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A TPD STUDY OF H_2 ON Ru/SiO_2 AND $Ru\text{-}Cu/SiO_2$

Tuo JIN, Sam K. JO and J.M. WHITE

Center for Materials Chemistry, Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

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Temperature Programmed Desorption (TPD), Auger Electron Spectroscopy (AES), supported metal catalysts Ru/SiO_2 and $Ru\text{–}Cu/SiO_2$

In H_2 TPD from Ru/SiO_2, two desorption peaks were observed. Both exchanged H for D in sequential dosing experiments. These hydrogen adsorption states were also found for $Ru\text{–}Cu/SiO_2$, along with another, higher temperature state at 400–500 K. This last state was neither exchangeable with nor replaceable by deuterium subsequently dosed at 150 K. The three chemisorption states are attributed to hydrogen held at the interface between Ru and SiO_2 ($<$ 300 K), adsorbed on Ru particles (310–380 K), and held at the Ru-Cu interface ($>$ 400 K).

1. Introduction

As potential catalysts for selective formation of long straight chain hydrocarbons from hydrogenation of CO [1], ruthenium and ruthenium-based samples have been widely studied. Single crystal samples provide good models for understanding the industrially important supported catalyst systems. For example, Hrbek reported new low temperature chemisorption state of hydrogen on Ru(001) in the presence of preadsorbed oxygen [2]. Tamaru et al. found that CO disproportionation proceeded rapidly on high index ruthenium surfaces (1, 1, 10) [3]. Goodman et al. found hydrogen spillover from Ru to Cu at 230 K for Cu deposited on a Ru(0001) surface [4].

Strengthening the connections between single crystal models and supported catalysts is an important enterprise and, very recently, SiO_2-supported Ru and Ru-Cu bimetallic catalysts were studied in our laboratory using UHV tools, e.g., Temperature-Programmed Desorption (TPD) and Auger Electron Spectroscopy (AES), and compared to Ru(001) [5]. Compared to single crystals, supported metals have a higher relative surface concentration of step or kink sites [6–8]. There is also evidence for spillover of adsorbed molecules to the support [6,9,10]. Even though electronic effects, such as SMSI [11], are not expected for SiO_2, we observed hydrogen desorption at lower temperature (160–220 K) from Ru/SiO_2

than from single crystal Ru (200–270 K for Ru(110), 300–340 K for Ru(0001)) [18], and at both higher temperature (> 500 K) and lower temperature for Ru–Cu/SiO_2.

Here we discuss this low temperature desorption in terms of a model in which the hydrogen is stored at the metal-oxide interface. In our previous work [5], spillover of hydrogen from Ru to the Ru–Cu interface was proposed for Ru–Cu/SiO_2, based on a variety of adsorption/desorption sequences at various temperatures. In the present work, this model is confirmed and extended by sequential H_2–D_2 exposure experiments which show that there is a barrier to exchange of H and D for that hydrogen desorbing above 400 K.

2. Experimental

The catalyst samples were supplied by Hong et al. [12]. Ru/SiO_2 was prepared by impregnation of SiO_2 (Cab-O-Sil, M-5) in a solution of $RuCl_3$. The bimetallic Ru–Cu/SiO_2 sample was prepared by co-impregnation of the same support in a mixed solution of $RuCl_3$ and $Cu(NO_3)_2$. For both samples, the loading of Ru was 1 wt% and that of Cu was 0.63 wt%. As a reference, 0.63 wt% Cu/SiO_2 was prepared in our laboratory from $Cu(NO_3)_2$ using the same method. The samples were dried at 393 K and treated in a H_2 flow at 723 K for 2 h. The dispersion of Ru was 0.16. For each mg of catalyst, the Ru surface area was about 10 cm^2 and the support surface area was 0.24 m^2.

The apparatus used for TPD has been described previously [13,14]. It is designed for surface science measurements (TPD and Auger electron spectroscopy) on high surface area materials. The base pressure was 5×10^{-9} Torr. The powder sample (8–10 mg) was pressed into a Ta mesh spotwelded to a Ta wire, enabling the sample to be heated resistively to 800 K and cooled to 150 K with liquid nitrogen [15,16]. H_2, D_2 and O_2 (CP grade, Linde) were passed through a liquid nitrogen trap during dosing.

