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Surface Structure Dependence of Reversible/Weak H_2 Chemisorption on Supported Ru

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Earlier work on highly dispersed NaY-supported Ru ($\bar{d}_p$ = 0.9–1.6 nm) showed that the reversible (weak) fraction of hydrogen chemisorption at 298 K is a function of average particle diameter, and it was suggested that this hydrogen is accommodated on lower-energy sites. In order to gain a more complete understanding of this weak chemisorption, an in-depth investigation of the effect of particle size on reversible H_2 chemisorption at 298 K was carried out using supported ruthenium catalysts with average metal particle diameters of 0.9–12.5 nm. Particular attention was paid to determining the reversibly chemisorbed hydrogen fraction under strictly the same conditions. It was found that this fraction exhibited a maximum of 30% of the total chemisorption for an average Ru particle size of 1.6 nm. This fraction decreased to zero as the average Ru particle size increased above 2.5 nm. These findings enable us to suggest that loosely chemisorbed hydrogen at equilibrium on Ru may be accommodated on multiatomic sites ("ensembles") of a similar type as the so-called B_5 sites described by R. van Hardeveld and F. Hartog (*Surf. Sci.* **15**, 189, 1969). Causes for deviations from this functionality are discussed. © 1985 Academic Press, Inc.

INTRODUCTION

Selective chemisorption has been used to estimate metal surface area, average particle size, and dispersion of supported metal catalysts (*1–4*). The calculation of average particle size from chemisorption measurements utilizes the amount of adsorbate needed for a monolayer coverage which can be converted into metal surface area. Two assumptions must be made. One is the ratio of adsorbate molecules or atoms to surface metal atoms at monolayer coverage. The other assumption concerns the area occupied by one surface metal atom (M_s) which can be established by chemisorption on a sample of unsupported metal whose surface area has already been determined by means of the BET method (*3*). The number of adsorbed molecules or atoms per surface metal atom at monolayer coverage may be a function of the particle size, as is the case for CO adsorption on supported ruthenium catalysts (*2, 6*). However, it has been found that the stoichiometry of H_2 chemisorption on Ru is not particle size dependent (*4, 7*), provided equilibrium is established and only the quantity of strong (irreversible) chemisorption used.

A recent study (*8*) has shown that the fraction of weak (reversible) H_2 chemisorption at 25°C appears to be a function of particle size in the range 1.0–1.6 nm and is not due to adsorption on the support. This study was undertaken to determine the relationship of fraction of reversible hydrogen chemisorption to Ru particle size over the wide range 0.9 to 12.5 nm. Different preparation methods, pretreatments, and supports were utilized in order to eliminate their effect on this reversible fraction and to permit a more comprehensive analysis of the effect of Ru particle size. No Ru catalysts were used which exhibited significant H_2 chemisorption suppression at 25°C (Ru/TiO_2 and ion-exchanged RuKL and RuNa mordenite (*9*)).

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While all chemisorption is reversible, use of the terms irreversible (strong) and reversible (weak) chemisorption will be made to denote that chemisorption which is not removed easily at 298 K as opposed to that which is easily removed (in 2 min of evacuation). This terminology conforms to that in general usage in the literature for these quantities.

EXPERIMENTAL

The supports were NaY, NaX, KL, SiO_2 (Strem), and Na mordenite (Norton). Ruthenium catalysts were prepared and pretreated according to the following methods:

(*a*) *Ion exchange* (*I.E.*). $Ru(NH_3)_6Cl_3$, obtained from Strem, was dissolved in a weakly hydrochloric solution (pH 4.5) and ion-exchanged with the support for 48 h at room temperature. The catalyst precursors were then filtered, washed several times with deionized water in order to free it of Cl ions, and dried overnight at 313 K. These precursors were decomposed under dynamic vacuum (10^{-6} Torr) by heating (0.5 K/min) to 693 K and reduced at this temperature in static hydrogen for 2 h. The reduction step was carried out even though this decomposition procedure has been shown to result in a completely reduced Ru in zeolites (*10*). The reduced sample was then evacuated at 693 K for 2 h and cooled under dynamic vacuum to room temperature. More details about this method of preparation are given in references (*4, 7–9, 11, 12*). In addition, it is worth noting that similar preparations have been shown to generate catalysts free of chlorine (*13*). These catalysts are designated as RuS, where S is the support used.

