

Alumina-Catalyzed Isotope Exchange in CO<sup>1,2</sup>

Catalytic isotope exchange in carbon monoxide has been found to occur over  $\gamma$ -alumina, 0.5% ruthenium/alumina, and molecular sieves. The exchange occurs readily at 400-500°C with little or no carbon dioxide formation.

## INTRODUCTION

Carbon-13 nuclear magnetic resonance spectroscopy has developed into an extremely powerful tool for the chemist. Thus, the demand for the isotope has increased rapidly. Fractional distillation of carbon monoxide has proved to be a convenient method for <sup>13</sup>C enrichment up to approximately 94%. Interference by the various oxygen isotopes prevents direct enrichment beyond this. Isotope exchange or scrambling is thus an important step in the ultimate production of >99% <sup>13</sup>CO (1). Although a variety of systems have been reported to promote this exchange, the great majority of the work has been performed with hot metal or metal-carbide filaments (2). These systems are not readily adaptable to flow conditions where large volumes of gases are involved. In order to obtain effective exchange rates, extremely high temperatures are often required and as a result, carbon deposits plague the system. Metal oxides have been found to catalyze this exchange at room temperature or below (3); however, the most effective systems are those where reduction of the catalyst might be occurring and carbon dioxide formation could present problems at higher temperatures.

Ruthenium on alumina is well known for carbon monoxide activation in the Fischer-

Tropsch generation of hydrocarbons and was thus suggested as a possible candidate for the isotope exchange in carbon monoxide. During the course of study described herein, we have found that 0.5% ruthenium/alumina is indeed active; however,  $\gamma$ -alumina itself has been found to be even more active at 500°C. The present study describes these systems and possible mechanistic implications.

## EXPERIMENTAL

Carbon-13-labeled CO was enriched at LASL ICONs facility. The material was analyzed by mass spectrometric techniques and found to contain approximately 94% <sup>13</sup>C and 4-5% <sup>18</sup>O with  $K = 0.0016$ , where  $K$  is defined as the following ratio of masses:

$$K = \frac{(28)(31)}{(29)(30)} \quad (28 = {}^{12}\text{C}^{16}\text{O};$$

$$29 = {}^{12}\text{C}^{17}\text{O}, {}^{13}\text{C}^{16}\text{O};$$

$$30 = {}^{13}\text{C}^{17}\text{O}, {}^{12}\text{C}^{18}\text{O}; 31 = {}^{13}\text{C}^{18}\text{O}).$$

Also 99.99% <sup>12</sup>CO was obtained from the ICONs facility. Ruthenium (0.5%) supported on alumina and 99%  $\gamma$ -alumina were obtained as  $\frac{1}{8}$ -in. pellets from the Strem Chemical Company. Molecular sieves (4A) were obtained from the Ventron Corporation as was 99.999% Al<sub>2</sub>O<sub>3</sub> (Puratronic, Johnson Matthey Chemicals Limited). Mass spectral analyses were performed on an Extranuclear Laboratories, Inc. mass spectrometer.

Spectral analyses were performed at LASL on the  $\gamma$ -alumina from Strem Chemical Company and the following analytical

<sup>1</sup> The U.S. Government's right to retain a nonexclusive royalty-free license in and to the copyright covering this paper, for governmental purposes, is acknowledged.

<sup>2</sup> This work was performed under the auspices of the U.S. Department of Energy.

results were obtained ( $\mu\text{g/g}$ );

Li 40	Ca 50	Ni 5
Na 400	Mn 4	Cu 30
Mg 8	Fe 40	Ga 50
Si 25	Co 5	Sn 50

The following analysis was supplied with the Puratronic alumina (ppm):

Fe 5	Cu 1	Ca <1
Si 3	Mg 1	

### *C-O Exchange in Closed System*

A quartz tube, 1 × 12 in., equipped with a greaseless stopcock was used in this study. The empty vessel was pressurized to 500 Torr with the  $^{13}\text{CO}$  described above and heated at 500°C for 1 hr. Mass spectral analysis revealed no degradation of the total  $^{13}\text{C}$  content and no exchange. The resulting  $K = 0.0016$  with less than 0.07%  $\text{CO}_2$ .

