

CO Isotopic Mixing Measurements on Nickel: Evidence for Irreversibility of CO Dissociation

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The isotopic mixing reaction, $^{12}\text{C}^{18}\text{O} + ^{13}\text{C}^{16}\text{O} \rightarrow ^{12}\text{C}^{16}\text{O} + ^{13}\text{C}^{18}\text{O}$, and the methanation reaction ($3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$) have been studied at 2 Torr CO pressure over a Ni(100) single crystal between 300 and 700 K. At 600 K the rate of the exchange reaction is a factor of 50 slower than CO hydrogenation indicating irreversibility of the CO dissociation reaction step. Below 850 K, the turnover number for the isotopic mixing reaction is less than 4×10^{-3} reactive events site⁻¹ sec⁻¹. This corresponds to a reactive sticking coefficient of $< 2 \times 10^{-8}$. The steady state reaction becomes significant at ~ 850 K at which temperature a graphite layer begins to decompose, opening up free Ni sites. Various models to explain these observations are discussed.

INTRODUCTION

The adsorption and dissociation of CO on Ni surfaces at temperatures above ~ 450 K is a particularly important heterogeneous reaction. The production of surface carbon by this reaction has been suggested as the first step in the catalytic production of CH₄ and higher hydrocarbons from CO and H₂ mixtures (1–6). Kinetic measurements of the absolute rates of CO dissociation on Ni (7) and Ru (8) have confirmed this step to be sufficiently rapid to account for all of the methane product. The reversibility of this dissociation step has been assumed in kinetic modeling of methanation (25); however, no experimental data addressing specific rates are available supporting this postulate.

Direct evidence for the thermal dissociation of CO on Ni surfaces was first obtained by Tracy (9) who found that Ni(100) behaved reversibly during CO adsorption/desorption cycles unless the Ni(100) was heated to temperatures above 475 K in the

presence of CO. Heating above 475 K led to dramatic changes in subsequent CO adsorption behavior which became irreversible. Auger spectroscopy showed that CO decomposed thermally, leaving surface carbon but little surface oxygen (9). Erley *et al.* (10) demonstrated that CO dissociates on a stepped Ni(111) surface at 430 K using high resolution electron energy loss spectroscopy. Following extensive CO dissociation, a high temperature thermal desorption peak at ~ 820 K was observed and was attributed to activated recombination of C(ads) and O(ads) on the stepped Ni(111) surface (11). For a flat Ni(111) surface, CO dissociation induced by electron impact led to the production of C(ads) and O(ads) species which desorbed as CO at ~ 620 K (11). Earlier, Madden and Ertl had observed that electron beam induced dissociation of CO on Ni(110) led to the production of high temperature CO thermal desorption states near 600 and 800 K (12).

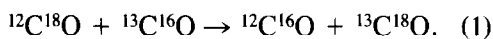
In this laboratory, a high pressure catalytic reactor system has been developed for studying single crystal catalysts. In addition to kinetic studies of reactions on these surfaces, it is possible to examine the crystals in a separate analysis chamber using

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Auger spectroscopy (5). This system has been extensively used to study the methanation reaction on Ni(100), Ni(111), Ru(110), and Ru(001) surfaces.

The work to be described here utilizes the high pressure reactor to study the catalytic isotope mixing reaction



This reaction may be utilized to investigate the details of the dissociation and recombination of surface carbon and oxygen produced by dissociation of CO. The use of the isotopic mixing reaction for investigation of CO dissociation extends back to early work of Madey *et al.* (13) who first observed isotopic mixing to occur rapidly on heated tungsten surfaces. Subsequent studies by others showed that this was indeed due to recombination of C(ads) and O(ads) produced by CO dissociation on W. The isotopic mixing method was extended to Re surfaces (14) and to Mo surfaces (15), yielding positive effects in both cases.