After being placed in the vacuum chamber, the sample was further treated in 10^{-3} Torr H_2 at 723 K for 30 min and evacuated at 800 K for 15 min. Prior to TPD, the sample was flash-heated to 800 K to remove species accumulated on the surface. The heating rate during TPD was 2 K/sec. When dosing at elevated temperatures, the sample was typically evacuated and then cooled to the base temperature (140 K before beginning TPD.

3. Results

Hydrogen adsorption on various components was examined; no desorption was detected when hydrogen (10^{-4} Torr, 150 K, 1 min) was dosed onto: (1) Ta mesh, (2) SiO_2 powder on Ta mesh, or (3) Cu/SiO_2 on Ta mesh. Hydrogen

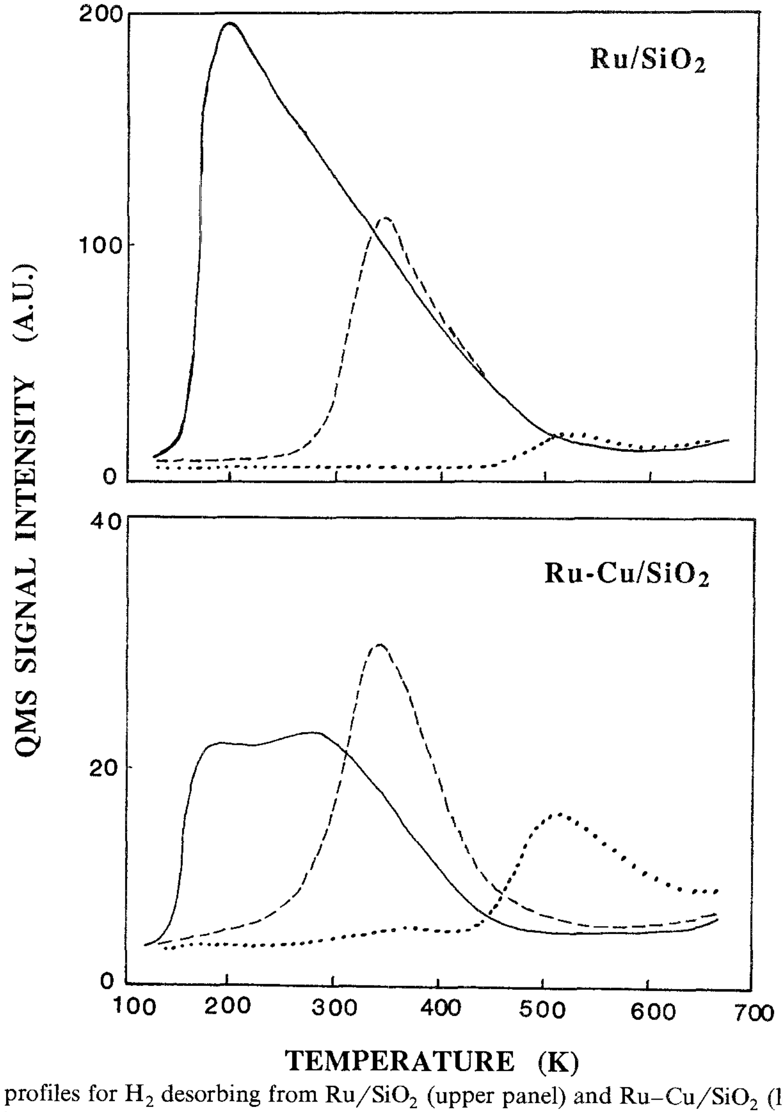


Fig. 1. TPD profiles for H_2 desorbing from Ru/SiO_2 (upper panel) and Ru–Cu/SiO_2 (lower panel) for various dosing temperatures: ——— 150 K, — — — 300 K, and · · · 450 K. The units of each curve in both panels are identical, permitting comparisons of intensities for the two samples.

desorption was observed only when ruthenium-containing samples, Ru/SiO_2 and Ru-Cu/SiO_2, were used.

