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Hydrogen adsorption states on silica-supported Ru–Ag and Ru–Cu bimetallic catalysts investigated via microcalorimetry

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Abstract

The nature of hydrogen adsorption states on silica supported Ru, Ru–Ag and Ru–Cu was investigated using microcalorimetry and selective hydrogen chemisorption. The differential heats of hydrogen adsorption as a function of hydrogen coverage were determined for Ru and bimetallics with varying Ag and Cu contents. The initial heats of hydrogen adsorption (differential heat at coverages approaching zero) were found to be similar on all three catalyst systems suggesting the absence of effects that directly alter the chemisorptive bond (e.g. electron transfer between Ru and the added metal). The addition Ag to Ru significantly reduced the total amount of hydrogen adsorbed per surface Ru atom. That is, the stoichiometry of adsorption was altered by the addition of Ag even though Ag does not adsorb hydrogen. Similarly, the addition of Cu reduced the amount of hydrogen adsorbed per surface metal atom. In both cases, the reduced amount of hydrogen adsorbed per surface atom (adsorptive stoichiometry) was associated with the loss of hydrogen adsorbed from weak and intermediate energy adsorption states (<80 kJ/mol). The population of sites with adsorption energies $\geq$80 kJ/mol were unaffected. From atomistic simulations it is known that, at low concentrations, Ag and Cu preferentially occupy the low coordination metal sites. The loss of the intermediate and low adsorption energy sites is correlated with replacement of Ru atoms at edge, corner and other defectlike sites by Ag and Cu. Possible reasons for this structure sensitivity are discussed. © 1998 Elsevier Science B.V.

Keywords: Ru bimetallic catalysts; Hydrogen adsorption; Microcalorimetry

1. Introduction

Bimetallic catalysts are used in a variety of important processes such as catalytic reforming in the petroleum industry and automobile emission control [1]. In principle, the adsorption properties and the catalytic behavior of bimetallic catalysts can be manipulated by varying the nature and relative composition of the component metals. Thus, by changing the concentration of the second element in bimetallic catalysts, it may be possible to control the selectivity, activity and/or stability of the catalytic process [2]. The Ru–Ag and Ru–Cu bimetallic systems are examples of model systems that are relatively simple and easy to study. One of the elements, Ru, is catalytically active while the second (Ag or Cu), is relatively inactive for most reactions [1–3]. Another advantage of these model systems is that at low concentrations the Group Ib element preferentially occupies the edges, corners and other low coordination metal sites on the catalyst surface [4]. This preferential segregation of Ag and Cu to the low metal coordination sites on the surface of the bimetallic catalyst can be used to manipulate the surface structure and study its influence on activity and selectivity (i.e. structure sensitivity). Such reactions as Fischer–Tropsch synthesis

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[3], ethane hydrogenolysis [5,6] and butane hydrogenolysis [7] have been investigated in our laboratory using this approach. In addition, other studies of hydrogenolysis and CO hydrogenation [1,8–11] provided valuable insight regarding the surface composition of the bimetallic catalysts and the nature of the catalytic site responsible for their activity.

Ru-Group Ib systems have been characterized with a variety of techniques including X-ray absorption fine structure (EXAFS) [12], X-ray photoelectron spectroscopy (XPS) [13], ultraviolet photoelectron spectroscopy (UPS) [14], temperature-programmed reduction (TPR) [15], temperature programmed desorption (TPD) [16], photoemission of adsorbed xenon (PAX) combined with angle resolved ultraviolet photoemission spectroscopy (ARUPS) [17], proton nuclear magnetic resonance (^{1}H NMR) of adsorbed hydrogen [18], and atomistic simulations [4]. One technique that has been quite useful in the study of other bimetallic systems is microcalorimetry of adsorbed hydrogen [19]. To date, there have been no studies on the thermodynamics of hydrogen adsorption on Ru bimetallics at conditions up to one atmosphere pressure.