Recently, a study of CO interaction with a Rh(111) surface using the isotopic mixing method gave a negative result up to 800 K, suggesting that rapid CO dissociation does not occur on Rh(111) below ~ 800 K (16). These results are in agreement with complementary AES studies (16), and with recent field emission investigations (17). These investigations confirmed that the rate of CO dissociation on polycrystalline Rh is vanishingly small below 1000 K (17).

All of the CO isotopic mixing studies cited above have utilized CO fluxes of the order of 1 CO (atomic site) $^{-1}$ sec $^{-1}$. The work to be described here has been carried out at CO fluxes at least 10^6 greater using the high pressure chamber. In this case, the use of high pressures coupled with precise mass spectrometry enhances the sensitivity of the method by about five orders of magnitude compared to the earlier work on Rh(111) (16). In addition, comparison of the rate of isotopic mixing with the rate of the methanation reaction at identical CO pressures is informative, as will be shown.

EXPERIMENTAL

The apparatus for this work is shown in Fig. 1. It consists of two bakeable ultra high vacuum chambers, connected by a metal valve and separately pumped. The base pressure in the analysis chamber and in the reactor chamber is 10^{-10} Torr. The single crystal Ni(100) disk (0.85 cm 2 surface area: 1.34×10^{15} Ni atoms exposed), mounted on Ni heating wires, may be cleaned by oxidation at 1400 K in 10^{-6} -Torr O $_2$ pressure followed by reduction at 800 K in 5 Torr H $_2$. Typical Auger spectra of the clean Ni(100) surface are given in Refs. (5) and (18). In position (1), AES spectra were measured using a double pass CMA spectrometer. Position (2) was not utilized in this experiment. In position (3) the clean catalyst crystal has been retracted into the evacuated reactor chamber; the valves to the analysis chamber and ion pump were closed, and the experiment was begun. A 50–50% mixture of $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ was admitted to the 727 cm 3 reactor chamber to a total pressure of 2 Torr. These gases have been previously purified by storage at 77 K prior to admission to the apparatus. A leak valve between the reactor chamber and the quadrupole mass spectrometer in the analysis chamber was opened and continuous measurements of the 4CO isotopic species were carried out with the Ni(100) crystal at 300 K. It was found that a small very constant rate of production of $^{13}\text{C}^{18}\text{O}(\text{g}) + ^{12}\text{C}^{16}\text{O}(\text{g})$ occurred as a background effect. The magnitude of this effect, expressed as the rate of change of the mole fraction of $^{13}\text{C}^{18}\text{O}$, is $d^{13}X/dt = 2.05 \pm 0.12 \times 10^{-6}$ sec $^{-1}$ at a total CO pressure of 2 Torr. All measurements of the rate of isotopic mixing on the Ni(100) crystal above 800 K have been corrected for this background effect which may be due to a slow exchange process on the stainless steel walls of the high pressure reactor system.

Results for the rate of the isotopic mixing reaction are expressed in two ways. From the measured time rate of change of the