Figure 1 gives the TPD profiles obtained after hydrogen was dosed on Ru/SiO_2 and Ru-Cu/SiO_2 at 150, 300 and 450 K. The results are similar to those we observed in our previous study [5]. Adding Cu clearly reduces, by about a factor of 3, the amount of desorbing hydrogen. For Ru/SiO_2, as the dosing temperature rises, the center of the desorption peak moves to higher temperatures, the lower temperatures desorption region is lost, but the high temperature

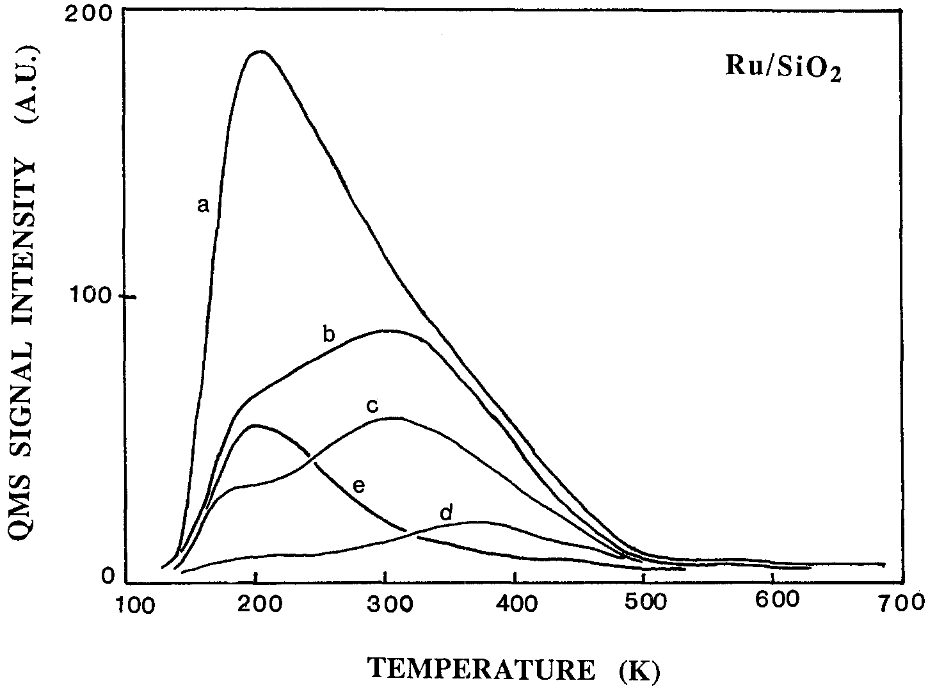


Fig. 2. TPD profiles of H_2 desorbing from Ru/SiO_2 for various dose pressures and 1 min exposures at 150 K: a) 10^{-4} Torr, b) 10^{-5} Torr, c) 5×10^{-6} Torr, d) 10^{-6} Torr, and e) 10^{-5} Torr on reoxidized Ru/SiO_2.

portions all overlap. For Ru–Cu/SiO_2, however, the situation is different [5]; as the adsorption temperature rises, the desorption signal in the high temperature region of the TPD spectrum grows.

Figure 2 shows the TPD profiles of hydrogen dosed at 150 K and various pressures on Ru/SiO_2. At high exposure (10^{-4} Torr), a desorption peak centered at 210 K was observed (fig. 2a). With a decrease in the hydrogen exposure, the one broad desorption profile became a two center (210 K and 340–380 K) curve (fig. 2b, 2c, 2d). With a reduction in hydrogen pressure, the low temperature peak decreased faster than the high temperature peak. When the sample was pretreated with oxygen (5×10^{-4} Torr, 723 K, 5 min, followed by evacuation at 773 K for 5 min) then dosed as in curve (b) 10^{-5} Torr hydrogen, the high temperature peak was suppressed but the low temperature peak retained its intensity (fig. 2e).