Many adsorption phenomena, including hydrogen adsorption on transition metals, are spontaneous and exothermic [20]. The amount of heat evolved during the adsorption process is called the heat of adsorption and has a characteristic value for a given gas–solid system. Factors which may influence heats of adsorption include the chemical nature of the gas and metal catalyst investigated, the amount of adsorbate present on the catalyst surface (coverage), temperature and pressure of adsorption, the size of the catalyst particles, the presence of additives, the nature of the support and the method used for heat determination. Most of the adsorption data in the literature are from surface science studies on single crystals [21] and have been obtained indirectly from kinetic studies of various phenomena (usually temperature-programmed desorption) or by applying the Clausius–Clapeyron equation to adsorption isotherm results [22]. A significant drawback of these methods is that many assumptions are made en route to calculating the heats of adsorption. For example, using adsorption isotherms for determining heats of adsorption is inherently limited by the assumptions which accompany the use of the Clausius–Clapeyron equation. Additionally, it is assumed that the surface state is unchanged during the adsorption process, i.e. the heat of adsorption is independent of adsorbate coverage, and that the heat of adsorption is not a function of temperature. These last two assumptions are the most flawed. It is well known that the heat of adsorption generally decreases with increasing adsorbate coverage [20,22]. The influence and importance of temperature on heats of adsorption measurements has been discussed in detail by Martinez and Dumesic [22]. The assumption of reversibility is also a moot point, particularly in cases of strong adsorption like that of hydrogen on clean transition metal surfaces, where the chemisorption process may be irreversible under experimental conditions [23].

The study presented here investigated the differential heat of adsorption of hydrogen on Ru, Ru–Ag, and Ru–Cu in order to characterize the catalysts themselves and to elucidate the interaction of this important reactant with the surface. A home-made Tian–Calvet microcalorimeter was used to determine the differential heat of adsorption for hydrogen as a function of hydrogen coverage. The amount of gas adsorbed onto the catalyst in a given dose was determined using a standard volumetric technique in conjunction with the microcalorimeter. The results of this work indicated that the states of hydrogen adsorption exhibited structure sensitivity.

2. Experimental methods

2.1. Catalyst preparation

All the supported catalysts used in this study had a Ru composition equal to 4% by weight of the total (Ru+SiO_2) content. A 4% Ru/SiO_2 was prepared from a 1.5% ruthenium nitrosyl nitrate solution (Strem Chemicals) using the incipient wetness impregnation method. A slurry was prepared by impregnating silica (Cab-O-Sil, 300 m^2/g) with the appropriate amount of salt solution. This slurry was dried overnight at room temperature and then at 110°C for two hours. It was then reduced in flowing hydrogen at 375°C. The Ru–Cu/SiO_2 and Ru–Ag/SiO_2 catalysts were prepared by coimpregnation of $CuNO_3$ or $AgNO_3$ with the ruthenium nitrosyl nitrate solution. The Ag and Cu contents are reported as atomic weight percent of the total metal (Ru+Ag or Cu) content. All the catalysts were washed 8-to-10 times with 60 ml of hot water in order to eliminate Na and Cl contamination. The catalysts were reduced in situ prior to measuring the differential heats of adsorption. Ru–Cu/SiO_2 catalysts with 5, 30, and 60 atomic % Cu and three Ru–Ag/SiO_2 samples with 10, 20 and 30 atomic % Ag were investigated.

2.2. Dispersion measurements

The dispersion of the 4% Ru/SiO_2 catalyst was determined by ^1H NMR and was found to be 11%. The dispersions of the Ru–Ag/SiO_2 and Ru–Cu/SiO_2 catalysts were obtained by selective hydrogen chemisorption using a home-made adsorption apparatus described elsewhere [24]. The optimized volumetric technique described by Uner et al. was used for the dispersion measurements [25]. About 1 g of the catalyst was placed in a Pyrex sample cell with a coarse frit to enable reduction in flowing hydrogen. Moisture was removed by heating for 30 min at ca. 400 K with helium gas flowing through the cell. The catalysts were then reduced in flowing hydrogen for 4 h at a temperature between 673 and 723 K, and then evacuated for 4 h at the temperature of reduction. Total hydrogen uptake measurements at 335 K were made by exposing the catalyst to progressively higher pressures, between 10 and 40 torr, and allowing to equilibrate for 10 to 15 min. At least four data points were obtained for all isotherms. The catalyst was then evacuated at 10^{-5} torr for 10 min to remove the weakly bond hydrogen. Subsequently, a second isotherm, corresponding to weak or reversible adsorption, was obtained using the same procedure. The linear portions of the total and reversible isotherms were extrapolated to zero pressure and the difference between the intercepts was taken as a measure of strongly bound hydrogen. This strongly bound hydrogen was used to calculate the dispersion of the catalysts. The dispersions of the various catalysts are given in Table 1.

