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Ultrahigh Vacuum Temperature-Programmed Desorption of CO and D_2 from Silica-Supported Ruthenium: Evidence for Spillover of D_2

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The ultrahigh vacuum temperature-programmed desorption of D_2 and CO from silica-supported Ru was studied. Features attributed to D_2 spillover were observed for doses at temperatures above 323 K. The CO desorption spectra were broad and indicated a very heterogeneous distribution of adsorption sites but no spillover. The desorption of predosed D_2 from coadsorbed D_2 + CO showed that CO displaces weakly bound D(a) causing the D_2 desorption peak to shift to higher temperatures. Preadsorbed D(a) caused no changes in the desorption of CO. A small amount of CD_4 desorbed when CO and D were coadsorbed. The potential catalytic role of the spillover D(a) is discussed.

INTRODUCTION

Ruthenium is one of the most studied methanation and Fisher–Tropsch (F-T) catalysts (*1–9*) because Ru catalysts produce mainly hydrocarbons, particularly heavier hydrocarbons and little, if any, oxygen-containing organics. CO activation is an important part of the reaction mechanism and has been the subject of a large number of investigations. In studies of the reaction mechanism, evidence for various intermediates have been developed using *in situ* IR and kinetic methods (*20–24*). Two basic mechanisms have been proposed: (1) hydrogenation of molecularly adsorbed CO followed at some point by subsequent dehydrogenation (*25*) or (2) dissociation of CO followed by hydrogenation of carbon and oxygen fragments (*26*). It is generally agreed that the dissociative adsorption of CO is important for the first step in the reaction.

The measurements of Ru surface areas using H_2 and CO chemisorptions do not agree and the existence of multiple-CO's coordinated to a single Ru atom has been suggested as one possible reason (*10–12*). Indeed, several types of adsorbed CO species have been observed by IR. Several models have been proposed, including a multiple-coordination model (*13, 14*), a ruthenium oxidation state model (*15–17*), and a particle size model (*18*). Recently, Chen and White (*19*) reinvestigated the CO/Ru system and proposed that coadsorbed species (e.g., OH, O, and Cl) play an important role in the character of the CO adsorption and the resulting IR spectra.

A few papers have dealt with the behavior of H(a) on supported Ru catalysts. Bossi *et al.* (*27*) reported that hydrogen had a strong inhibiting effect on the CO isotope exchange reaction. Yamasaki *et al.* (*28*) observed hydrogen exchange between molecular H_2 and methylene ($>CD_2(a)$) and methyl($-CD_3(a)$) in the absence of inhibition by adsorbed CO. Recently, Miura *et al.* (*29*) reported that the surface concentration of CO on Ru/SiO_2 increased by a factor of about 3 in the presence of H_2. Chen and White also observed that the CO infrared absorption intensities on Ru/SiO_2 tended to increase in the presence of coadsorbed H_2 (*30*).

The role of adsorbed H on supported Ru catalysts is thus of continuing interest. In this paper we report on the desorption of CO and D_2 from Ru/SiO_2 catalysts by UHV temperature-programmed desorption (TPD). In addition to a comparison of sup-

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ported and unsupported Ru, we report D(a) spillover on Ru catalysts.

EXPERIMENTAL

A 4.1 wt% Ru/SiO_2 catalyst was prepared by impregnating Cab-O-Sil, grade HS-5 (Cabot Corp.), with an aqueous solution of ruthenium trichloride. The slurry was air-dried at 373 K for 16 h.

The experiments were carried out in a two-chamber (preparation and analysis) ultrahigh vacuum system described in a previous paper (*31*). The base pressure of both chambers was 2×10^{-9} Torr after bake out, and the working pressure in the preparation chamber was 2×10^{-8} Torr after dosing.