The vessel was loaded with 1.4 g (~30 pellets) of 0.5% Ru/alumina and heated to 800°C under vacuum for 6 hr to remove any absorbed gases and water. The vessel was then cooled and loaded with 500 Torr  $^{13}\text{CO}$  and heated for 1 hr at 500°C. Mass spectral analyses revealed a  $K = 0.6$  and 1.2%  $\text{CO}_2$  with no degradation of the total  $^{13}\text{C}$  content. A slight darkening of the catalyst was observed.

The vessel was reevacuated and filled with 500 Torr of fresh  $^{13}\text{CO}$ . The catalyst from the previous run was reused in this experiment. The vessel was heated for 35 min at 500°C. Mass spectral analysis yielded a  $K = 0.36$  and 0.15%  $\text{CO}_2$ . No further change in the appearance of the catalyst was observed. A third run using the same catalyst gave a  $K = 0.64$  and only 0.6%  $\text{CO}_2$  after 1 hr at 500°C. In all runs a slight degradation of the  $^{18}\text{O}$  content was observed.

To check for the involvement of carbon on the surface of the catalyst in the exchange, we loaded the vessel with 50 g 0.5% Ru/alumina pellets and pretreated the catalyst as before. To ensure complete re-

moval of absorbed gases, the catalyst was heated to 500°C under vacuum for an additional 24 hr. The vessel was loaded with 500 Torr  $^{13}\text{CO}$  and was heated to 500°C for 3 hr. Analysis gave a  $K = 0.5$  and 25.5%  $\text{CO}_2$ . Again some darkening of the catalyst was observed. The vessel was evacuated and heated for 12 hr at 500°C to remove any residual  $^{13}\text{CO}$ . The system was then filled with 500 Torr 99.99%  $^{12}\text{CO}$  and heated for 1 hr at 500°C. Mass spectral analyses indicated 0.6%  $^{13}\text{C}$  incorporation and 0.3%  $\text{CO}_2$  formation.

The quartz tube was loaded with 1.4 g  $\gamma$ -alumina pellets (99%) and heated to 800°C for 6 hr under vacuum to remove any absorbed gases. The vessel was filled with the  $^{13}\text{CO}$  (500 Torr) and heated at 500°C for 1 hr. Analysis gave a  $K = 0.76$ , 0.008%  $\text{CO}_2$  and 3.9%  $^{18}\text{O}$ . A repeated reaction with the same catalyst gave a  $K = 0.83$ , 0.007%  $\text{CO}_2$ , and 4.7%  $^{18}\text{O}$ . A few dark spots suggestive of carbon deposits were observed in the catalyst. This same catalyst was heated to 500°C under vacuum for 6 hr to remove any residual  $^{13}\text{CO}$  and then reacted with 500 Torr 99.99%  $^{12}\text{CO}$  (<0.002%  $^{18}\text{O}$ ) for 1 hr at 500°C. The resulting gas was found to contain 0.15%  $^{13}\text{C}$  and 0.8%  $^{18}\text{O}$ .

The tube was loaded with 1.4 g alumina (99.999%) powder and pretreated as usual. The vessel was then pressurized with 500 Torr  $^{13}\text{CO}$  ( $K = 0.0011$ ; 28 = 1.277, 29 = 93.647, 30 = 4.711, 31 = 0.365, and 5.1%  $^{18}\text{O}$ ) and heated at 500°C for 1 hr. Analysis gave  $K = 0.84$  (28 = 5.780, 29 = 89.349, 30 = 0.371, 31 = 4.501), 0.004%  $\text{CO}_2$ , and 4.9%  $^{18}\text{O}$ . A repeated reaction with the same catalyst yielded  $K = 0.80$ , 0.004%  $\text{CO}_2$ , and 5.0%  $^{18}\text{O}$ . Again to check for carbon deposition the catalyst was reacted with 99.99%  $^{12}\text{CO}$  (<0.006%  $^{18}\text{O}$ ) for 1 hr at 500°C. Mass spectral analysis of the resulting gas found 0.15%  $^{13}\text{C}$  and 0.3%  $^{18}\text{O}$ .