Figure 3 shows TPD results for Ru/SiO_2 and Ru-Cu/SiO_2 which were sequentially exposed, first to H_2 and then to D_2 at 150 K, each for 1 min. On both samples, desorption of HD (dashed curves) and replacement of H_2 (dotted curves) by D_2 (solid curves) were observed over the temperature range below 400 K. However, for both samples, the D_2/H_2 and HD/H_2 ratios were greater than unity below, and less than unity above 210 K. In other words, the hydrogen

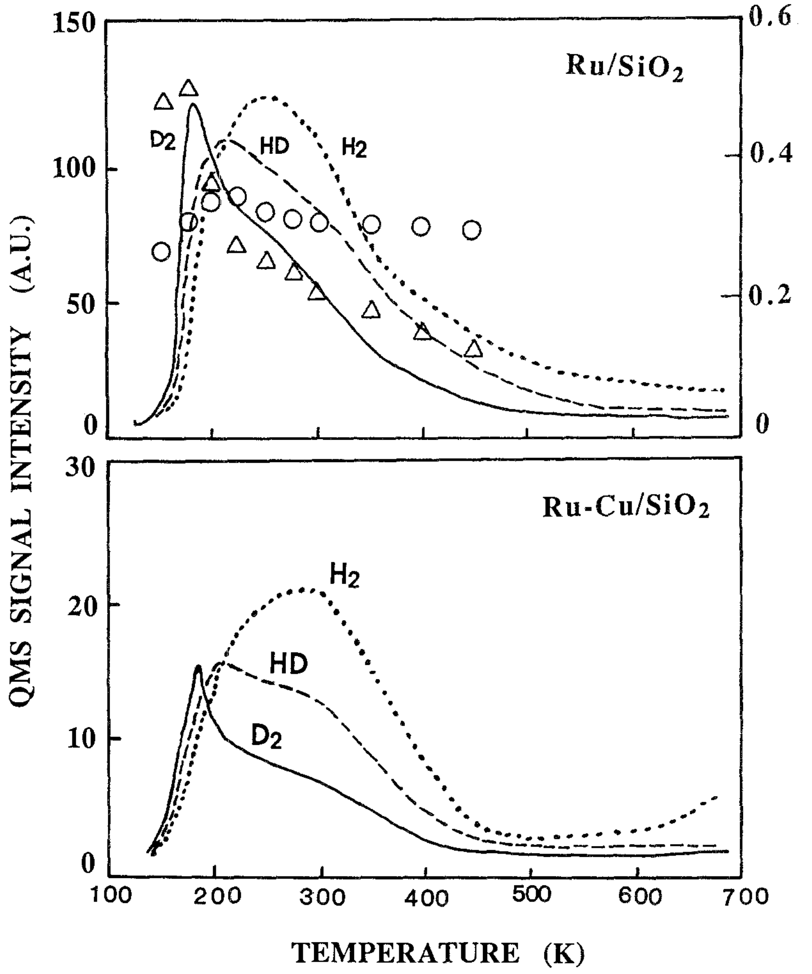


Fig. 3. TPD profiles after sequential dosing of 10^{-4} Torr of H_2 and 10^{-4} Torr of D_2 for 1 min at 150 K. Upper panel is for Ru/SiO_2 and the lower panel for Ru–Cu/SiO_2. The three curves in each panel are profiles for D_2 (———), HD (— — —) and H_2 (···). Open circles (triangles) are the fraction desorbing as HD (D_2) at each temperature.

desorbing at low temperatures was replaced by or combined with deuterium more easily than the hydrogen desorbing at high temperatures.

When the dosing temperature was raised to 300 K (fig. 4), hydrogen was completely replaced by or reacted with deuterium on Ru/SiO_2. For Ru–Cu/SiO_2, however, considerable hydrogen was left on the sample. These results point to the distinct character of the sample containing Cu; displacement/exchange is more difficult in the presence of Cu.

Figure 5 gives the TPD profiles after dosing of H_2 at 300 K followed by D_2 at 150 K. For both Ru/SiO_2 and Ru–Cu/SiO_2, the H_2 and D_2 peaks overlap, and HD formation was observed. Moreover, we detected H_2 desorption (as well as