(*b*) *Vapor impregnation* (*V.I.*). $Ru_3(CO)_{12}$, also obtained from Strem, was introduced onto the support via vacuum impregnation. The resulting light-yellow catalyst precursors were decomposed under dynamic vacuum (10^{-6} Torr) at 693 K without being exposed to air, yielding a completely reduced Ru. The 1.3% $Ru_3NaY(F)$ catalyst was decomposed in flowing hydrogen as the temperature was raised at 0.5 K/min to 693 K where reduction was continued for 2 h before the catalyst was evacuated at that temperature. These catalysts are designated as Ru_3S. More details about this method of preparation are given in references (*4, 7, 14–17*).

(*c*) *Incipient wetness* (*I.W.*). $RuCl_3 \cdot 1.5H_2O$, from Strem, was dissolved in distilled water at a concentration sufficient to yield the desired metal loading when each gram of support was impregnated with 0.77 cm^3 of solution. The catalyst precursors were then dried overnight in air at 313 K. Reduction was carried out in flowing H_2 following the same procedure as used for the 1.3% $Ru_3NaY(F)$ sample. These catalysts are designated as Ru/S.

A conventional gas volumetry system was used for the chemisorption measurements. The procedures employed to determine the amount of total and reversible H_2 chemisorption have been described elsewhere (*8*). The catalysts were evacuated for 2 min at room temperature following determination of the total H_2 chemisorption isotherm, and then the reversible H_2 isotherm was measured. Gases used were UPC-grade hydrogen and helium (Air Products) which were passed through a liquid–nitrogen trap before being admitted to the gas reservoirs. Helium was used for dead-space determination.

The average particle size of catalysts was determined by the amount of irreversible H_2 chemisorption which was obtained by subtracting the reversible quantity from the total uptake. The stoichiometry of chemisorption used was $H(irr)/Ru_s = 1$, and the particles were assumed to be cubic with five sides exposed to the gas phase (*4, 8*). The use of H(irr) has been found to be necessary for highly dispersed Ru (ca. 100%) since H(tot)/Ru(tot) can greatly exceed 1 (*4*).

RESULTS AND DISCUSSION

The H_2 chemisorption characteristics of the supported Ru catalysts are presented in

TABLE 1

Characteristics Based on Chemisorption

Catalyst[a]	$\bar{d}$[b] (nm)	D[b] (%)	H_r/H_T
0.19% RuNaY[c]	0.87	96	0.13
0.68% Ru_3NaY	0.89	94	0.07
1.3% Ru_3NaY	0.93	90	0.072
0.43% Ru_3SiO_2	0.93	90	0.082
2.5% RuNaX	1.0	83	0.12
1.1% Ru_3NaY	1.1	76	0.16
0.24% Ru_3NaY	1.1	76	0.16
0.76% RuNaY[c]	1.1	76	0.22
2.17% RuNaY	1.2	68	0.22
3.0% RuNaY[c]	1.3	67	0.27
3.0% RuNaY	1.3	67	0.22
1.5% RuNaY[c]	1.5	55	0.30
1.1% RuNaY	1.5	55	0.18
0.38% RuNaY[c]	1.6	51	0.30
3.1% RuNaY	1.6	51	0.22
0.74% Ru_3NaM	1.7	48	0.17
1.4% Ru_3KL	1.8	46	0.14
0.2% Ru_3NaX	1.8	45	0.14
0.27% Ru_3NaX	2.2	37	0
0.49% RuNaY	2.3	35	0.08
1.3% Ru_3NaY(F)	2.4	35	0
0.77% Ru/NaY	2.8	29	0
2.0% Ru/NaY	5.4	16	0
2.24% Ru/NaY	6.0	14	0
3.0% Ru/NaY	6.0	14	0
3.0% Ru/NaY	9.0	9	0
3.92% Ru/NaY	12.4	7	0

[a] RuS, Ru_3S, and Ru/S indicate catalysts prepared by ion exchange, vapor impregnation of $Ru_3(CO)_{12}$, and incipient wetness, respectively; S being the support.

[b] $\bar{d}$ (av particle diameter) and D (% dispersion) were determined from the amount of the irreversible H_2 chemisorption.

[c] From Ref. (*8*), evacuated 10 min between isotherms.

