Adsorption of Hydrogen, Carbon Monoxide, and Nitrogen on Rhenium(0001) and Copper Overlayers on Rhenium(0001)

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The interaction of hydrogen, carbon monoxide, and nitrogen with Re(0001) and with Re(0001) covered with submonolayer Cu has been studied by thermal desorption spectroscopy (TDS) and low-energy electron diffraction (LEED). The adsorption of H₂ on clean Re(0001) induces a 2 × 2 superstructure that can be produced by H₂ exposure over a wide temperature range (110-300 K). Cu deposition on Re(0001) induces a new hydrogen desorption state with a higher binding energy than that from bulk Cu. The population of this new hydrogen state is significantly reduced on the annealed Cu-Re(0001) surface and is believed to correlate with hydrogen adsorbed on the Cu overlayer perturbed by the Re substrate. Cu overlayers result in the attenuation of the H₂ desorption peak associated with the Re substrate. On a 4.6 ML (ML = monolayer) Cu-covered Re(0001) surface, a new desorption state at ~337 K is evident and is interpreted to arise from hydrogen desorption from 3-D Cu clusters. The TD spectrum of CO adsorbed on clean Re(0001) reveals four states with peak desorption temperatures at 175, 390, 961, and 1123 K. The initial adsorption of CO and annealing result in dissociation and leads to surface C and O. Subsequent CO adsorption on this C- and O-covered surface gives rise to two additional TDS features at ~280 and 358 K. Adsorption of CO at 115 K induces a 5 × 1 structure, which upon annealing to ~1000 K, produces another square structure with a lattice constant 7 times that of the Re(0001) surface. This structure is likely composed of a superlattice of C formed from the dissociation of CO upon the annealing. Adsorption of CO on a Re(0001) surface with varying amounts of Cu shows that at low Cu coverages (<2 ML), a new desorption state is present, with a corresponding binding energy higher than that for bulk Cu and lower than that for clean Re(001). This state is interpreted to correspond to CO adsorbed at Cu sites perturbed by the underlying Re. At higher Cu coverages (~5 ML), the CO TDS features are essentially the same as those found for bulk Cu. No new TDS states of nitrogen have been observed following nitrogen adsorption on Cu-covered Re. The TDS features from the Re substrate are greatly reduced by Cu deposition, consistent with Cu serving as a simple site-blocking agent to the adsorption and dissociation of nitrogen on Re.

1. Introduction

The structural, electronic, and chemisorptive properties of metal overlayers grown on single-crystal substrates have been the focus of considerable recent work. These metal overlayer systems are particularly exciting because they frequently demonstrate unique chemisorptive properties compared with either of the bulk metal components. For example, it has been found that CO on chemisorption of a monolayer Ni or Pd film on W(100) and W(110) has been found to form stable, uniform layers at a Cu coverage of 2 ML. (1) In contrast to this behavior, the bonding of CO on a W(110) Cu-covered Ni surface and is believed to correlate with hydrogen adsorbed on the Cu overlayer perturbed by the Re substrate. Cu overlayers result in the attenuation of the H₂ desorption peak associated with the Re substrate. On a 4.6 ML (ML = monolayer) Cu-covered Re(0001) surface, a new desorption state at ~337 K is evident and is interpreted to arise from hydrogen desorption from 3-D Cu clusters. The TD spectrum of CO adsorbed on clean Re(0001) reveals four states with peak desorption temperatures at 175, 390, 961, and 1123 K. The initial adsorption of CO and annealing result in dissociation and leads to surface C and O. Subsequent CO adsorption on this C- and O-covered surface gives rise to two additional TDS features at ~280 and 358 K. Adsorption of CO at 115 K induces a 5 × 1 structure, which upon annealing to ~1000 K, produces another square structure with a lattice constant 7 times that of the Re(0001) surface. This structure is likely composed of a superlattice of C formed from the dissociation of CO upon the annealing. Adsorption of CO on a Re(0001) surface with varying amounts of Cu shows that at low Cu coverages (<2 ML), a new desorption state is present, with a corresponding binding energy higher than that for bulk Cu and lower than that for clean Re(001). This state is interpreted to correspond to CO adsorbed at Cu sites perturbed by the underlying Re. At higher Cu coverages (~5 ML), the CO TDS features are essentially the same as those found for bulk Cu. No new TDS states of nitrogen have been observed following nitrogen adsorption on Cu-covered Re. The TDS features from the Re substrate are greatly reduced by Cu deposition, consistent with Cu serving as a simple site-blocking agent to the adsorption and dissociation of nitrogen on Re.