Table 1
Dispersion of catalysts

Catalyst [a]	Dispersion (%)
Ru/SiO_2	11 [b]
Ru–10 at.% Ag/SiO_2	12
Ru–20 at.% Ag/SiO_2	8.8
Ru–30 at.% Ag/SiO_2	7.6
Ru–5 at.% Cu/SiO_2	35
Ru–30 at.% Cu/SiO_2	19
Ru–60 at.% Cu/SiO_2	8.3

[a] All catalysts contained 4% by weight Ru.
[b] Via ^1H NMR

2.3. Microcalorimetry

A home-made Tian–Calvet differential heat flux microcalorimeter, based on the design of Handy et al. [26], was used in this work. The catalyst was loaded in a thin-walled Pyrex NMR tube (Wilmad Glass) connected to a stainless-steel manifold with greaseless fittings. In-situ static reduction was carried out with the catalyst at 375–400°C using hydrogen at ≈1 atm pressure. The hydrogen was replenished every 30 min. This was followed by evacuation at the reduction temperature for a period of time equal to the total time of reduction. The samples were lowered into the calorimeter (while still connected to the manifold) and the system allowed to thermally equilibrate overnight. All differential heats of adsorption measurements were made at 403 K to ensure the hydrogen adsorbate had sufficient mobility to probe the energetics of the entire sample surface [22]. The differential heats of adsorption are reported in terms of heat evolved per mole of hydrogen gas adsorbed (kJ/mol).

3. Results

The differential heats of hydrogen adsorption on the various Ru, Ru–Ag and Ru–Cu catalysts are shown in Fig. 1. The amount of hydrogen adsorbed is given per surface metal (for Ru–Cu) or per surface Ru (for Ru and Ru–Ag). On Ru–Ag, the only surface metal which can adsorb hydrogen is Ru since hydrogen does not adsorb on Ag or spillover to the Ag from Ru [24]. On the other hand, for the Ru–Cu catalysts spillover from the Ru to Cu does occur [11] and, therefore, the entire surface can accommodate hydrogen. The initial heats of hydrogen adsorption were found to be similar for all the catalysts at 90–95 kJ/mol. All catalysts displayed a decrease in differential heats of adsorption with increasing hydrogen coverage. Furthermore, Ru/SiO_2 displayed a coverage as high as 4.0 before the differential heats of adsorption fell below 5 kJ/mol.

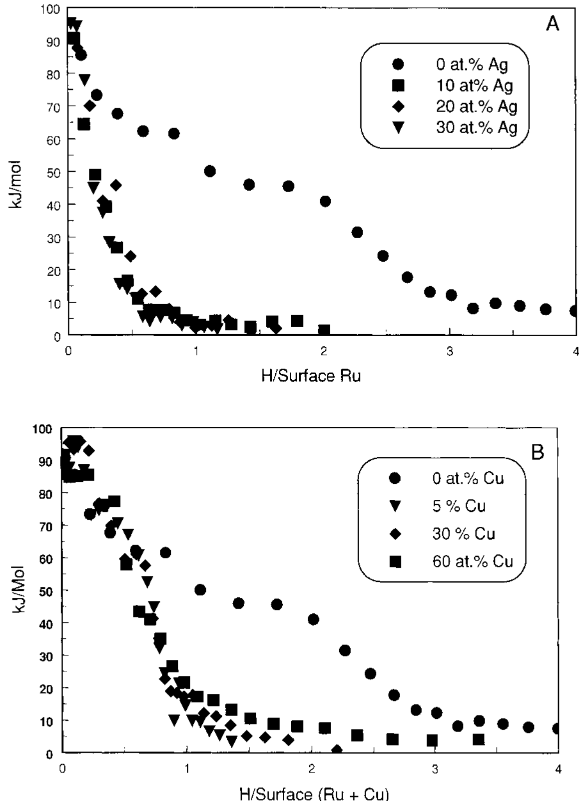

Fig. 1. Differential heats of hydrogen adsorption at 403 K on (a) 4% Ru/SiO_2 compared with a series of $Ru–Ag/SiO_2$ catalysts, and (b) 4% Ru/SiO_2 compared with a series of $Ru–Cu/SiO_2$ catalysts.