The air-dried powder sample was mixed with H_2O to form a slurry which was applied on the central 0.5-cm section of a W wire loop. After drying, the sample (200 μg) was outgased in the preparation chamber, heated at 577 K for 15 min, and then was reduced in 0.1 Torr H_2 at 577 K for 0.5 h. This relatively low reduction temperature was chosen to minimize sintering, but does not completely reduce Ru. This procedure also leaves Cl on the surface. Finally, the sample was evacuated at 577 K and cooled to room temperature. Prior to TPD experiments, the sample was flash-heated to 700 K to remove species accumulated from the background gases. TPD spectra were obtained by resistively heating the W wire at a linear rate of 4 K/s with a temperature programmer. As previously noted (*31*), the contributions from the background (i.e., with SiO_2 with no Ru) were negligible. Thus, contributions to the hydrogen assigned as spillover cannot be due to desorption from the W support wire, unless that H migrated from Ru to SiO_2 to W, which we consider unlikely.

CP grade lecture bottles of D_2, H_2, and CO were purchased from Linde. All gases were introduced to the chamber through separate liquid-nitrogen-trapped inlet lines.

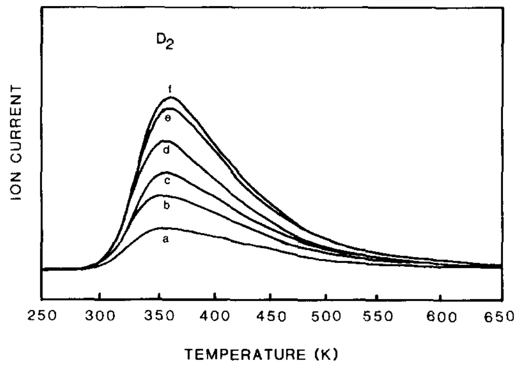

FIG. 1. TPD of D_2 adsorption on Ru/SiO_2 at 1.0×10^{-5} Torr and 305 K for various dose times: (a) 20, (b) 50, (c) 100, (d) 200, (e) 500, and (f) 800 s.

RESULTS AND DISCUSSION

Deuterium

D_2 TPD spectra after exposure (1.0×10^{-5} Torr) at 303 K and cooling under vacuum to 140 K are shown in Fig. 1 as a function of D_2 exposure time. A single desorption peak is observed with a peak temperature (360 K) that is independent of dosing time. We expect associative recombination and desorption of D_2 to be second order and thus the TPD peak should shift to lower T as coverage increases. That it does not suggests first-order kinetics. An activation energy of desorption of 21.5 kcal/mol was calculated based on first-order kinetics, using a preexponential factor of 10^{13} s^{-1}. This is slightly higher than the results (17.5 kcal/mol) from single-crystal Ru (*35*). H_2 or D_2 desorption from the Ru(001) surface shows two desorption peaks (322 and 361 K) that are well-characterized by second-order kinetics (*32–34*). Desorption from a Ru(110) surface shows a single peak (~360 K) which obeys first-order kinetics (*35*). Our results for Ru/SiO_2 are not inconsistent with these results. We expect the Ru particles to expose a range of crystallite faces and the desorption spectrum will thus be an average over all of them with the added complexity of a large number of steps and kinks. Empirically, our results resemble most closely those for the (110) face. Regardless of the kinetic order, all these Ru samples give D_2 desorption at very close to the same T. This indicates that differences due to Cl and/or incompletely reduced Ru are minimal.

In another set of experiments, the sample was exposed to D_2 at 1.0×10^{-5} Torr for 100 s at various temperatures ranging from 305 to 573 K. After evacuation and cooling to 140 K, TPD (Fig. 2) shows no significant intensity below the adsorption temperature but important increases in desorption as the exposure temperature increases. This thermally activated process is ascribed to spillover from Ru particles to the SiO_2 support. The relative amount of D_2 adsorbed in the activated process was calculated from the data of Fig. 2 using spectrum a as a reference (i.e., assuming there is no spillover at 306 K). As the exposure temperature increases there is a steady growth in the additional amount of D_2 desorbed (Fig. 3). This is similar to our previous results for Pt/TiO_2 (*31*).