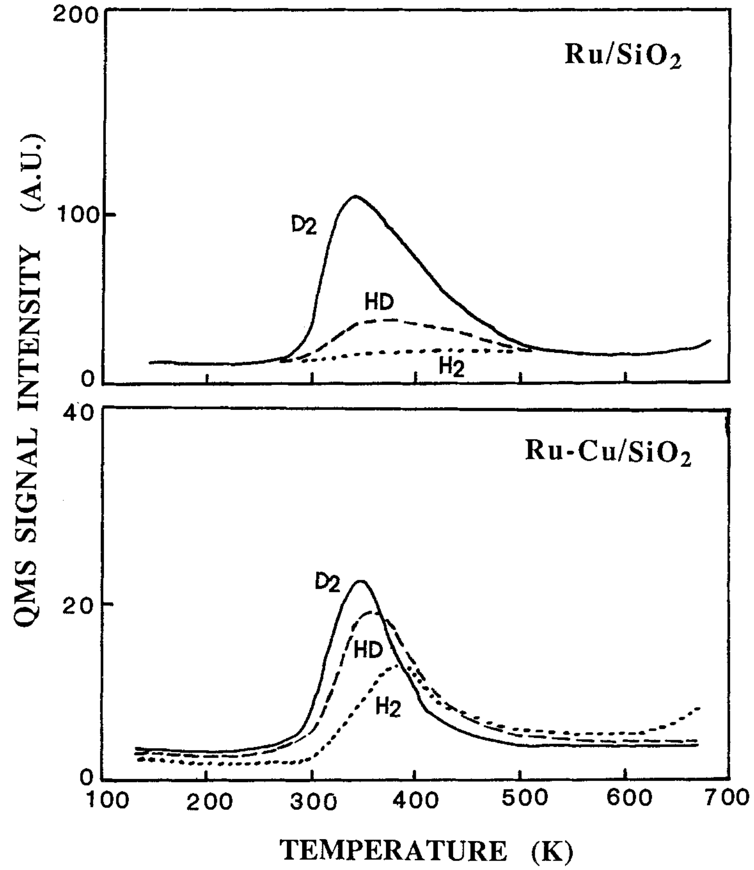


Fig. 4. TPD profiles after sequential dosing of 10^{-4} Torr of H_2 at 300 K and 10^{-4} Torr of D_2 for 1 min at 300 K. Upper panel is for Ru/SiO_2 and the lower panel for $Ru-Cu/SiO_2$. The three curves in each panel are profiles for D_2 (———), HD (— — —) and H_2 (· · ·).

HD formation) below 300 K. Dosing at 300 K (fig. 1), did not produce this desorption. This indicates that some shifting of hydrogen from the high to the low temperature state is induced by the low temperature exposure. Comparing the two samples and data from figs. 1 and 5, it is evident again that it is more difficult to exchange/displace H when Cu is present.

In another sequential dosing experiment, fig. 6 shows TPD of sequentially adsorbed H_2 (at 450 K) and D_2 (at 150 K). On Ru/SiO_2, the peaks for H_2 and D_2 overlapped; the qualitative description is like that of fig. 5, although the hydrogen uptake at 450 K was much less (< 20%) than that at 300 K. For the bimetallic sample, $Ru-Cu/SiO_2$, the results are different; only a very small amount of HD desorption was found below 400 K, there was no overlap of the H_2 and D_2 peaks, and the high temperature hydrogen peak (500 K) was in the same position and had the same intensity as when only H_2 was dosed at 450 K (fig. 1e).