2. Experimental Section

The experiments were carried out in a conventional UHV chamber equipped with LEED, double-pass cylindrical mirror analyzer for AES, and a mass spectrometer for TDS. This system has been described in detail previously. The sample was spot-welded to two 0.5-mm Ta wires that allow resistive heating to 1500 K and sample cooling to 110 K. A W/5% Re-W/26% Re thermocouple was spot-welded to the sample edge. The Re(0001) surface was cleaned by heating to 1200 K in O₂ (10⁻² Torr) for several hours and then flashing under vacuum to 1900 K. After this cleaning process, AES indicated an impurity free surface (<1 atom % C, S), and LEED showed a sharp hexagonal pattern with a low background intensity. Cu deposition was performed by resistively heating a filament wrapped with a high-purity Cu wire. Prior to each Cu deposition, the source was degassed extensively. AES detected no impurity accumulation during metal deposition.

3. Results and Discussion

3.1. Hydrogen Adsorption on Re(0001)

Over the past decade, there have been a number of studies on the interaction of hydrogen dimensionsal clusters with the (111) plane parallel to the substrate surface. The details of the Cu overlayer growth on Re(0001) have been published elsewhere.

In this paper, we report the interaction of hydrogen, carbon monoxide, and nitrogen with clean Re(0001) and with the Cu-Re(0001) system studied by TDS and LEED. The emphasis of this work has been to address the unique properties of the Cu-Re(0001) system toward the adsorption of key probe molecules. Also we present new relevant data for the adsorption of hydrogen and carbon monoxide on clean Re(0001).

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~1 langmuir and appear to saturate at ~2 langmuirs. Here, we will characterize this LEED pattern as a 2 x 2 structure, although the missing spots at \((m + 1/2, n + 1/2)\) yield an incomplete 2 x 2 lattice. The fractional spots are sharp with weak intensities. Annealing the 2 x 2 phase to ~300 K, then cooling to 110 K, does not change the pattern. Heating the 2 x 2 phase to 510 K results in its disappearance due to desorption of H₂. The H_ads coverage of the 2 x 2 structure corresponds to 0.25 monolayer (ML).

H₂ exposures were also carried out at substrate temperatures of 193, 260, and 300 K. The 2 x 2 pattern was observed with H₂ adsorption at all three temperatures with subsequent cooling of the exposed surface to <200 K. The formation of the 2 x 2 phase of H_ads on Re(0001) was not observed in previous studies of H₂ adsorption at 300 K. This discrepancy regarding the observation of the 2 x 2 phase is believed to be caused by Debye-Waller effects.

In a study of the 2 x 1 phase of H_ads on a Pd(110) surface, the LEED intensity of the half-order beams decreased considerably upon heating the 2 x 1 phase from 130 to 210 K. At 230 K, the half-order spots were hardly discernible. In the present work, heating of the 2 x 2 phase of H_ads on Re(0001) to 300 K results in its disappearance. However, upon cooling to 110 K, the 2 x 2 pattern reappears. The disappearance of the 2 x 2 structure at 300 K then apparently arises from thermally induced disorder of the H_ads with an increase in sample temperature rather than from a change in the surface coverage of H_ads.

The disagreement of the present work with previous studies might also be caused by imperfections of the substrate surface. It has been proposed that H_ads first adsorbs on Re(0001) at defect sites. The subsequent population of H_ads at other surface sites arises via migration of H_ads from these defect sites. However, there is no evidence that the sample used in the present studies had a higher surface concentration of defects than the Re samples employed in the previous work.