In considering these spectra, it is important to account for the possibility that a kinetically slow approach to equilibrium adsorption at 198 K could account for the data of Fig. 3. We do not believe this is the case for the following reasons. (1) There is no evidence for high temperature desorption peaks of H_2 (like those in Fig. 2) from either single crystal or supported Ru. (2) The data of Fig. 1 shows no trend toward the preferential filling of more strongly bound activated adsorption sites as the exposure time is increased by a factor of forty. Thus, even though the approach to full thermodynamic equilibrium may be relatively slow (Fig. 1, curves e and f, indicate that under our conditions there is very little coverage increase between 500- and 800-s exposure), the data of Fig. 3 cannot be understood in this way.

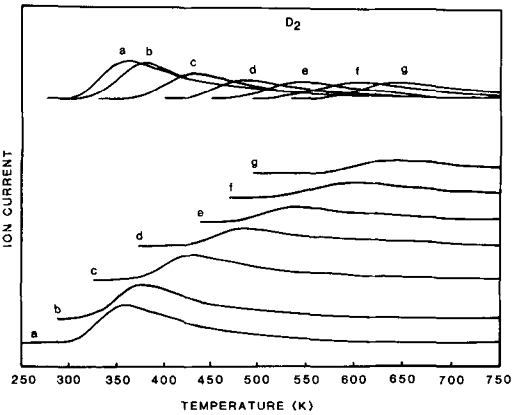

FIG. 2. TPD of D_2 adsorption on Ru/SiO_2 at 1.0×10^{-5} Torr and 100 s for various dose temperatures: (a) 305, (b) 323, (c) 373, (d) 423, (e) 473, and (f) 523, and (g) 573 K.

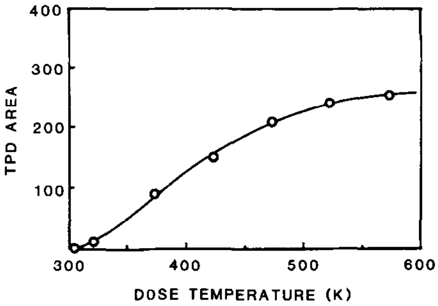

FIG. 3. Relative amount of spillover as a function of dose temperature.

It is generally accepted that there is insignificant hydrogen activation on irreducible oxides (e.g., Al_2O_3, SiO_2, MgO, etc.) unless metal is present (*36*). Kramer and Andre (*37*) and Chen and White (*38*) observed the amount of the activated hydrogen was negligible on Al_2O_3 without metal. Bianchi *et al.* reported that there was no activated hydrogen on SiO_2 even for H_2 exposures at 430°C for 12 h (*39*). Thus we expect that direct D_2 adsorption on SiO_2 is negligible and that gas-phase D_2 interacts with the dispersed Ru particles. The former has been confirmed in blank experiments in our apparatus. Further support comes from the fact that H_2 chemisorption at 298 K has proven to be an acceptable method for determining the Ru dispersion (*40*).

We propose that the activated process reflected in the data of Fig. 3 is due to the migration of D atoms from Ru to SiO_2. Since the amount is a steadily increasing function of the exposure temperature, this spillover must be considered under methanation and/or F-T conditions.

Carbon Monoxide

TPD spectra taken from Ru/SiO_2 exposed to CO at 305 K and cooled to 140 K are shown in Fig. 4. For all exposures the spectrum is broad, indicating several CO adsorbed states and suggesting a very heterogeneous surface. The existence of several kinds of adsorbed CO (at least three states) is in good agreement with previous work (*19*). Although the data do not permit detailed kinetic analysis since separate states cannot be resolved, first-order kinetics, as generally observed on single-crystal Ru, provides an adequate description.