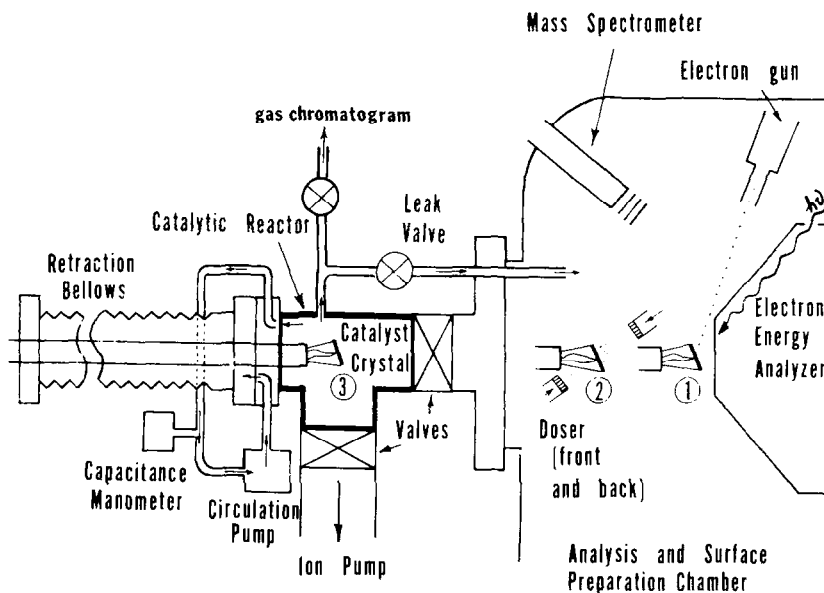


FIG. 1. Ultrahigh vacuum apparatus for studying single crystal catalysts before and after operation of high pressure catalytic reactor.

mole fraction of $^{13}\text{C}^{18}\text{O}$, $d^{31}X/dt$, the rate of production of $^{13}\text{C}^{18}\text{O} = d^{31}N/dt$, may be calculated. A turnover number, defined as N_{CO}^* , is

$$N_{\text{CO}}^* = \frac{d^{31}N}{dt} / 1.34 \times 10^{15} \text{ Ni sites.} \quad (2)$$

The results may be expressed differently in the static reactor as a reactive sticking coefficient (16), S_{R}^* , defined as

$$S_{\text{R}}^* = \frac{d^{31}N}{dt} / \frac{P_{\text{CO}} \cdot 0.85 \text{ cm}^2}{(2 \text{ mm } kT)^{1/2}} \quad (3)$$

where the denominator in Eq. (3) is the collision rate with the Ni(100) crystal surface. While it is not quite correct to assume molecular flow conditions at 2 Torr CO pressure, the error is not large (19).

RESULTS

By raising the temperature of the Ni(100) crystal it was found that an appreciable rate of isotopic exchange between the CO molecules did not occur until about 850 K. The results of a sequence of measurements between 700 and 938 K are shown in Fig. 2.

The steep temperature dependence of the rate corresponds to an activation energy of about 98 kcal mole $^{-1}$. For comparison, the rate of the catalytic *methanation* reaction by the same Ni(100) crystal is also shown in Fig. 2, both rates being expressed as turnover numbers. These data are from a comprehensive study covering a wide range of reaction conditions (5). Both the temperature range and the activation energy for the two reactions on this crystal differ significantly, with the *methanation* reaction occurring at lower temperatures with a lower activation energy (24.7 kcal mole $^{-1}$) (5). Previous work (7) has directly correlated the rate of CO dissociation on this surface with the methanation rate. Assuming this mechanism, it is clear from the methanation turnover numbers of Fig. 2 that at $T \geq 500$ K the rate of methanation and consequently CO dissociation on Ni(100) is high enough to have been detected by isotopic mixing unless some other factor interferes with the isotopic mixing reaction.

The rate of the isotopic mixing reaction is plotted vs temperature in a linear fashion in Fig. 3. Previous work (7) has shown that

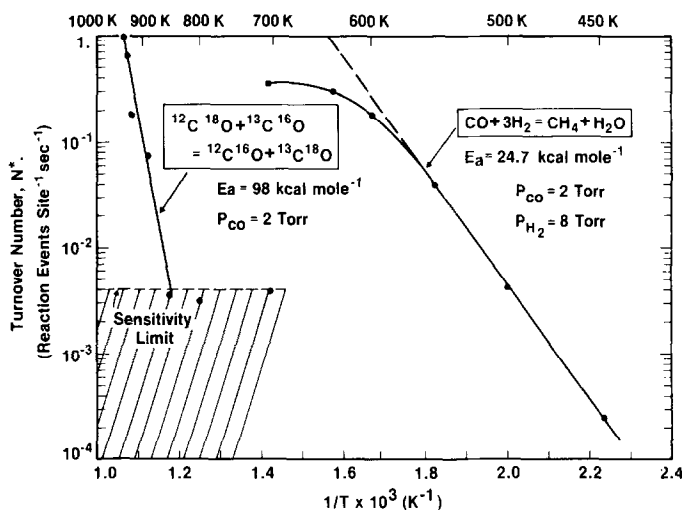


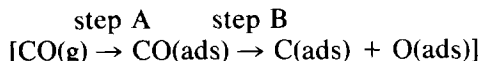
FIG. 2. Comparison of the turnover number for the CO isotopic mixing reaction on Ni(100) and the catalytic methanation reaction on Ni(100).