### 3.2. Hydrogen Adsorption on Cu/Re(0001)

#### Figure 1.

TD spectra of hydrogen from Re(0001) following hydrogen exposures of (a) 0.05, (b) 0.10, (c) 0.30, (d) 0.60, and (e) 2.0 langmuirs. (f) TD spectra of H₂, D₂, and HD from Re(0001) after exposure to ~0.3 langmuir of H₂ and then ~1 langmuir of D₂ at 110 K. The heating rate for all TDS was ~10 K/s.

The mass 2 TD spectra from a Re(0001) surface following various exposures of H₂ at 110 K. The TD spectra show peak maxima that vary from ~575 K for a 0.05-langmuir (1 langmuir = 10⁻⁶ Torr-s) H₂ exposure (Figure 1a) to 490 K for a 2-langmuir exposure (Figure 1e). The 2-langmuir exposure results in saturation of the H_ads TD spectra.

The TD spectrum of Figure 1e is in general agreement with that reported by Ducros et al. However, in addition to the primary feature at ~490 K, a small shoulder at ~420 K is also evident, which appears only at an intermediate hydrogen coverage (Figure 1c,d). This shoulder is not apparent in the spectra obtained subsequent to either high exposure (Figure 1e) or low exposure (Figure 1a) of H₂. A shoulder found by Kelly et al. at ~240 K was not observed in this work. Figure 1a shows that the peak maximum shifts toward lower temperatures as the adsorbed hydrogen (H_ads) coverage is increased. This is consistent with second-order kinetics arising from a recombination of atomic hydrogen during the desorption.

Deuterium isotope exchange experiments to verify atomic hydrogen recombination were carried out, and the results of one of these experiments (Figure 1f) are inset in Figure 1. The Re(0001) surface at 110 K was first exposed to ~0.3 langmuir of H₂ and then to ~1 langmuir of D₂. Figure 1f indicates clearly that the desorption features in Figure 1a-e correspond to atomic hydrogen recombination. If we assume that the desorbed molecules of H₂, D₂, and HD are accurately represented by the corresponding areas in Figure 1f, an equilibrium constant of 4.5 can be derived for the isotope exchange reaction, consistent with complete exchange.

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Figure 2. (a) LEED pattern of the 2 x 2 phase of $H_{ads}$ on Re(0001) and (b) a schematic drawing of its structure. This pattern was induced by a 2-langmuir exposure of $H_2$ at 110 K. The primary energy of the incident electrons was 284 eV. In b, the filled circles correspond to integral spots, the open circles to $H$-induced spots, and the dashed circles to missing spots.

Figure 3. (a) TDS of $H_2$ from a 1.1-ML Cu-covered Re(0001) surface following a ~20-langmuir $H_2$ exposure. The Cu overlayer was unannealed and deposited at 115 K. (b) TDS of $H_2$ from a 1.1-ML Cu-covered Re(0001) surface following a ~20-langmuir $H_2$ exposure. The Cu overlayer, annealed to 900 K, was deposited at 115 K. (c) TDS of $H_2$ from a clean Re(0001) surface following a ~20-langmuir $H_2$ exposure at 115 K.

Figure 4. TDS of $D_2$ from a Re(0001) surface with varying amounts of unannealed Cu. The Cu coverages are (a) 0.2, (b) 0.6, (c) 1.8, (d) 4.6, and (e) 0 ML. The $H_2$ exposure in each case was ~20 langmuirs and was carried out at 115 K.

Figure 5. TDS of $D_2$ from a Re(0001) surface with varying amounts of Cu annealed to 900 K. The Cu coverages are (a) 0.2, (b) 0.6, (c) 1.8, and (d) 4.6 ML. The $H_2$ exposure in each case was ~20 langmuirs and was carried out at 115 K.

higher than the 300 K feature of $H_2$ from Cu, suggests that the overlayer Cu to which the hydrogen of the $\gamma_1$ state is bonded is significantly altered by its interaction with the underlying Re. Hydrogen is therefore bonded to the overlayer Cu more strongly than to bulk copper but considerably weaker compared to hydrogen on clean Re(0001) ($E_\gamma$ for the $\beta$ state of hydrogen on clean Re(0001) is estimated to be ~32 kcal mol$^{-1}$). It is also possible that the hydrogen of the $\gamma_1$ state is associated with hydrogen adsorbed at mixed Cu-Re sites at the perimeter of 2-D Cu islands.

