2(T)}$	$H_{2(r)}$	$H_{2(ir)}$	$CO_{(T)}$	$CO_{(r)}$	$CO_{(ir)}$	R_H[a]	$CO_{(ir)}/H_{(ir)}$
0.19	10.4	1.4	9.0	108.0	20	88.0	0.13	4.89
0.38	13.8	4.1	9.7	112.5	25	87.5	0.30	4.51
0.76	37.2	8.1	29.1	276.1	22	254.1	0.22	4.38
1.5	60.0	19.0	41.0	—	—	—	0.32	—
3.0	133.0	35.8	97.2	927.0	30	897.0	0.27	4.61

[a] Fraction of reversibly chemisorbed H_2, $R_H = H_{(r)}/H_{(T)} = H_{2(r)}/H_{2(T)}$.

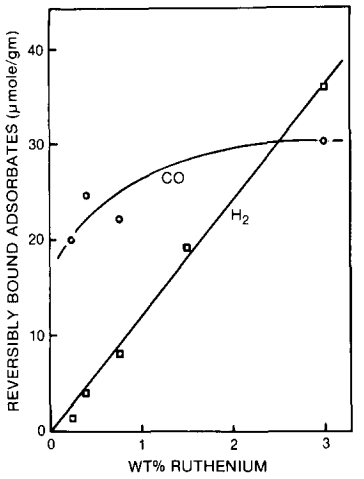

FIG. 3. The effect of Ru metal loading on the reversible quantities of H_2 and CO chemisorption from RuY catalysts at 25°C.

dispersion, particle size, and support–metal interactions.

In this study, for the highly dispersed RuY catalysts, the quantity of reversibly bound hydrogen varied from 1.4 to 35.8 μmole/g of catalyst while that of CO was relatively constant for all the RuY catalysts studied (as shown in Fig. 3). This behavior is similar to the reversible chemisorption results for Ir found by McVicker *et al.* (*7*). As can be seen in Fig. 3, reversibly bound CO does not vary greatly as the Ru weight percentage (and consequently surface area) increases suggesting that this quantity is mainly due to the interaction with the total catalyst surface, including the zeolite support's surface. On the other hand, reversibly bound hydrogen would seem to be a linear function of the Ru weight percentage. Certainly, the Ru surface area increased with increasing Ru metal loading (see Table 1). However, in order to prevent all properties from varying directly with metal loading, slight differences in the rate of temperature-programmed decomposition (0.5–1.5°C/min) were used. This produced a variety of Ru dispersions not directly related to metal loading.

The fraction of reversibly chemisorbed H_2, R_H, was observed to increase from 13 to 32% of the initial value as the average Ru particle size increased from 0.87 to 1.59 nm (Fig. 4). A similar variance was also observed as expected when metal dispersion was plotted instead of average particle size (Fig. 5). This indicates that a greater portion of hydrogen is strongly chemisorbed on smaller Ru particles than on larger ones. From the concept that the extent of reversibility is associated with lower-energy sites and/or sites for multiple hydrogen chemisorption, such sites on the larger Ru particles would be predominantly responsible for the reversible chemisorption (*13*). It is evident that the small Ru particles must possess a greater fraction of sites which do not chemisorb hydrogen weakly at room temperature. It is as yet difficult to say whether this is a structural effect solely or an effect due to support–metal interactions having a greater influence on the properties of the smaller clusters. On the basis of previously compared E.M. and chemisorption results (*6*) where $H/Ru_{(s)} = 1$ was found (based on $H_{(ir)}$), it would seem highly likely that at least some of the reversibly chemisorbed hydrogen at room temperature is due to multiple hydrogen chemisorption on certain Ru sites.

Another possibility to be considered for the appearance of reversible chemisorption is hydrogen spillover. An unoccupied site on the Y-zeolite in the vicinity of a Ru particle may function as a hydrogen-acceptor

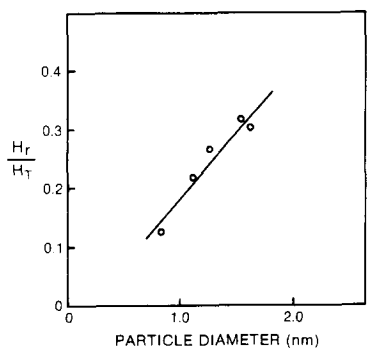

FIG. 4. The effect of particle size on reversibility of hydrogen chemisorption on RuY catalysts.

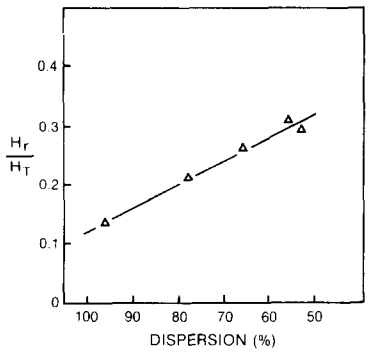

FIG. 5. The effect of dispersion on reversibility of hydrogen chemisorption on RuY catalysts.

site (*14, 15*). Thus the amount of hydrogen spillover onto the support would be directly proportional to the quantity of neighboring sites and to the surface area and particle size of the metal. However, it has been suggested that hydrogen spillover should only be significant beyond ambient temperature (*14*). In the present case, hydrogen spillover would seem to be of minor importance.

CONCLUSIONS

A detailed picture of reversible adsorptive properties of ion-exchanged RuY catalysts has been obtained. For highly dispersed RuY catalysts prepared by ion exchange, the fraction of reversibly (weakly) chemisorbed hydrogen is directly related to average particle size and dispersion. This fraction increases approximately linearly with average Ru particle diameter for diameters between 0.9 and 1.6 nm; however, it probably eventually attains a constant value for large particles. This reversible hydrogen chemisorption may be related to multiple chemisorption on certain Ru sites. These results for reversible H_2 chemisorption are surprising since one might expect that highly uncoordinated sites on smaller particles would be more likely to exhibit multiple chemisorption.

Reversible (weak) CO chemisorption, unlike that of H_2, is a function only of total catalyst surface area. In other words, it seems due to an interaction with both the metal and the support.

The reversibility of hydrogen chemisorption may depend upon other factors besides particle diameter. Preliminary results of chemisorption on zeolite-supported Co catalysts indicate that the fraction of reversibly chemisorbed hydrogen is sensitive to the preparation method. Several other factors which might affect reversible hydrogen chemisorption are the temperature of adsorption, the presence of impurities, and support–metal interactions.

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