The sample also was exposed at various temperatures ranging from 305 to 472 K (Fig. 5). Unlike D_2, no activated desorption was observed, and we conclude that there is no spillover. Some CO_2 desorption was observed in these experiments. This indicates dissociative adsorption of CO followed by reaction with a second CO to form the product which desorbs. This is commonly observed and is one route to surface carbon (*1*). The amount of CO_2 desorbed is ca. 0.01 of the amount of CO desorbed and the desorption is broad (350–600 K) and peaks at 500 K.

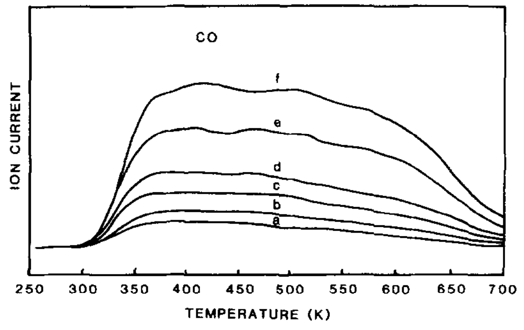

FIG. 4. TPD of CO adsorption on Ru/SiO_2 at 1.0×10^{-5} Torr and 306 K for various dose times: (a) 20, (b) 50, (c) 100, (d) 200, (e) 500, and (f) 800 s.

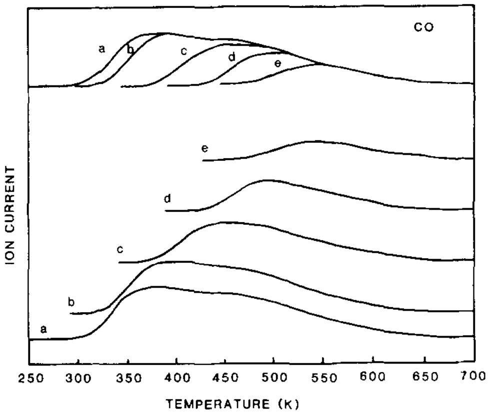

FIG. 5. TPD of CO adsorption on Ru/SiO_2 at 1×10^{-5} Torr and 100 s for various temperatures: (a) 306, (b) 323, (c) 372, (d) 423, and (e) 472 K. Upper part superimposes curves from lower part.

In other work, focused on elucidating the rate-determining step for CO activation, TPD has been used. Miura *et al.* (*29*) obtained three CO desorption peaks from Ru/SiO_2 (peak temperatures were 405, 473, and 698 K). McCarty and Wise (*41*) observed a broad desorption spectrum (~350–700 K) from Ru/Al_2O_3 and, on the basis of isotope exchange, concluded that reversible CO dissociation was significant. Two CO desorption peaks (~400 and 600 K) were observed by Low and Bell (*22*) on Ru/SiO_2 and by Zagli and Falconer (*42*) on Ru/SiO_2. The relative intensities of the TPD peaks are not consistent in these studies indicating that sample preparation variables are not all under adequate control. In the absence of direct evidence, several explanations have been proposed to account for these results, including metal dispersion (*43*), surface defects (based on single-crystal experiments) (*44*) and the water-gas shift reaction from H_2O contamination (*21*). Based on single-crystal results, there is general agreement that the high-temperature desorption of CO arises from the recombination of dissociated (or sideways bonded) CO. There are two interpretations for the lower temperature peaks, molecularly (*22*) or dissociatively (*41*) adsorbed CO. Generally, the evidence points to molecularly adsorbed CO. Unfortunately, we could not clearly distinguish these adsorbed states. Our observation of CO_2 desorption clearly indicates dissociation and the broad CO desorption indicates a very heterogeneous distribution of particle sizes and morphologies.