The last point to note in Figure 3 is that for the annealed Cu-Re surface, the population of hydrogen in the $\gamma_1$ state is significantly reduced. Annealing will undoubtedly lead to a decrease in the defect population, and, perhaps, to the nucleation of 2-D islands with larger effective diameters than for the unannealed surface. Since the population of the $\gamma_1$ state in Figure 3 is determined by the kinetics of hydrogen diffusion from free Re sites to the Cu overlayer, larger Cu islands will lead to a significant reduction of the effective Cu perimeter and thus will inhibit the population of the $\gamma_1$ state.

Figure 4 shows the desorption spectra of $D_2$ from Re(0001) with varying amounts of Cu, unannealed, following ~20 langmuirs of $D_2$ exposure at 115 K. As the Cu coverage is raised from 0.2 to 1.8 ML, the $\gamma_1$ state at ~390 K becomes increasingly populated. At a high Cu coverage (~4.6 ML), a new state ($\gamma_2$) appears at ~337 K with $E_\gamma$ ~20 kcal mol$^{-1}$. For a $D_2$ exposure to a Cu-Re(0001) surface annealed to 900 K, the $\gamma_1$ states become much less discernible (Figure 5). On the unannealed surface, the intensity of the desorption peak from clean Re(0001) decreases as the Cu coverage increases. The overlayer Cu therefore blocks the Re sites for $D_2$ adsorption, as observed for hydrogen adsorption on Cu-covered Ru(0001).#23 The $\gamma_2$ state in Figure 4e may be

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Figure 6. TD spectra of CO from a clean Re(0001) surface following varying exposures at 115 K: (a) 0.3, (b) 0.6, (c) 0.8, (d) 1, and (e) 1.5 langmuirs.

Figure 7. TD spectra of CO from Re(0001) on a C- and O-covered surface following an ~2-langmuir CO exposure at 115 K. The C and O were created (a) by exposure to 2 langmuirs of CO at 115 K and then annealing the surface to 1000 K and (b) by exposure to 2 langmuirs of CO at 606 K.

Figure 6 shows the CO TD spectra following varying exposures of CO at 110 K. The spectra show four peaks located at 175, 390, 561, and 1123 K and labeled as $\alpha_1$, $\alpha_2$, $\beta_1$, and $\beta_2$, respectively. Each TD spectrum was collected following exposure to CO after first flashing the Re(0001) to 1900 K to produce a Re(0001) surface free of C and O. Figure 6a indicates that, at low coverage, CO particularly dissociates at room temperature and recombines as CO at $T > 900$ K. Figure 6 also shows that the dissociated CO state saturates with a ~0.6-langmuir CO exposure at 115 K. The $E_p$ for $\alpha_1$, $\alpha_2$, $\beta_1$, and $\beta_2$ are estimated to be 10.1, 23.2, 58.9, and 69.2 kcal mol$^{-1}$, respectively.

The present work differs in several respects to the previous studies: (1) The desorption spectra near room temperature reveals only one state (the $\alpha_1$). (2) Two $\beta$ states are observed at temperatures $>900$ K. (3) One TD feature ($\alpha_2$) at temperature ~2 K has been detected. The $\alpha_1$, likely corresponds to physically adsorbed CO that has been identified previously by XPS and UPS. In contrast, the multiple states near 300 K, we will show, correlate with the presence of C and O surface impurities.