Table 1. It has been shown that different methods of preparation produce NaY-supported Ru catalysts differing in average particle size (*7, 8*). The average particle size for RuNaY catalysts prepared by ion exchange or vapor impregnation of $Ru_3(CO)_{12}$ is not dependent upon Ru concentration in the range 0.2–3 wt% while that for those catalysts prepared by incipient-wetness is (*7*). The average Ru particle size for ion-exchanged RuNaY is a strong function of the rate of temperature increase during decomposition of the precursor (*8*). In Table 1, it can be seen that the average particle sizes for Ru_3NaY (V.I.) catalysts have values between 0.9 and 1.1 nm. Based on the size of the supercages in NaY zeolite, the high Ru dispersion, and a previous examination by TEM (*4*), it has been suggested that most of the Ru crystallites are inside the NaY zeolite (*7, 10, 18, 19*).

Ru_3NaX, Ru_3KL, and Ru_3Na mordenite prepared by V.I. had average particle sizes greater than the diameters of the pores of these zeolites. Since the pore diameters are on the order of the estimated critical diameter of $Ru_3(CO)_{12}$ (*20*), it has been suggested (*14*) that a significant part of the ruthenium carbonyl clusters are not able to diffuse into these zeolites. The metal clusters on the external zeolite surfaces are able to sinter more easily upon decomposition and reduction. On the contrary, Ru_3SiO_2 has a small average particle size and good dispersion. This is partly due to the larger pore diameters and high surface area, and partly due to some retention of the cluster structure (*15, 16*).

While the majority of the metal crystallites were probably encaged within the zeolite cavities in most of the RuNaY (I.E.) catalysts, the 0.49% RuNaY sample exhibited an unexpectedly high average particle diameter of 2.3 nm. This catalyst may have been inadvertently reduced at too high a heating rate. The heating rate for the initial decomposition of these catalysts is probably the most important parameter affecting final Ru dispersion (*8*).

The effect of ruthenium particle size on the fraction of reversibly chemisorbed hydrogen at room temperature is shown in Fig. 1. The fraction of reversibly chemisorbed H_2 was observed to increase from 7 to 30% of the total chemisorption as the average Ru particle size increased from 0.9 to 1.5 nm and then to decrease to zero as the average Ru particle size increased from 1.5 to 2.2 nm.

Since H_r/H_T is very small for particles

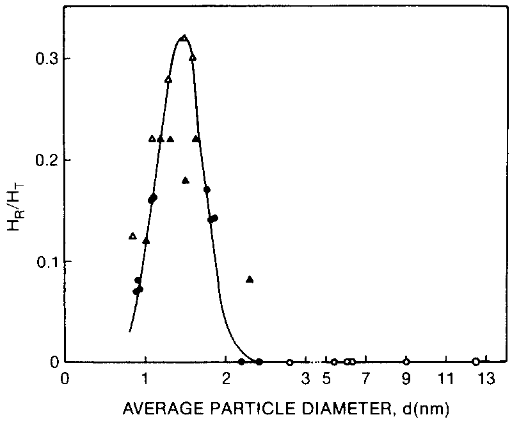

FIG. 1. The effect of particle size on reversible hydrogen chemisorption on zeolite-supported ruthenium catalysts. ●, V.I.; ▲, I.E.; ○, I.W.; △, from Ref. (*8*).

having diameters less than 1.0 nm or more than 2.0 nm, it can be concluded that the weakly chemisorbed hydrogen at room temperature is *mainly associated with the metal*. This result is in agreement with those reported by McVicker *et al.* (*21*) and Yang and Goodwin (*8*) who studied Ir/Al_2O_3 (totally dispersed) and RuNaY (70–95% dispersions), respectively.

Furthermore, given that the weakly chemisorbed hydrogen occurs exclusively on the surface of metallic Ru within a well-defined range of particle sizes, one would reasonably seek a possible explanation of the relationship $H_r/H_T = f(d)$ in the modification of surface topography of small metal particles as a function of their diameter. In this respect, several authors have dealt with the statistics of various types of surface atom sites as a function of metal particle diameter and shape using perfect crystal models. In the case of platinum, Poltorak and co-workers (*22, 23*) considered a series of octahedra with increasing edge length. They developed statistics versus particle size for three types of surface atoms (at corners, on edges, and on faces), having, respectively, coordination numbers (x) of 4, 7, and 9. Figure 2 is drawn based on the results of these calculations. As was pointed out (*22, 23*), the major modifications in the relative number of the various types of surface atoms occur for particle sizes less than 4 nm. For larger crystallites all surface atoms can be considered as belonging to a flat surface ($x = 9$). The validity of these conclusions has been extended to many other regular geometric forms (*24–26*). From a geometric standpoint, it is obvious that regular polyhedra can exist only for set numbers of atoms. There is no indication at all that, during the preparation process the metallic atoms assemble together precisely in such numbers. However, model calculations performed on "incomplete" octahedra (*22*) and other crystal shapes (*25*) show that variations similar to those reported in Fig. 2 occur if one considers arbitrarily three types of surface coordination; namely, high, intermediate, and low. Therefore, such variations are expected to be operative even when the shape of the metal particles is not very uniform.