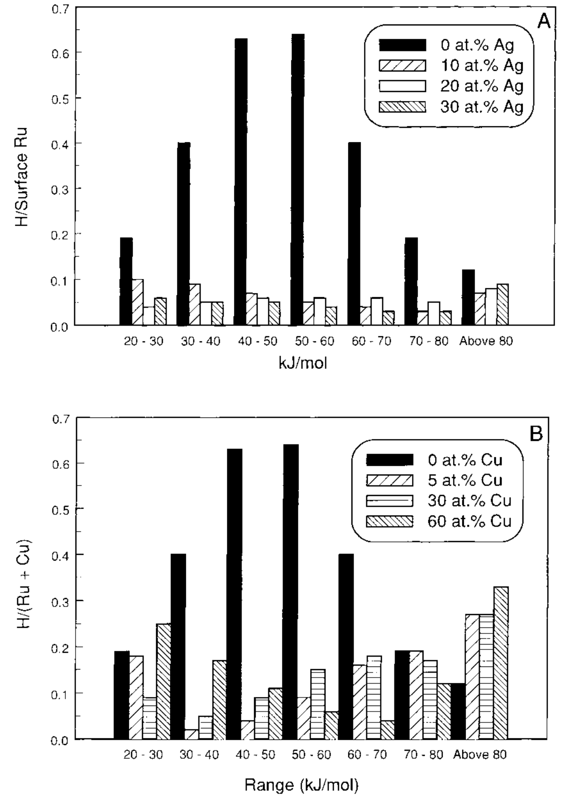

Fig. 2. Histogram of differential heat distributions for hydrogen adsorption at 403 K on (a) 4% Ru/SiO_2 compared with a series of $Ru–Ag/SiO_2$ catalyst, and (b) 4% Ru/SiO_2 compared with a series of $Ru–Cu/SiO_2$ catalysts.

Adding Cu or Ag to Ru/SiO_2 significantly reduced the stoichiometry of hydrogen per surface metal. The decrease was greater with Ag than with Cu. The bimetallics with 10, 20, and 30 atomic % Ag displayed similar differential heat of adsorption trends. Note that, for all the Ru–Ag catalysts, the differential heat values fell to negligible values at a coverage of $\approx$1.0 hydrogen per surface Ru atom. Similarly, up to a hydrogen-to-surface metal ratio of $\approx$1.0, the differential heat curves for all the Ru–Cu catalysts had a similar shape. However, the amount of very weakly bound hydrogen (differential heat <15 kJ/mol) increased with increasing amounts of Cu.

Histograms of the amount of hydrogen adsorbed within specific ranges of differential heats, called site distributions, are given in Fig. 2. The site distributions for Ru–Ag and Ru–Cu, respectively, are compared with the distribution for Ru/SiO_2. These histograms were obtained with a method described by Cortright and Dumesic [27]. The site distributions were essentially the same for all three Ru–Ag catalysts studied.

Of all catalysts studied, Ru/SiO_2 adsorbed more hydrogen per Ru (or surface metal) and most of this hydrogen was between 30–70 kJ/mol. Adding more than 10 atomic % Ag caused a significant reduction in the population of sites with intermediate and low heats of adsorption (<80 kJ/mol). The population of sites with heats of adsorption >80 kJ/mol showed a slight increase.

Adding Cu to Ru also significantly reduced the amount of hydrogen adsorbed per surface metal site (Ru+Cu), especially in the differential heat range between 30–70 kJ/mol (see Fig. 2(b)). Similar to Ru–Ag catalysts, the population of sites which adsorb hydrogen with a heat of adsorption greater than 80 kJ/mol was not greatly affected by adding Cu, although an increase was noted. Thus, adding either Cu or Ag to Ru/SiO_2 decreased the stoichiometry of adsorption by depopulating the low and intermediate energy adsorption states. Consequently, the integral heats of adsorption averaged over all coverages was increased by both,. Cu and Ag.

4. Discussion

Two features of the results of hydrogen adsorption on Ru and Ru bimetallics are notable. First, the initial heats of adsorption are the same (within experimental error) on all catalysts investigated here. Second, both Ag and Cu had the effect of reducing the population of hydrogen adsorbed at low and intermediate energies, i.e. below 80 kJ/mol. These features and their implications for catalysis are discussed in the following.