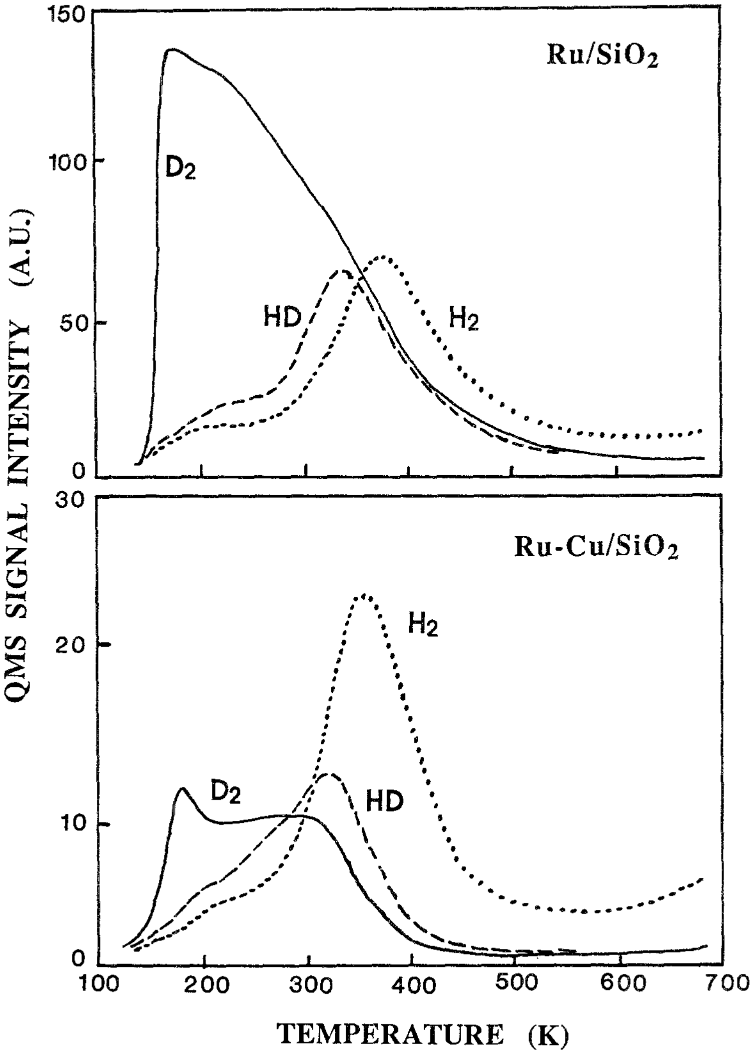


Fig. 5. TPD profiles after sequential dosing of 10^{-4} Torr of H_2 at 300 K and 10^{-4} Torr of D_2 for 1 min at 150 K. Upper panel is for Ru/SiO_2 and the lower panel for Ru–Cu/SiO_2. The three curves in each panel are profiles for D_2 (———), HD (— — —) and H_2 (· · ·).

4. Discussion

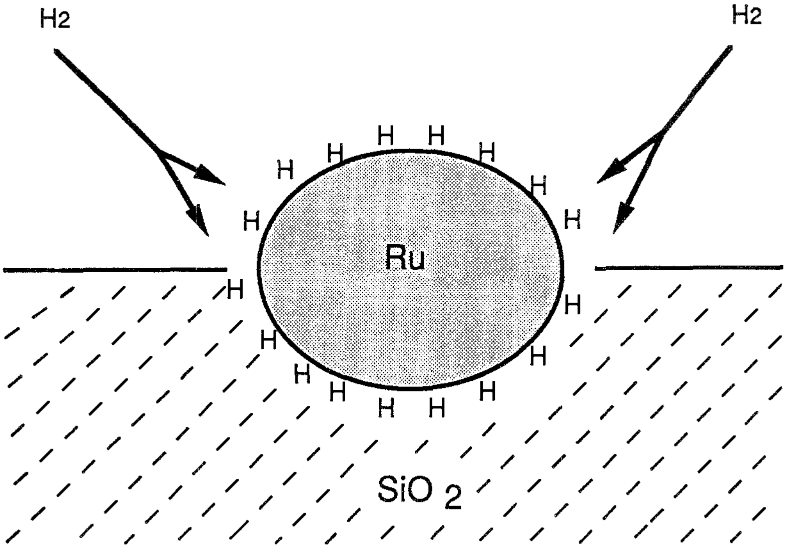
Since the experiments on Ta mesh, SiO_2 and Cu/SiO_2 did not show any hydrogen desorption, we attribute the observed desorption to Ru and *combinations* of Ru with SiO_2 and/or Cu. Since hydrogen desorption from single crystal Ru occurs mainly above 300 K, with small amounts at lower temperatures on high index and chemically modified regions [4,5,8], we attribute the intense signals below 300 K to sites involving SiO_2. These could be spillover sites and Ru sites controlled by SiO_2.

Less thermal energy may be required to desorb hydrogen adsorbed on small particles of Ru containing high index facets, than hydrogen on low index single crystal Ru [8]. If this were the case and if the distribution of Ru particle size followed the binomial expression, we would expect a broad, unstructured hydrogen distribution. Figure 2, however, shows two broad peaks in the TPD spectra, suggesting the existence of at least two distinct hydrogen adsorption states.