It has been suggested (*8*) that reversible H_2 chemisorption on ruthenium at room temperature occurs on lower-energy sites. To the best of our knowledge, no more accurate information concerning the nature of those sites is presently available. As has already been mentioned, the relative

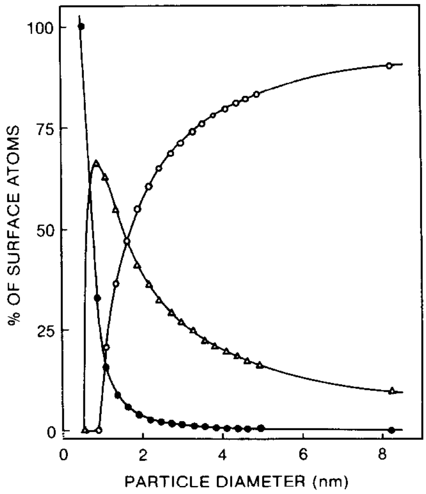

FIG. 2. Variation in the concentrations of different types of surface atoms with particle size for fcc octahedron. ●, coordination number $x = 4$; △, $x = 7$; ○, $x = 9$.

amount of the weakly held hydrogen passes through a maximum for Ru particles having a mean diameter of about 1.5 nm. The maximum density of intermediately coordinated surface atoms also occurs in the same region of particle size. Thus, it may be suggested that weakly chemisorbed hydrogen is bound to this kind of surface atom.

However, it is known that, on highly dispersed Ru, the strongly held hydrogen forms a complete monolayer, assuming $H(irr)/Ru_s = 1$ (*4*). The reversibly chemisorbed hydrogen is then in excess with regard to this strongly chemisorbed monolayer. There is strong evidence that weakly chemisorbed hydrogen on Ni, Pt, and Pd is in excess of a surface stoichiometry of $H/M_s = 1$ (*27*). In TPD experiments this weakly chemisorbed species leaves the metallic surface around room temperature (*27*). Therefore, it is believed to be of the same kind as the reversibly chemisorbed hydrogen we are dealing with. Based on this, it is possible that this hydrogen (H_r) is "shared" between a certain number of adjacent atoms (an ensemble). For example, Shimizu *et al.* (*28*), based on a study of H_2 chemisorption on clean and Cu-covered Ru(0001) single crystal surfaces, suggested that ensembles of up to 5–10 adjacent Ru atoms are involved in hydrogen chemisorption.

Van Hardeveld and co-workers (*24–26*) have constructed a large series of models of crystallites with different diameters and counted the different types of surface sites on crystals with fcc, bcc, and hcp structures, with and without the complete outer layers of atoms. They considered the number, n, and coordination of atoms constituting the ensemble sites, B_n, as well as the geometry of these ensembles. For calculations based on cubooctahedra of nickel crystallites with an incomplete outer layer, they reported that the concentrations of B_3 and B_4 sites show monotonic decreases upon increasing the particle diameter. However, the surface density of B_5 sites, which occur at the steps of the outer layer, increases steeply with increasing particle size for particle sizes less than 1.5 nm and reaches a maximum for particle sizes ca. 1.8 nm. For larger particles, the concentration of B_5 sites decreases monotonically with increasing particle diameter. The maximum in the B_5 site concentration occurs for a particle size near that where the maximum in the reversible hydrogen chemisorption fraction is also observed. Nickel has an fcc structure while Ru has an hcp one. Because both crystal systems are structured from layers with hexagonal packing, the bonding geometry with regard to neighbor and next nearest neighbor is the same. Therefore, if one assumes the reversible chemisorption of hydrogen to be multicentered, the B_5 sites would seem to be the most likely sites where such chemisorbed species could be accommodated. It is noteworthy that sites of the same kind exist on the stepped surfaces of single crystals and they have high activities for chemisorption as well as for catalysis (*29, 30*).