4.1. Initial heats of adsorption

It was noted that the initial heats of adsorption for all catalysts, regardless of bimetallic composition, was $\approx$90 kJ/mol (see Fig. 1). A similar observation was made by Cortright and Dumesic [27] for hydrogen adsorption on a series of Pt–Sn/SiO_2 catalysts. The similarity of the initial heats of adsorption suggests the absence of effects that directly alter the chemisorptive bond or chemisorption site. Possible mechanisms by which the chemisorptive bond or surface site on a bimetallic can be modified include electronic effects, ensemble effects, or surface segregation induced structure sensitivity. For example, the last item refers to the possibility that Ag and Cu preferentially populate edge, corner and other low metal coordination sites, and thus hydrogen may be blocked from those adsorption sites in the bimetallics. If those sites were associated with high binding energy, and if the adsorbed hydrogen was relatively immobile, then one would expect that the initial heats of adsorption would be less with the bimetallics. On our systems, however, we know from ^{1}H NMR that adsorbed hydrogen is mobile on individual metal particles [28] and, under the conditions of our experiments, hydrogen atoms sample all available adsorption sites (see, also, the Appendix A). Hence, any decrease observed would be an average of all adsorption sites sampled by the hydrogen atoms. Since the observed initial heats of adsorption were not changed by presumably blocking low metal coordination sites, we conclude the following:

(i) low coordination sites (predominately edges and corners) do not have significantly different heats of adsorption; and
(ii) too few low coordination sites exist so as to resolve them in the calorimetry.

Ensemble effects are not likely because these bimetallic pairs are immiscible in the bulk and do not experience micromixing on the surface even though the two elements are in contact. That is, neither Cu nor Ag break up Ru ensembles to any extent [4–6].

A more expected mechanism that could alter initial heats of adsorption on our bimetallic catalysts involves the transfer of electron density from Ru to, or from the second metal. The premise of this electronic (sometimes called ligand) effect is that the chemical environment of the adsorbing metal is determined by free metal electrons as well as vacant *d*-orbitals which can accommodate electrons [29]. The chemisorption process involves bonding of the adsorbate through electron transfer and is a function of the density of electrons at the catalyst surface (e.g. see Refs. [30] and [31]). The initial heats of adsorption are a measure of bond strength, and since electrons are involved in bonding, any influence of the Group Ib metal on electron transfer is expected to alter the initial heats of adsorption. Prinsloo and Gravelle [32] determined the differential heats of hydrogen adsorption on a series of silica-supported Ni–Cu catalysts of various compositions. They attributed the observed decrease in the initial heats of adsorption with increasing Cu amounts to a transfer of electrons from the Cu to the vacant *d*-orbitals of Ni. However, in magnetic studies, Ni–Cu alloys with high Cu contents displayed strong paramagnetic behavior ([33], and references therein). This result suggested that Ni retained its paramagnetic behavior even in the Cu rich environment and no electron transfer occurred from Cu to Ni in the alloys. The Ru–Ag/SiO_2 catalysts of this study were previously investigated using ^{1}H NMR [34]. No change in the proton Knight shift, a measure of the density of bonding states at the Fermi level, was observed with increasing amounts of Ag. Thus, it was concluded that the density of bonding states at the Fermi surface does not change upon addition of Ag to Ru/SiO_2. This view is also supported by XPS and XAES results for Ag monolayers supported on Ru(0001) reported by Rodriguez [16].

In the case of Ru–Cu catalyst, the studies probing electronic effects using other techniques are not as conclusive. Infrared [35–37] and thermal desorption ([38] and references therein) studies using CO as a probe molecule have been used to investigate electronic effects in the Ru–Cu bimetallic systems [39]. Chemisorption of CO is more complicated than hydrogen because it involves donation of electrons from the 5σ orbitals of CO to the metal as well as "back donation" from the metal *d*-orbitals to the antibonding $2\pi^*$ orbitals of CO [40]. However, the temperature shifts in peak maxima, reported from the thermal desorption studies, have been criticized as being insignificant and because these studies did not account for reductions in the preexponential factor in the rate of desorption resulting from a decrease in the sticking coefficient of CO [41]. Similarly, caution should be exercised in interpreting the peak shifts reported in the early IR results because high CO coverages were used in these studies and the results did not account for dipole–dipole interactions [42]. The electron energy loss spectroscopy results of Kiskinova et al. [43], and the XPS study by Helms and Sinfelt [13], also suggested no electronic interactions between Ru and Cu.

