

Isotopic Exchange of Carbon Dioxide and Its Interaction with Carbon Monoxide over Copper Catalysts

The adsorption/isotope exchange of carbon dioxide was studied over two copper-based catalysts by means of a pulse-flow isotopic-tracer technique. The catalysts used were Cu:ZnO:Al₂O₃ (60:30:10) and Cu:Al₂O₃ (80:20), both prepared by coprecipitation (1). The total surface areas of the catalysts and the surface areas of the components have been reported previously (2). The apparatus used throughout this study is detailed elsewhere (3). 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 activated palladium bronze, to remove oxygen, and Carbosorb AS (BDH) to remove water. Typically 1 g of the catalysts was reduced by heating in a stream of 5% hydrogen in nitrogen overnight at 513 K. While still at this temperature the flow was switched to helium, GHSV 2000 (v/v), for 0.25 h; the samples were then cooled to 293 K in flowing helium. Immediately following the reduction sequence, pulses (typically 4 cm³, 1.33 × 10⁴ Pa) of carbon dioxide (¹³CO₂, C ¹⁸O₂ mixtures) were introduced into the helium carrier gas and passed over the catalysts.

Carbon dioxide adsorbed on both the Cu/Al₂O₃ and the Cu/ZnO/Al₂O₃ catalysts. However, that portion of each pulse which was not adsorbed, i.e., which was detected in the eluent stream, was delayed by passage through the catalyst by 1 min for the Cu/Al₂O₃ catalyst and 2.5 min by the Cu/ZnO/Al₂O₃ catalyst. This occurred even when there had been no detectable adsorption of the pulse. The ratio of the isotopic

masses for the input carbon dioxide, which was pulsed over the Cu/Al₂O₃ catalyst, and for the carbon dioxide detected in the eluent gas is shown in Fig. 1. The ratios obtained indicate that the carbon dioxide in the eluent gas has scrambled. Analysis of the ¹²C:¹³C ratio gave 1.4:1 for the reference and eluent gas; however, the ¹⁸O:¹⁶O ratio was 1.2:1 for the reference gas but 0.2:1 for the eluent gas indicating that there had been significant incorporation of [¹⁶O]oxygen into the eluent carbon dioxide. The ratio of the isotopic masses for the input carbon dioxide, which was pulsed over the Cu/ZnO/Al₂O₃ catalyst, and for the carbon dioxide detected in the eluent gas is shown in Fig. 2. The ratios obtained indicate that the carbon dioxide in the eluent gas has scrambled. The ratio of ¹²C:¹³C was the same in both reference and eluent gas at 2.2:1; however, analysis of the ¹⁸O:¹⁶O ratio gave 1.6:1 in the reference but 0.1:1 in the eluent, again indicating that there had been considerable incorporation of [¹⁶O]oxygen into the eluent carbon dioxide.

The samples were heated, in flowing helium, to 523 K and the isotopic profile of the desorbing gas continuously monitored. The desorption peak maxima were 378 K for the Cu/alumina catalyst and 423 K for the Cu/ZnO/alumina catalyst. In both cases the gas was scrambled with a ¹⁸O:¹⁶O ratio of 0.1:1, cf. reference values of 1.2:1 and 1.6:1, respectively. While at temperature, pulses of isotopically labelled gas were passed over the catalysts. Carbon dioxide was the only species detected; no delay was observed on passage through the catalyst bed and no carbon dioxide was retained by the catalyst. However, after passing through the catalyst bed the carbon dioxide

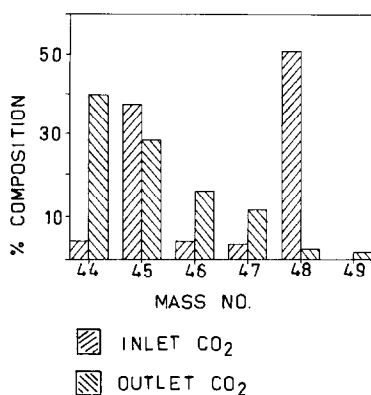


Fig. 1. Isotopic distribution of CO₂ before and after pulsing over the Cu/alumina catalyst.

was scrambled and had a ¹⁸O:¹⁶O ratio of 0.1:1 compared with 1.2:1 in the inlet.

Carbon [¹⁸O]dioxide was pulsed over a reduced Cu/ZnO/alumina catalyst at 293 K and subsequently thermally desorbed (maximum temperature 523 K); the catalyst was then cooled and carbon [¹⁶O]monoxide (no detectable carbon [¹⁸O]monoxide) pulsed over the catalyst at 293 K. The carbon monoxide adsorbed and as reported previously (4) began to "bleed" off the catalyst; on analysis of the "bleed" gas, carbon [¹⁸O]monoxide was detected with a ¹⁶O:¹⁸O ratio of 15.1:1. On thermal desorption of the carbon monoxide the ¹⁶O:¹⁸O ratio was 9.3:1. Therefore the [¹⁸O]oxygen exchanged during the carbon dioxide adsorption/desorption is subsequently available for reaction with carbon monoxide.