Chemisorbed oxygen and oxidized Ru must be considered. Hrbek [2] found that precovering a Ru(001) surface with oxygen ($\theta = 0.09$ to 0.46) resulted in the generation of two new hydrogen adsorption states which desorbed below 250 K. The fact that, in our work, only one distinct peak appeared in this temperature range may be due to the heterogeneity of the supported sample. In our earlier work [19], a Ru{001} sample, treated with 35 L of O_2 at 865 K, was reduced (first order kinetics) by treatment with 10^{-7} Torr of H_2 at 600–900 K for 30–60 min. The present sample, which was reduced in 760 Torr H_2 at 723 K as part of its pretreatment, was treated again with H_2 (10^{-3} Torr, 723 K, 30 min) after insertion into the vacuum chamber. This treatment removes surface oxygen accumulated by exposure to air [17]. Thus, only those Ru atoms in contact with the SiO_2 support are likely to have contact with oxygen. Moreover, high exposure retreatment with O_2 (723 K, 5×10^{-4} Torr, 5 min) should fully reoxidize the surface of the Ru particles. Since oxidized Ru does not chemisorb H_2 under these conditions [2], the fact that only the high temperature part of the H_2 desorption is suppressed (fig. 2e) points to the importance of Ru atoms that are intrinsically strongly coupled to the support, probably through Si–O–Ru bonds. These sites are not removed by either oxidation or reduction treatments.

Hydrogen spillover to SiO_2, after dissociation on Ru, must also be considered. As noted above, silica alone shows no adsorption of H_2 so direct adsorption on SiO_2 can be ruled out. Spillover from supported metals is generally important only at relatively high temperatures (> 500 K) [9]. Furthermore, the spillover model can not easily explain the TPD of H_2 dosed onto a heavily oxidized sample (fig. 2e). The metal surface, deactivated for dissociative adsorption by oxidation, cannot supply the atomic hydrogen to the support. There must be some sites for adsorption which remain protected throughout the oxidation/reduction cycles used here. We speculate, as shown by Scheme 1, that these sites, which are responsible for the H_2 desorption below 250 K, involve partially oxidized Ru located at the interface between metallic Ru and bulk SiO_2, including buried sites. The nature of these sites could be similar to those on partially oxidized single crystal Ru [2].

The two desorption peaks in fig. 2 also indicate that there is an energy barrier between the high and low temperature hydrogen adsorption states. The isotope scrambling [13] results (figs. 5 and 6) suggest that the energy barrier is not high enough to completely block the transfer between the two states. The low temperatures hydrogen, however, is more readily replaced by subsequently adsorbed deuterium (fig. 3).



Scheme 1.

There is some question about whether the low temperature hydrogen is adsorbed atomically or molecularly. The fact that maximum HD desorption occurred at 200 K after the sequential dosing of H_2 and D_2 (fig. 3) supports the former. Even if the HD that desorbs below 300 K were from H and D migrating from the high temperature state, this migration mechanism would not explain the fact that the *maximum* desorption intensity of HD was at 200 K (see fig. 3 and fig. 5).

Comparing Ru/SiO_2 with Ru-Cu/SiO_2 in fig. 1, we note that Cu preferentially blocks the low temperature hydrogen TPD that we have attributed to sites at the Ru–SiO_2 interface. Within the framework of this model, Cu is located preferentially at the interface between Ru and SiO_2.

On the bimetallic, Ru–Cu/SiO_2, we previously reported evidence for hydrogen spillover from Ru to the interface between Ru and Cu [5]. In the present study, this model is supported by the sequential adsorption of H_2 and D_2 (figs. 4 and 6). Successive dosing of D_2 at 300 K replaced almost all the preadsorbed hydrogen on Ru/SiO_2 but not on Ru–Cu/SiO_2, indicating that the high temperature adsorption states are different, at least kinetically, for the two samples (fig. 4). This can be accounted for by a new type of hydrogen adsorption site on Ru, probably involving Ru–Cu bonded together, generated by addition of Cu. The complete temperature separation and lack of isotope mixing in fig. 6b indicates that on Ru–Cu/SiO_2 there is an energy barrier, between the populated high temperature state and the low temperature region, high enough to strongly inhibit the exchange between hydrogen adsorbed at 450 K and deuterium adsorbed at 150 K. This energy barrier was found only when Cu was present (fig. 6a).