Wu et al. [18] reported only a single ^1H NMR resonance for adsorbed hydrogen, varying from -49 to -62 ppm, for $Ru–Cu/SiO_2$ catalysts containing <45 atomic % Cu. At higher Cu contents, an additional peak, attributed to hydrogen chemisorption on Cu particles, was observed at ca. 95 ppm. The shift in the upfield peak position with increasing Cu content was attributed to fast exchange of hydrogen between Ru and Cu environments, and not to changes in the density of bonding states at the Fermi level. An electronic perturbation of the Cu by the underlying Ru, especially at Cu concentrations >45 atomic % was not ruled out. Theoretical analysis of the Knight shifts in this system also do not suggest any electronic interactions [44,45].

The calorimetry results presented here agree with the view that electronic effects are not operable in these bimetallics, at least with regard to hydrogen adsorption. The results suggest that the hydrogen chemisorption bond strength on a Ru atom is not altered by the presence of Cu or Ag.

4.2. Hydrogen adsorption at higher pressures: Amounts and energies

Hydrogen chemisorption on transition metals, including Ru, have been extensively investigated at low pressures [46]. However, there are few fundamental studies investigating hydrogen chemisorption on supported catalysts at pressures >100 torr. Using ^1H NMR, Wu et al. [24] identified two distinct adsorbed states on Ru in Ru/SiO_2: irreversible and reversible. The strongly bound, irreversible state was observed at pressures $<10^{-5}$ torr and showed no interactions with hydrogen in the silica support. In later studies, Engelke et al. [28,47] used 2D NMR to show that the irreversibly adsorbed hydrogen showed intraparticle mobility at a coverage of ≈ 0.5 and below. The more mobile, reversibly adsorbed hydrogen was observed at higher pressures and was shown to exchange with deuterium on the silica support at the relatively low pressure of 5 torr.

Bhatia et al. [48] reported H-to-surface metal ratios >1.0 for pressures exceeding 100 torr. Further, at pressures >100 torr an additional ^1H NMR resonance, not seen at lower hydrogen pressures, was observed. The weakly bound hydrogen on the metal, comprising the resonance observed only at high pressures, was in fast exchange with the gas phase and perhaps with the hydrogen spilled over to the support (revealed by the pressure dependence of its resonance shift). The exact location of the weakly bound hydrogen on the metal was not determined. In addition to the weakly and strongly bound hydrogen on Ru, ^1H NMR studies clearly showed that hydrogen spills over from the Ru particles to the silica support, particularly at higher pressures [25]. The amount of hydrogen spillover on the support is quite large for the Ru/SiO_2 system.

From the site distribution plots, shown in Fig. 2, it was observed that on Ru/SiO_2 the population of sites with intermediate and low heats of adsorption, i.e. characterized by <70 kJ/mol, was high. Hence, it is not surprising that the pure Ru catalyst generates considerable spillover (see Fig. 1) with heats below 10 kJ/mol. The weakly bound hydrogen on the metal can spillover the support without a large energy penalty. Also, hydrogen from the gas phase quickly replenishes the metal with weakly bound hydrogen.

In contrast, on the Ru–Ag and Ru–Cu catalysts, the sites displaying adsorption heats <70 kJ/mol were significantly depopulated (see Fig. 2). Since the intermediate and weakly bound states have significantly lower amounts of hydrogen, there is less weakly bound hydrogen available for spillover to the support in these catalysts. Possible reasons for the significant depopulation of the intermediate and weak adsorption states on Ru–Ag and Ru–Cu are discussed in Section 4.3.

4.3. *Comparison of Ru/SiO$_2$ and Ru-Group Ib metallics: reduction in hydrogen chemisorbed at high pressures*

Possible explanations for the depopulation of the intermediate and weak sites on Ru–Ag and Ru–Cu bimetallics include:

(i) electronic effects;
(ii) changes in site geometry including blocking of sites; and
(iii) altered kinetics of hydrogen adsorption.

Since electronic effects were not important at low coverages, it is improbable that the depopulation can be accounted for by using this explanation at higher coverages.

It is possible that Ag blocks Ru adsorption sites that can accommodate large amounts of hydrogen. However, in this work, we know that the adsorbed hydrogen is highly mobile at these conditions. Also, in order to account for the large amount of hydrogen on the metal, these ''special'' adsorption sites would need to accommodate unreasonably high stoichiometries, between 12 to 20 hydrogen atoms per surface metal atom. Thus, even though Ag and Cu selectively blocked low coordination sites, blocking of sites exhibiting high adsorption stoichiometries cannot account for all the depopulation observed.