CO dissociation on Ni(100) at pressures comparable to that used in these studies leads to an increasing coverage of "carbide" carbon up to approximately one-half monolayer at ~ 650 K. With increasing reaction temperatures a carbon phase change to "graphitic" carbon is observed. This "graphitic" carbon is thermally stable up to ~ 900 K where dissolution into the bulk occurs (20). It may be seen that the onset of the CO isotopic mixing process at 850 K closely corresponds to the temperature at

which graphitic carbon begins to dissolve in Ni. It is also interesting to note that the thermal conversion of "carbide" surface carbide to graphitic carbon near 650 K does not seem to cause the rate of CO isotopic mixing on Ni(100) to vary from its value of zero.

DISCUSSION OF RESULTS

The striking experimental finding here is that the isotopic mixing reaction for CO does not occur at Ni(100) temperatures where it is known (Fig. 2) that the methanation reaction proceeds rapidly. This observation has important implications in modeling kinetic reactions such as methanation and Fischer-Tropsch synthesis since these reactions are currently believed to be initiated via a "carbide" intermediate derived from the dissociation of CO (7). This lack of isotopic mixing indicated that step B in CO dissociation



is irreversible in that the rate of the recombination reaction is insignificantly small compared to the forward reaction. Reversibility of step B should result in isotopic scrambling since the rate of step A is at

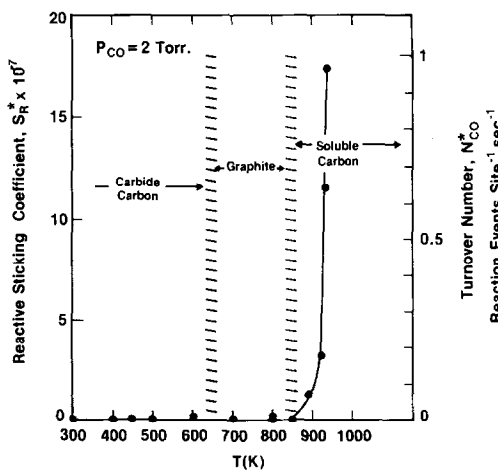


FIG. 3. Temperature behavior of the CO isotopic mixing reaction.

these temperatures and pressures several orders of magnitude faster than step B as estimated from known CO binding energies (21). Previous work (18) has shown that isotopic mixing does not occur in a monolayer of CO(ads) at temperatures up to 450 K. The reverse of step B is known to occur at ~ 820 K following dissociation of CO at 620 K (11); therefore, the association of C(ads) and O(ads) should not be kinetically limited at temperatures ≥ 820 K. Several models may be offered to explain this lack of CO isotopic exchange:

Model 1. CO dissociation on the surface is followed by reaction of O(ads) with CO(g) to yield CO₂. This prevents C(ads) + O(ads) recombination.

Model 2. The reaction of C(ads) + O(ads) is a highly activated process whose rate does not successfully compete with O(ads) reduction by CO until a critical temperature is achieved.

Model 3. Processes (1) and/or (2) are responsible for the lack of isotopic mixing below ~ 650 K. Above ~ 650 K, the presence of graphite impedes the dissociation of CO. As graphite begins to dissolve at ~ 850 K, the isotopic mixing reaction is initiated on clean Ni sites. The activation energy measured is the activation energy for graphite dissolution into Ni.

We believe that Model 3 best explains the temperature dependence of the mixing reaction between CO molecules.