Figure 7 shows the desorption spectra of CO from Re(0001) with surface C and O impurities. The surface C and O in Figure 7a was produced by first exposing the Re(0001) surface to 2 langmuirs of CO at 110 K and followed by an anneal to 1000 K. The annealed surface (with ~8% atomic C, estimated from the AES spectrum) was then cooled to 110 K and reexposed to 2 langmuirs of CO. The TD spectrum then acquired (Figure 7a) exhibits additional peaks at 280 and 358 K, compared to CO desorption from clean Re(0001) (Figure 6). These two CO desorption states have been previously observed. Heating a CO-covered Re(0001) surface to 1000 K leads to dissociation of CO and the formation of surface C and O, as shown by previous XPS and UPS and HREELS studies. The AES line shape of C on the annealed surface in the present study also indicates that the carbon is of the "carbide" type. The above experiment clearly shows that the $\alpha_2$ and $\alpha_3$ states of Figure 7 are associated with a presence of surface impurities of C and O. The $E_p$ for the $\alpha_2$ and $\alpha_3$ states are estimated to be 16.5 and 21.2 kcal mol$^{-1}$, respectively.

To further demonstrate this, the following experiment was carried out: First, the surface was exposed to 2 langmuirs of CO at 610 K where CO is known to adsorb on Re(0001) dissociatively, the surface was then cooled to 110 K and reexposed to 2 langmuirs of CO, and the TD spectrum measured (Figure 7b). As in Figure 7a, three desorption states near room temperature are evident. This experiment also concludes that the $\alpha_2$ and $\alpha_3$ are related to the presence of surface C and O. Furthermore, the bonding of CO to the C- and O-contaminated Re(0001) in the $\alpha_2$ and $\alpha_3$ states apparently is weakened relative to CO on the clean Re(0001) surface (the $\alpha_1$ state).

Two ordered structures have been observed on Re(0001) following a 2-langmuir CO exposure and a subsequent anneal. In Figure 8 is shown the 5 × 1 LEED structure, together with a...
Figure 8. (a) $5 \times 1$ LEED pattern of CO on Re(0001) and (b) its schematic drawing. The Re(0001) surface was first exposed to 3 langmuirs of CO at 115 K and then annealed to 340 K. The primary energy of the electron beam was 225 eV. In b, the filled circles correspond to integral spots and the open circles to CO-induced spots.

Figure 9. (a) LEED pattern from dissociated CO and (b) its schematic drawing. The Re(0001) was exposed to 3 langmuirs of CO at 115 K and then annealed to 1000 K. $E_p = 235$ eV. In b, the filled circles correspond to integral spots and the open circles to fractional order spots.

schematic drawing of the pattern, induced by CO adsorption at 110 K and a subsequent anneal to 300 K. The fractional order spots are weak and diffuse at 110 K, probably due to a low mobility of CO at this temperature. Heating the $5 \times 1$ phase to room temperature sharpens the fractional spots. When the $5 \times 1$ structure is annealed further to 400 K, the fractional spots disappear, leaving lines along the (1010) direction. The lines are an indication of one-dimensional disorder of adsorbates along this direction. Annealing to $\sim$1000 K produces a pattern shown in Figure 9. This pattern appears to be square with the lattice constant $8a$ where $a$ is the lattice constant of the Re(0001) surface. Oxygen is known to form a $2 \times 2$ structure on Re(0001), thus, the square pattern likely is associated with surface carbon rather than oxygen, although it is possible that oxygen may form a different surface structure in the presence of surface C. This pattern disappears upon heating the surface to 1200 K, the temperature at which recombination of C and O occurs as the CO states. The LEED patterns observed in this work differ from the previously reported $\sqrt{3} \times 4$ structure found following CO adsorption at 110 K and the $(\sqrt{2} \times 3)R30^\circ$ structure observed following CO exposure at 550 K. The reason for this disagreement is not clear.

3.4. CO Adsorption on Cu/Re(0001). The TD spectra of CO from Re(0001) with varying Cu coverages, deposited at 115 K, are shown in Figures 10 and 11. CO exposure was carried out at a substrate temperature of 115 K following Cu deposition (without a subsequent anneal). For Cu coverages below 0.3 ML, the intensity of the $\alpha_4$ state from Re(0001) is gradually attenuated, a new state $\gamma_1$ is $\sim$15.9 kcal mol$^{-1}$ at a Cu coverage of 0.8 ML. A new peak, labeled as $\gamma_1$, begins to appear at $\sim$220 K. As the Cu coverage increases above 0.8 ML, the $\gamma_1$ state gradually becomes dominant and its peak maximum shifts to a lower temperature.