CO on Samples Precovered with D

Exposure of CO onto a surface exposed to varying amounts of D_2 at 305 K and 1.0×10^{-5} Torr was investigated. For D_2 dose times between 100 and 1000 s, there was no change in the CO desorption peak area or peak shape. Even D_2 exposure at 1.0×10^{-4} Torr did not alter the CO desorption. These results show that the CO is desorbing from the same states throughout and these are not altered by the presence of preadsorbed hydrogen, in good agreement with the data from Ru(110) (*35*) and Ru(001) (*32*).

Figure 6 shows how the desorption of D_2 is altered by postdosed CO. The shift to higher temperatures is clearly the result of displacement of D_2 into the gas phase by CO during CO exposure. Moreover, these spectra indicate a heterogeneous distribution of hydrogen desorption energies consistent with the above discussion of a heterogeneous distribution of particle morphologies. These results indicate a repulsive interaction between CO and D which destabilizes D(a) (on Ru at these temperatures and exposures) causing it to recombine and desorb. In other work, both attractive (*35, 45*) and repulsive (*32, 46*) interactions have been reported.

A very small amount of CD_4 was detected in desorption when CO and D were coadsorbed. The peak temperature was ca. 425 K and the peak area was 0.004 of the CO desorption. No hydrocarbon formation on Ru/SiO_2 at room temperature has been reported by Rabo *et al.* (*23*) and by Kobori *et al.* (*47*). Our results are consistent with this.

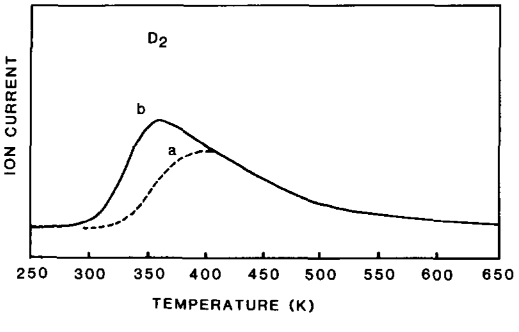

FIG. 6. TPD of D_2 adsorbed on Ru/SiO_2 after doses of 1×10^{-5} Torr, 305 K, and 100 s: (a) D_2 followed by CO postdose at 1×10^{-5} Torr, and 305 K for 150 s, and (b) D_2 without CO postdose.

Based on results for unsupported Ru, Ekerdt and Bell (*48*) and Kobori *et al.* (*47*) proposed that the hydrocarbon species were formed on and desorbed from Ru particles of Ru/SiO_2. However, King (*24*) proposed that the support played a significant role. Since unsupported Ru is more selective toward methane production than supported Ru (*49*), the detailed reaction mechanism might be different for unsupported and supported Ru catalysts. For example, spillover hydrogen could participate. In support of this idea, we note that oxides (Al_2O_3, SiO_2) after exposure to H_2 in the presence of a catalyst (Pt/Al_2O_3, Pt/SiO_2) at 300°C or higher, acquire catalytic activity for hydrogenation of olefins (*50, 51*). This has been attributed to the reaction of the olefin with spillover hydrogen on oxides. Recently, Yang and Goodwin reported that SiO_2 in the presence of a Ru/Al_2O_3 catalyst catalyzed the CO hydrogenation reaction (*52*). They did not ascribe this to hydrogen spillover, but the phenomenon is very similar to the hydrogenation of hydrocarbons by activated SiO_2. By analogy with these results, we propose that some of the CO which is held on Ru can react with spillover hydrogen to form hydrocarbons and/or CO_2 and water under reaction conditions and that spillover hydrogen on supported Ru catalysts might play a role in the formation of $—CH_x—$ and $—C_nH_x—$ intermediates. We envisage this reaction as occurring on Ru sites and involving H migration from SiO_2 to Ru.

CONCLUSIONS

(1) Hydrogen spillover occurs for temperatures above 323 K on Ru/SiO_2; (2) there is no spillover of CO on Ru/SiO_2; (3) CO exposure at 300 K displaces some D_2 from

Ru/SiO_2; (4) the potential role of spillover in the formation of hydrocarbons from CO and H_2 is identified.

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