Let us examine the evidence that dissolution of graphite into Ni is the factor which is responsible for the initiation of the isotopic mixing reaction. Sau and Hudson (22) have studied the kinetics of carbide and graphite formation and solution on Ni(110), using an ethylene molecular beam to produce surface carbon at various steady temperatures. Auger spectroscopy was used to determine the kinetics of the various processes involved, and to discriminate between "carbide" carbon and graphite. Their work is summarized in Fig. 4. Here it may be seen that a steady coverage of carbide (1×10^{15} C cm⁻²) exists up to about ~ 600 K; above

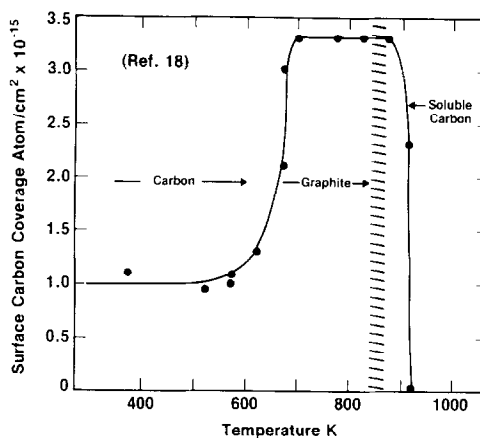


FIG. 4. Thermal behavior of carbon on Ni(110).

~ 600 K, conversion into graphite occurs and the steady carbon coverage rises steeply to 3.5×10^{15} C cm⁻². At about 850 K, the graphite suddenly begins to dissolve in the Ni and the steady state carbon coverage drops to almost zero. It is believed that the rate of graphitic carbon dissolution is controlled by the transport of the adsorbed layer to the bulk at $T > 873$ K. The activation energy measured for this process is 89 kcal mole⁻¹ and is thought to represent the energy required to remove a carbon atom from a graphite layer (22). The activation energy measured for the rate of isotopic mixing between CO molecules on Ni(100) in the same temperature range is 98 kcal mole⁻¹, suggesting that the carbon dissolution kinetics may be governing the rate of the CO-isotopic reaction above ~ 850 K. Unfortunately, we do not have data similar to that of Sau and Hudson for Ni(100). Equilibrium segregation studies of "carbide" carbon on Ni(100) surfaces have been carried out by Isset and Blakely (23, 24).

At the present time we cannot determine what factors govern the lack of CO isotopic mixing in the "carbide" region below ~ 650 K. Qualitative experiments indicate that the availability of O(ads) is severely limited by its interaction with CO(g) to produce CO₂. It may also be true that the activation energy for C(ads) + O(ads) \rightarrow CO is too high to permit a measurable reaction to oc-

cur in the "carbide" region below 650 K. This is suggested by the high CO desorption temperatures (600–800 K) observed when $C(ads) + O(ads)$ recombine (10–12).

SUMMARY

1. The isotopic mixing reaction $^{12}C^{18}O + ^{13}C^{16}O \rightarrow ^{12}C^{16}O + ^{13}C^{18}O$ and the methanation reaction $3H_2 + CO \rightarrow CH_4 + H_2O$ have been studied at 2 Torr CO pressure over a Ni(100) single crystal between 300 and 700 K. At 600 K the rate of the exchange reaction is a factor of 50 slower than CO hydrogenation indicating irreversibility of the CO dissociation reaction step.

2. The CO isotopic exchange reaction exhibits a sudden onset at 850 K which is thought to be associated with graphite dissolution into the bulk of the Ni crystal, making Ni sites available for rapid CO dissociation/recombination.

3. Below 850 K, the turnover number for the isotopic mixing reaction is less than 4×10^{-3} reactive events site⁻¹ sec⁻¹ in 2 Torr CO. This corresponds to a reactive sticking coefficient of $< 2 \times 10^{-8}$.

4. Below ~650 K, where "carbide" carbon is present, the isotopic mixing reaction is also retarded. This may be due to a reaction with CO(g) or another process removing O(ads) from the surface, or to a high activation energy for the process $C(ads) + O(ads) \rightarrow CO(ads)$.

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