The TDS of CO from Cu(110), reported previously, consists
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Figure 11. TD spectra of CO from Cu-Re(0001) surfaces following a ~20-langmuir CO exposure at 115 K. Cu coverages are (a) 0, (b) 0.3, (c) 0.5, (d) 1.3, and (e) 2.7 ML.

Figure 12. TD spectra of N₂ between 100 and 300 K from unannealed Cu-Re(0001) surfaces following a ~20-langmuir N₂ exposure at 115 K. Cu coverages are (a) 0, (b) 0.3, (c) 0.5, (d) 1.3, and (e) 2.7 ML.

of a single peak located at 200–220 K. The activation energy of the desorption was found to be coverage-dependent (Eₐ = 12.9 kcal mol⁻¹ for ~0.3 ML of CO), and the sticking coefficient was constant for CO coverages between 0 and 0.5 ML.²⁹ ³⁰ The γ₁ state then, found in the present study for the 5.2-ML Cu-covered Re(0001), is consistent with the previous work for bulk Cu. The activation energy for the γ₁ is estimated to be 13.0 kcal mol⁻¹ for the peak at 222 K and 9.1 kcal mol⁻¹ for the peak at 157 K. The decrease in the activation energy with Cu coverage may either be due to a reduction in the substrate perturbation of the overlayer Cu or to the overall increase in CO surface coverage.

The γ₂ desorption state at ~277 K is evident in Figures 11 and 12 at low Cu coverages. This state may arise from CO adsorption on a Cu overlayer that binds CO more weakly compared to the clean Re(0001) surface (Figure 6) and more tightly than to a surface of bulk Cu.²⁹ ³⁰ As the Cu coverage increases, the adsorption sites on the mixed perimeter sites become less prevalent and the population of the γ₂ state is correspondingly reduced through a kinetic effect as discussed in the desorption of hydrogen from Cu-Re(0001) in section 3.2.

Figure 11 also shows that the desorption states (α₂, β₁, and β₂) from the Re(0001) substrate are still apparent even with Cu coverages as high as 5.2 ML. This is probably caused by the formation of 3-D clusters during the deposition and heating. If this is the case, the accessible surface sites of Re likely are formed below 220 K, the temperature at which CO has completely desorbed from Cu. This result is consistent with the AES results,

indicating 3-D nucleation of Cu at 115 K.¹¹

3.5. Nitrogen Adsorption on Cu-Re(0001). In a previous study, we have shown that the TD spectrum of N₂ from Re(0001) consists of two peaks, one at ~160 K, corresponding to molecularly adsorbed N₂, and a second between 900 and 1300 K, that relates to the recombination of dissociated nitrogen. In this work, two ordered surface structures were observed by LEED. The low-temperature state at 160 K is associated with a 4 × 1 structure. Heating this 4 × 1 phase to >300 K dissociates N₂ to form the 2 × 2 structure.²³

It has been established that nitrogen does not dissociatively chemisorb on Cu surfaces [ref 32 and references cited therein]. However, atomic nitrogen, generated by e⁻-beam dissociation of molecular nitrogen, is found to adsorb on Cu and form ordered structures.²² ²³

In Figures 12 and 13 are shown the TD spectra of N₂ from Re(0001) with varying coverages of Cu deposited at 115 K. The N₂ exposure was carried out at 115 K on the unannealed Cu overlayer. For reference, the TD spectrum for N₂ adsorption on clean Re(0001) is presented in Figures 12a and 13a. The desorption spectra for the Cu-covered surfaces show two peaks at ~170 and 1220 K. (No desorption peaks are observed between 300 and 1000 K.) Compared to clean Re(0001), it is noteworthy that no new peak is induced by Cu deposition, indicating that nitrogen does not spill over from the Re to the Cu overlayers. Also, importantly, the population of both the α and β states are considerably reduced by the presence of Cu. At a Cu coverage of 2.7 ML, the β state is barely discernible from the background. Obviously, the Cu overlayers block the Re surface sites for nitrogen adsorption and dissociation. At a Cu coverage of 2.7 ML, the α-state population is still ~20% that of clean Re(0001). These results suggest that the site requirements on Re(0001) for N₂ dissociation are more demanding than the site requirements for molecular adsorption.