The third possibility is that a kinetic phenomenon controls the amount of intermediate and weakly bound hydrogen on the Ru–Ag and Ru–Cu bimetallics. It is possible that the adsorption process may proceed primarily via rapid dissociative adsorption at the edges, corners and other similar sites on the Ru surface in a structure-sensitive manner. Hydrogen adsorption on Ru/SiO$_2$ may be structure-sensitive and may occur more efficiently through the low coordination defect-like sites, than on the high coordination terrace atoms in much the same way as noted for Pt [49]. The term coined for this rapid, site-specific adsorption is ''portal'' mediated adsorption [50]. It is likely that this process is zero-order in hydrogen pressure and initially produces weakly bound, highly mobile hydrogen that migrates to stronger binding states. Likewise, the desorption process requires two hydrogen atoms combining to form the desorbing molecule. The two atoms may be both strongly adsorbed (SS), both weakly adsorbed (WW), or a combination of weakly and strongly adsorbed species (WS). The relative rates of the elementary desorption processes should be WW>WS>SS, based solely on the energy barriers.

When the portals are systematically closed, for example, by allowing Ag or Cu to distribute to edges and corners, the elementary adsorption process at those sites is shut down, by the desorption process still can occur to the extent that the populations of surface hydrogen exist. Note that adsorption directly onto basal plane facets still occurs but at its intrinsically slower rate [49]. Hence, the qualitative picture that emerges is that the weakly bound states are systematically depopulated due to a reduced adsorption rate coupled with desorption favoring the more weakly bound states. The net result is a metal surface with less total hydrogen and an adsorption energy distribution more heavily weighted to the higher energy states (Fig. 2). In addition, spillover of hydrogen to the support is diminished because little weakly bound hydrogen on the metal is available. Note that, in this picture, the calorimetry results are not truly at equilibrium because microscopic, detailed balance is not achieved. Rather, these experiments probe a stationary state.

It should be highlighted that the portal mediated adsorption, described in detail for the Ru–Ag till now, can also describe the results noted for the Ru–Cu system. However, the model must account for spillover from the Ru to the Cu [18]. As mentioned earlier, Cu unlike Ag, can accommodate spillover hydrogen. This spillover of hydrogen to Cu also contributed to the significantly larger populations of sites with low heats of adsorption, observed at high pressures, on Ru–Cu compared to Ru–Ag. The extent of this spillover from Ru to Cu can be quantified and modeled [50].

The Tian–Calvet calorimeter used in the present study had a much larger time constant than the adsorption processes investigated, and thus, it does not provide information on the rates of the various processes. Furthermore, the calorimetric method probed the system at equilibrium conditions and this method cannot be used to provide information on the influence of Ag or Cu on the kinetics of hydrogen adsorption on Ru/SiO_2. However, experimental evidence that the kinetics of hydrogen adsorption and desorption are affected by addition of Ag was provided by ^1H NMR studies on $Ru–Ag/SiO_2$ catalysts [51]. These studies found that the rates of hydrogen adsorption and desorption were lowered by a factor of 20–100 on the bimetallic catalysts. Hydrogen sticking coefficients, determined as a function of H-to-surface Ru stoichiometries, were also lower on the Ru–Ag catalysts than on pure Ru/SiO_2 and corresponded to values observed on Ru(0001) surfaces [52].

A correlation of entropies of adsorption with enthalpy of adsorption observed in this work is given in Appendix A. Although not directly related to the above discussion, these results may suggest that the underlying mechanism of adsorption is dominated by kinetic effects common to all catalysts studied here.

5. Implications for catalysis

The foregoing portal-mediated adsorption model can explain catalytic variations previously observed for some bimetallic systems. For example, Smale and King [5,6] noted that even though Ag is catalytically inert, it does not adsorb hydrogen and cannot produce an ensemble effect; it can significantly alter the ethane hydrogenolysis reaction on Ru. Ru–Ag catalysts yielded a significantly more negative order of reaction with respect to hydrogen on Ru–Ag compared to Ru catalysts, -2.5 vs. -1.5. In a simple mechanism, the effect is the same as if the heat of adsorption of hydrogen was increased [5,6]. The results presented here reveal that the average heat of adsorption is indeed higher on the Ru–Ag bimetallic.

