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Isotopic Exchange of Carbon Monoxide over Copper Catalysts

Carbon monoxide adsorption on transition metals is regularly studied by a variety of techniques (*1*), but the technique of pulse–flow adsorption coupled with isotopic tracers is relatively rarely used (*2*). In this study we have used this technique to examine the adsorption and the retention (or otherwise) of the molecular integrity of carbon monoxide on copper catalysts. Our expectation, and indeed that of the literature (*3*), was that there would be no exchange reaction at room temperature and that even at elevated temperatures, e.g., 473 K, exchange would still be unlikely. The data presented below show a result which was totally unexpected.

The adsorption of carbon monoxide was studied over two copper-based catalysts by means of a pulse–flow isotopic-tracer technique. The catalysts used were a Cu/ZnO/alumina and a Cu/alumina, both prepared by coprecipitation (*4*). The apparatus used throughout this study is detailed elsewhere (*5*). Adsorptions and desorptions were continuously monitored using a TCD gas chromatograph coupled to a mass spectrometer (Spectramass SM100D fitted with a high-resolution RF head). The carrier gases (helium, 99.998%; hydrogen/nitrogen, 99.9998%) were further purified by passing through a bed of reduced Pd/WO_3 and Carbosorb AS (BDH) to remove oxygen and water impurities. The catalysts were reduced by heating in a stream of 5% hydrogen in nitrogen overnight at 513 K. While still at that temperature the flow was switched to helium, GHSV 2000, for 0.25 h; the samples were then cooled to 293 K in flowing helium. Immediately following the reduction sequence, pulses (typically 4 cm^3, 1.33×10^4 Pa) of carbon monoxide (^{13}CO, $C^{18}O$ mixtures) were introduced into the helium carrier gas and passed over the catalysts.

Carbon monoxide adsorbed on both the Cu/alumina and the Cu/ZnO/alumina catalysts but after a period of approximately 0.1 h adsorbed carbon monoxide began to "bleed" off both catalysts. When this process started, pulsing of the carbon monoxide was discontinued. The input carbon monoxide, pulsed over the Cu/alumina catalyst, had a mass 28 : 29 : 30 : 31 ratio of 1 : 8.2 : 9.9 : 1 while the gas "bleeding" off the catalyst was found to be partially scrambled having a 28 : 29 : 30 : 31 ratio of 1 : 3.8 : 4.4 : 1. The carbon monoxide pulsed over the Cu/ZnO/alumina catalyst had a 28 : 29 : 30 : 31 ratio of 1 : 19.9 : 32.3 : 2.8 while the "bleed" gas was completely scrambled with a ratio of 1.1 : 1 : 1.9 : 1.4. The $^{12}C : ^{13}C$ and the $^{18}O : ^{16}O$ ratios were the same, in both cases, for input and "bleed" gases.

The samples were heated, in flowing helium, to 498 K and the isotopic profile of the desorbing gas was continuously monitored. Both catalysts gave desorption peak maxima at approximately 365 K. On desorption from the Cu/alumina catalyst the carbon monoxide started with a 28 : 29 : 30 : 31 ratio of 1 : 2.3 : 2.6 : 1 and ended with a ratio of 2.7 : 3.7 : 2.1 : 1; similarly the $^{18}O : ^{16}O$ ratio started at 1.1 : 1 (as per reference) but ended at 0.5 : 1. The $^{12}C : ^{13}C$ ratio remained constant, at 1.1 : 1, throughout. Desorption from the Cu/ZnO/alumina was similar with the 28 : 29 : 30 : 31 ratio starting at 0.6 : 0.8 : 1.3 : 1 and ending at 5.1 : 4.1 : 1.5 : 1. The $^{18}O : ^{16}O$ ratio also changed during the course of the desorption, going from 1.6 : 1 (as per reference) to finish

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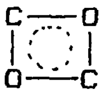
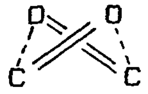
at 0.3 : 1; again the $^{12}C:^{13}C$ did not alter from the reference value.

Clearly from these results there is isotopic exchange between carbon monoxide weakly adsorbed on copper at 293 K. It seems unlikely, given the nature of bonding between copper and carbon monoxide (*1*, *3*), that there is dissociation and recombination; therefore a concerted mechanism between two (or more) adsorbed species appears more likely. For such an interaction to take place the carbon monoxide molecules must either lie flat on the surface (a) or be at an angle to the surface so that even though the oxygen is not bonded to the surface it can interact with another carbon atom, (b).


(a)


(b)

The existence of species such as (a) and (b) on copper has been inferred from an angle-resolved UPS study of carbon monoxide on copper single-crystal surfaces (*6*) and from a recent study on polycrystalline copper (*7*),

However, surface oxygen, remaining after reduction, may play a part in facilitating the exchange process. Clearly, at 293 K, there is no exchange between residual oxygen and adsorbed carbon monoxide and this also suggests that the exchange reaction is concerted, as some incorporation would be expected if the carbon monoxide dissociated. As the temperature is raised, however, there is exchange with residual surface oxygen. This exchange process, too, does not require a dissociative mechanism, but only an equivalence in the bonding between the oxygens and the carbon. The effect of oxygen on catalytic reactions has recently been detailed (*8*) and we will be examining this aspect in more detail.

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