4. Summary

(1) For H₂ on clean Re(0001), the TD spectrum shows one peak that follows second-order kinetics. Isotope exchange experiments confirm that this TDS feature arises from the recombinination of dissociated hydrogen. Exposure of H₂ at 110 K induces a LEED pattern, described as a 2 × 2 structure of H on Re(0001).

(2) The TD spectrum of H₂ from a Re(0001) surface covered by Cu reveals a new hydrogen desorption state with a higher binding energy than that from a surface of bulk Cu. This state is attenuated by annealing the Cu prior to hydrogen adsorption and likely corresponds to hydrogen desorption from overlayer Cu sites perturbed by the underlying Re substrate. For a Cu coverage of ~4 ML, a new desorption state at ~337 K is induced, very likely corresponding to desorption of hydrogen from 3-D Cu clusters.

References:

Dissociation of CO by annealing.

square structure with a lattice constant 7 times that of the Re-

resorption of CO on Re(0001) at

lying between that for CO on bulk Cu and that for CO on clean

adsorption reveals a new desorption state that has a binding energy
to the substrate lattice and likely arises from C produced via

features observed in previous work between 280 and 358 K cor-

Prediction of Low Occupancy Sorption of Alkanes in Silicalite

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Alkane sorption in a pentasil zeolite has been studied through molecular simulations. A series of alkanes, including methane, n-butane, and three hexane isomers, were studied in silicalite by using a detailed atomistic representation that allows for torsion around skeletal bonds. Statistical mechanical principles have been employed to predict sorption equilibria at low occupancy. Henry's constants and isosteric heats of sorption were calculated through the evaluation of configurational integrals with a Monte Carlo integration scheme. Results are in good agreement with experiment. The spatial distribution of sorbate molecules within the pore network, as well as perturbations to their conformation due to confinement in the pores, were determined via Metropolis Monte Carlo algorithm. Simulations of sorbate spatial distributions show that linear alkanes, such as n-butane and n-hexane, prefer to reside in the channels and avoid the channel intersections; on the contrary, bulky side groups in branched alkanes, such as 2- and 3-methylpentane, force these molecules toward the more spacious channel intersections. An analysis of sorbate conformations indicates that molecules are perturbed from the ideal gas dihedral angle distribution toward the more linear trans states when confined in silicalite.

Introduction

Zeolites are crystalline aluminosilicates consisting of covalently bonded networks of SiO4 and AlO4 tetrahedra arranged in such a way as to form a network of connected cavities and channels with dimensions commensurate with molecular diameters (3–10 Å). Because of their unique structure, zeolites have found wide application in processes such as adsorption, ion exchange, and catalysis.6–8 For the optimization of many of these applications, knowledge of the effects of zeolite structure and composition on adsorptive properties is essential. While such properties can be established experimentally, it would be highly desirable to develop theoretical methods for predicting zeolite adsorption behavior, so as to facilitate selection and optimization of zeolites for a given purpose. An attractive approach to this goal is the use of computer simulation based on an atomistic description of sorbate–zeolite interactions.

Previous atomistic models of molecular sorption into narrow pores have been of two types: those dealing with idealized pore systems and those dealing with zeolites or similar cage-like structures. Simulation techniques, including molecular dynamics, grand canonical ensemble Monte Carlo, and Gibbs ensemble Monte Carlo among others, have been employed to study phenomena such as fluid structure, phase transitions, hysteresis effects, and wetting2-14 for simple Lennard-Jones fluids in idealized pores. Theoretical studies15,16 involving the application of mean field approximations have also been employed to examine the phase behavior of fluids in micropores.

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Simulation methods have also been used to investigate sorption in zeolites. Grand canonical ensemble Monte Carlo simulations have been employed to determine sorption equilibria over a full range of occupancies in model zeolite structures by Soto and others.1-3


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