It is not clear how generally one can apply the explanation of portal-mediated chemisorption processes coupled with surface segregation to bimetallic and structure-sensitive reactions. But, in cases such as Ru–Ag, where electronic and ensemble effects are unlikely, it remains an attractive rationale.

6. Conclusions

Microcalorimetry and selective hydrogen chemisorption were used to investigate the energetics and extent of hydrogen chemisorption on Ru/SiO_2, and a series of $Ru–Ag/SiO_2$ and $Ru–Cu/SiO_2$ bimetallic catalysts. It was observed that addition of Ag or Cu to Ru/SiO_2 significantly reduced the amounts of hydrogen adsorbed as well as the stoichiometry of hydrogen adsorption. Both Cu and Ag reduced the population of adsorbed hydrogen with intermediate and weak heats of adsorption. The initial heats of adsorption were similar on all the catalysts studied, indicating that processes which directly alter the chemisorption bond strength, such as electron transfer from Ag or Cu to Ru, did not play a noticeable role.

The depopulation of the intermediate and weak sites was attributed to a structure-sensitive kinetic effect. It was proposed that hydrogen adsorption occurred more efficiently through edges, corners and other low-coordination metal sites than basal planes. The intrinsic rate constants for desorption from the basal planes were assumed to be unaffected and, thus, were the same on Ru/SiO_2 as well as the bimetallics. Since Ag and Cu preferentially segregate to the low metal coordination sites, it was postulated that the addition of Ag or Cu resulted in reduced rates of hydrogen adsorption while the rates of desorption were not affected. Thus, there was a net depletion in the population of hydrogen residing on the surface, resulting in the reduced hydrogen-to-metal ratios observed on the Ru–Ag and Ru–Cu bimetallic catalysts. The reduced amounts of weakly bound hydrogen on the bimetallics also decreased the spillover to the silica support.

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Appendix A

The relationship between differential entropy and differential heats of adsorption for silica-supported Ru, Ru–Cu and Ru–Ag

An interesting observation is that the differential entropies of adsorption plotted against the differential heat of adsorption gave the same straight line for all catalysts (see Fig. 3). The linear relationship between the heats and entropies of adsorption was considered to be interesting enough to be presented here as thermodynamic adsorption data of this nature is scarce in the literature. Assuming ideal gas behavior, the differential entropy, s_a (in J mol^{-1} K^{-1}), was calculated using the following equation [53]

$$\overline{s_a} = s_g - R\ln P - \frac{q_{st}}{T} \tag{A1}$$

where s_g is the reference entropy of the gas at the standard pressure of 1 atm (for hydrogen, s_g=139.22 J/(mol K) [54]), q_{st} the differential heat of adsorption obtained experimentally, P the equilibrium pressure, R the gas constant, and T the temperature, 403 K, at which the differential heat of adsorption takes place. The values for the slope and intercept of the line shown in Fig. 3 are −0.00166 K^{-1} and 163.5 J/(mol K), respectively. The standard errors for the slope and intercept are 0.000026 K^{-1} and 1.2 J/(mol K), respectively. It was noticed that, at higher heats of adsorption, a greater scatter occurred about the regression line. A possible explanation for the scatter is that, for high heats of adsorption, the adsorption is irreversible while Eq. (A1) strictly applies to reversible adsorption.

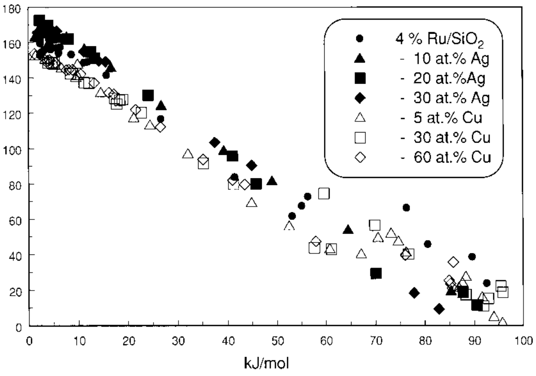

Fig. 3. Plot of differential entropies of adsorption against differential heats of adsorption. All data determined at 403 K.

The similarity in the variation of the differential entropy with differential heats displayed by all the catalysts suggests that the adsorbed hydrogen is mobile at all coverages and, consequently, there is no configurational difference between the catalysts. The results observed in Fig. 3 are analogous to, but not the same as, the compensation effect observed in kinetic studies [55].

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