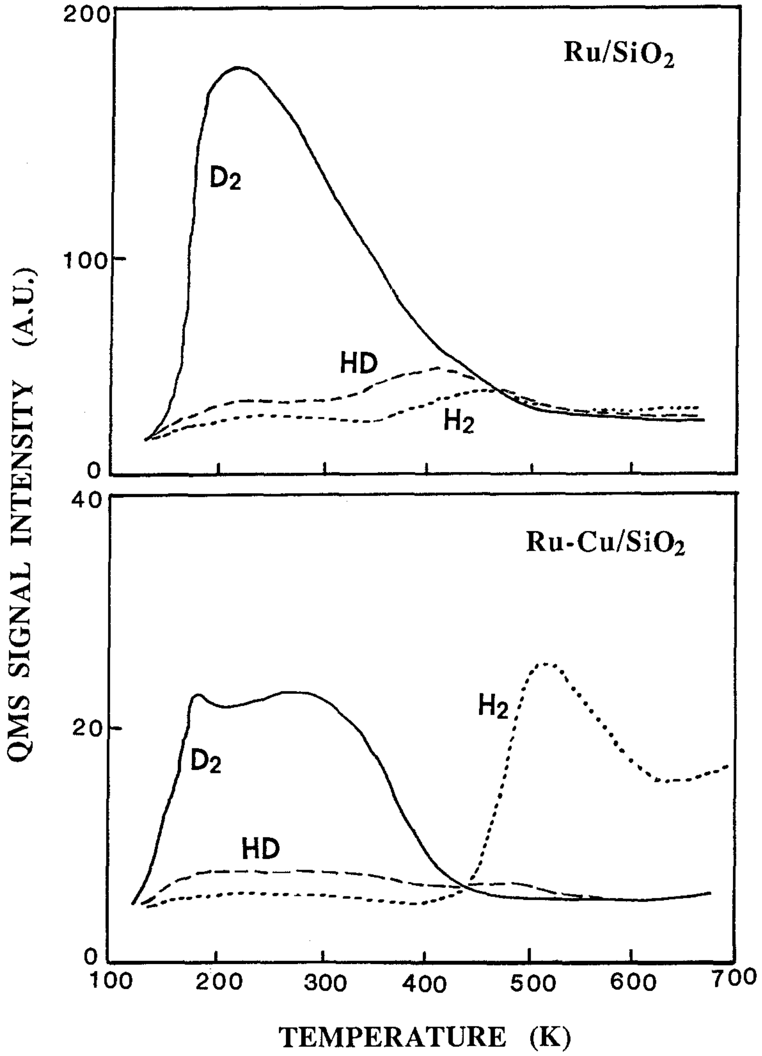


Fig. 6. TPD profiles after sequential dosing of 10^{-4} Torr of H_2 at 450 K and 10^{-4} Torr of D_2 for 1 min at 150 K. Upper panel is for Ru/SiO_2 and the lower panel for $Ru-Cu/SiO_2$. The three curves in each panel are profiles for D_2 (———), HD (— — —) and H_2 (· · ·).

5. Summary

The study reported here can be summarized as follows:

1. For Ru/SiO_2, two very broad but distinguishable desorption states for hydrogen were found. One (> 250 K) is assigned to metallic Ru sites, not influenced by the support while the other (< 250 K) is assigned to Ru sites that are partially oxidized through interactions at the interface with the support and to sites associated with high index regions of the Ru particles. The breadth of the TPD peaks is ascribed to a heterogeneous distribution of sites.

2. Based on isotope scrambling, both desorption states involve recombination of atomically adsorbed hydrogen.

3. While there is an energy barrier, of variable height, between the two hydrogen chemisorption states, the two types of hydrogen exchange, to some extent, even at 150 K.

4. For $Ru-Cu/SiO_2$, as compared to Ru/SiO_2, there is a kinetically distinct type of hydrogen adsorption state ascribed to Ru–Cu sites.

5. The energy barrier between atomic hydrogen adsorbed on metallic Ru and adsorbed at the interface between Ru and Cu is high enough to completely block atom transfer between the two states when the high temperature region is preferentially populated by dosing at 450 K and the low temperature region by dosing at 150 K.

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