The study of crystallite models showed that hardly any B_5 surface sites can occur on very small particles (diam. ca. 1 nm) (*25*). However, reversible hydrogen chemisorption was observed on catalysts with Ru particles as small as 0.9 nm. This can be explained since average particle diameter is used, although there is obviously a metal particle size distribution and hence a presence of some larger particles. In addition, ideal particle geometries are not to be expected since particle geometry is determined to some extent by metal–support interactions.

Two types of arguments are often used to criticize the validity of using ideal crystal models to explain surface phenomena on small metal crystallites (*31, 32*). The first one is related to the geometry of small metallic particles. Even though it is difficult in practice to have direct information concerning the symmetry of clusters, theoretical calculations have shown that icosahedral (fivefold symmetry) packing is the most stable shape for isolated and bare small particles (*33–35*). However, experimental evidence of such nonperiodic structures has only been achieved in very special cases and only for a few fcc metals, e.g., gold and silver (*31, 32, 36*). Conversely, in the case of supported metallic clusters and from a crystallographic standpoint, Pt particles as small as 1 nm have been shown to be identical to the bulk metal (*37*). Reinen and Selwood (*38*) have reported that for 2.6-nm Ni crystallites, the saturation magnetization, which depends greatly on the crystal structure, is the same as that for bulk nickel.

The second criticism is centered on the fact that modifications in the electronic and energetic properties of small particles as their diameters decrease are not taken into account. Based on growing evidence stemming from theoretical considerations as well as experimental results (*39, 40*), we expect such behavior for Ru crystallites. However, their properties in general, increase or decrease more or less regularly when the particle size decreases. Therefore, since the amount of reversible chemisorption of hydrogen passes through a maximum at about 1.5 nm, our findings cannot be completely explained by a modification in the surface energetics of the Ru crystallites.

Reversible H_2 chemisorption can represent an important fraction of the hydrogen held by the catalyst. It is easily desorbed, but whether it is adsorbed associatively or dissociatively is not known. Moreover, it is always hard to make a clear distinction between reversible and irreversible H_2 chemisorption. The distinction is made on the grounds of some criterion like the specificity of the adsorption, temperature range of adsorption, time for desorption, etc. Furthermore, in spite of the tremendous volume of published work dealing with H_2 adsorption on metals, few figures have been reported concerning the reversibly or weakly chemisorbed fraction of H_2. This makes any comparison of our findings with other published data very difficult. However, some values of H_r/H_T have been reported for Ru catalysts, mostly without any further comment (*41–44*). Most of the H_r/H_T ratios do not fit the same trend as that displayed by our Ru samples. However, the explanation for these apparent discrepancies lies with the fact that H_r/H_T depends upon a great number of parameters. Some of these are: temperature of chemisorption, time allowed to reach "equilibrium," time of evacuation, reduction temperature, promoters, impurities, alloying effects, presence of physisorption, hydrogen spillover, support–metal interactions, etc. In order to carry out a quantitative study, all these factors should be strictly monitored. Variation of one or more of these parameters may greatly affect the expected value of H_r/H_T leading to such discrepancies. For example, in Ref. (*41*), H_T corresponds to the total amount of adsorption of hydrogen at an equilibrium pressure of 100 mm Hg and therefore contains an unknown fraction of physisorbed molecules. Thus, it is easy to demonstrate that this leads to an overestimated value of H_r/H_T. In addition to that, the time of evacuation was 10 min instead of the 2 min used in this work, and no information was reported about the time allowed for adsorption. Based in another work done in our laboratories, the presence of even small quantities of alkali species or of SMSI increases the reversibly (weakly) chemisorbed fraction. Commercially prepared catalysts are often contaminated with such small quantities of alkali species.

CONCLUSIONS

The main conclusion of the present study is that the presence of special surface sites appear to be responsible at equilibrium for most of the reversible or weak H_2 chemisorption at room temperature on highly dispersed ruthenium catalysts. Reversible H_2 chemisorption at room temperature was found to occur in appreciable amounts only on crystallites having average sizes within the limited range 0.9 to 2.2 nm.

More generally, the results of this study point to the possibility of using reversible H_2 chemisorption to determine specific site concentrations. The influence which particular types of sites on supported metal catalysts have on the catalytic activity is of great interest, and further research of this influence would be greatly aided by a better means of characterization of surface sites.

Finally, these results suggest that use of total chemisorption at 298 K is in order when characterizing Ru catalysts having metal dispersions less than ca. 30%. For such catalysts, the existence of weak chemisorption may be more related to experimental conditions or catalyst formulation than to the presence of special sites permitting hydrogen to be weakly held in excess of $H/M_s = 1$.

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