A mixture of ¹³C¹⁶O, ¹²C¹⁸O, and ¹²C¹⁶O₂, in a ratio of monoxide to dioxide of 1:1, was pulsed over a reduced Cu/ZnO/alumina catalyst at 293 K. Both gases were adsorbed but their adsorption was affected by the presence of the other gas. The amount of carbon monoxide adsorbed was decreased by 33% from that in the absence of carbon dioxide, while the amount of carbon dioxide adsorbed was reduced by 50% from that when no carbon monoxide was present. There was also found to be no delay in the passage of nonretained carbon

dioxide through the catalyst bed. As previously (4), the carbon monoxide began to "bleed" from the catalyst; ¹²C:¹³C and ¹⁶O:¹⁸O ratios, however, were the same for both the inlet and the bleed gases, indicating no exchange between coadsorbed CO and CO₂.

From the results presented above it is clear that there are two types of adsorbed carbon dioxide at 293 K. One is sufficiently strongly adsorbed for the CO₂ to be retained under dynamic flow conditions, the other only strongly enough adsorbed to cause a chromatographic effect on the gas pulse. However, although each of the catalyst components may adsorb CO₂, it is possible to show that the isotopic exchange phenomenon is associated with the copper component. The Cu/alumina catalyst behaves similarly to the Cu/ZnO/alumina catalyst and therefore the ZnO component is not required to enable scrambling/exchange for either the strongly or the weakly adsorbed gas. The alumina in these catalysts has been shown (2) not to adsorb carbon monoxide even in a static system but coadsorption with carbon monoxide results in a loss of the weakly bound species and therefore the weakly bound species must be associated with the copper. These two species can also be identified with ones detected in the CO₂ desorption spectra (desorption peak maxima 309 and 417 K) ob-

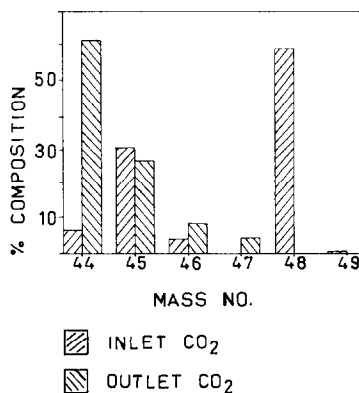


Fig. 2. Isotopic distribution of CO₂ before and after pulsing over the Cu/ZnO/alumina catalyst.

tained after subambient adsorption of CO₂ on unsupported copper which had surface oxygen present (5).

It is interesting that even the weak interaction allows the carbon dioxide to scramble (¹³C ¹⁸O₂ detected) and to exchange with residual surface oxygen. This oxygen has been shown to remain on the copper surface even after reduction (4–6). In a recent paper Kinnaird *et al.* (2), using carbon-14 radiotracers in a static system, also detected two forms of adsorbed carbon dioxide on copper. They suggested that the weakly held carbon dioxide was CO₂(ads) while the strongly bound was the dissociated species CO(ads) + O(ads). However, from the above results the weakly held species must interact with surface oxygen to facilitate fast exchange. Therefore we propose that the weakly held species is CO₃(ads). If the equilibration C¹⁸O₂(g) + O(ads) ⇌ CO¹⁸O₂(ads) ⇌ CO¹⁸O(g) + ¹⁸O(ads) is fast, then it is possible to achieve both the degree of exchange and the scrambling observed. From the results of Kinnaird *et al.* (2) and Wachs and Madix (7) the strongly adsorbed species is the dissociated CO₂(g) ⇌ CO(ads) + O(ads). When carbon monoxide and carbon dioxide are coadsorbed there is no evidence for exchange; however, there is a reduction in the amount of each gas adsorbed and the chromatographic effect on the carbon dioxide is lost. These results indicate that there are two discernible adsorption regions, (i) sites which adsorb carbon monoxide strongly and carbon dioxide weakly, and (ii) sites which adsorb carbon dioxide strongly and carbon monoxide weakly; therefore on coadsorption only the strongly adsorbed

species are present on the surface. However, when labelled carbon dioxide was used to exchange [¹⁸O]oxygen with the surface, carbon monoxide subsequently adsorbed was able to incorporate the [¹⁸O]oxygen. These results are in excellent agreement with a study by Lui *et al.* (8) who examined the role of CO₂ in methanol synthesis using C¹⁸O₂. They suggested that there was no exchange between CO and CO₂ when coadsorbed, but showed that if C¹⁸O₂ was used in one experiment, then in subsequent experiments, with the same catalyst, the label could be detected in carbon monoxide.

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