Molecular sieves (1.4 g) were loaded into the quartz tube and pretreated at 600°C for 6 hr. The vessel was then pressurized to 500 Torr with  $^{13}\text{CO}$  and heated at 500°C for 1 hr. Analysis gave a  $K = 0.25$ , 0.95%  $\text{CO}_2$ , and

3.2%  $^{18}\text{O}$ . A slight darkening of the catalyst was observed.

#### *C-O Exchange in Flow System*

A type 347 stainless-steel tube ( $11 \times 1$  in. o.d.) was loaded with 118 g 0.5% Ru/alumina pellets and pretreated at  $800^\circ\text{C}$  under vacuum. The catalyst bed was then placed on line and heated by a standard tube furnace. The temperature was controlled using a Honeywell Dialapak controller with a chromel-alumel thermocouple inserted into a well in the center of the bed. With an approximate flow rate of 10 moles of  $^{13}\text{CO}$  per day, the following results were obtained:

$T$ ( $^\circ\text{C}$ )	$K$
215	0.43
275	0.52
315	0.55
370	0.73
415	0.81

No decrease in activity has been observed over a period of several months.

The ruthenium/alumina was removed from the above tube and after thorough clearing, the tube was repacked with 99%  $\gamma$ -alumina. Under the same conditions described above (flow of 0.3 SCFH) the following results were obtained:

$T$ ( $^\circ\text{C}$ )	$K$
228	0.15
310	0.60
343	0.84
390	0.83
422	0.83

After initial pretreatment, the carbon dioxide observed was negligible and no loss of activity has been observed over a period of several months.

#### RESULTS AND DISCUSSION

Previous studies at room temperature had found only slight activity for  $\gamma$ -alumina in the isotope exchange of carbon monox-

ide. High catalytic activity had been observed in the more easily reduced systems such as the Ni, Cu, and Fe oxides (3). At higher temperatures, however, we have found that  $\gamma$ -alumina is an excellent catalyst for this exchange, and because it is not easily reduced, little or no carbon dioxide is formed.

Because Ru/alumina has been observed to be an effective Fischer-Tropsch catalyst where the CO is activated toward reaction with hydrogen, we had expected that this would also be a good catalyst for the isotope exchange in CO; and, indeed, we observed  $K$ 's between 0.6 and 0.7 after 1 hr at  $500^\circ\text{C}$  in a closed system. This  $K$  is defined as the ratio of masses given in the experimental section and as complete exchange occurs, this should approach unity. However, due to varying amounts of oxygen-17 in an enriched  $^{13}\text{CO}$ ,  $K$ 's in excess of 0.9 are not observed. Much to our surprise, however, 99%  $\gamma$ -alumina was found to be an even better catalyst, yielding essentially complete exchange ( $K = 0.83$ ) under the same conditions. Analytical data on this alumina did not indicate the presence of substantial amounts of impurities, such as iron and copper oxides that might be expected to catalyze the CO exchange. However, to further minimize the possibility that an impurity might be the active species in the exchange, an ultrapure grade of alumina (99.999%) was examined under the same conditions. Essentially identical results were obtained ( $K = 0.84$ ).

For both Ru/alumina and alumina some preferential site exchange between oxygen in the catalyst and CO is observed. This phenomenon was observed earlier in the room temperature studies on alumina (3). No indication of bulk oxygen exchange with the catalyst has been observed. Likewise extremely small amounts of carbon appear to be deposited on the catalysts and exchange with the carbon in the CO occurs. It is unlikely that these two mechanisms would account for all of the isotope exchange that we are observing,

and because no appreciable amount of CO<sub>2</sub> is formed, we feel that CO/CO<sub>2</sub> exchange is also not a major contribution.

The exact nature of the exchange process is thus unknown. But it is interesting that the exchange occurs readily on pure  $\gamma$ -alumina. Since this is the choice of support for many metal systems that are active in the conversion of CO/H<sub>2</sub> to hydrocarbons, one has to wonder what role the alumina might be playing in the overall reaction scheme, and whether some activation of the CO might not be coming from the support. Similarly, the use of zeolites as supports is becoming more commonplace, and although not as active as  $\gamma$ -alumina, molecular sieves have also been found to catalyze this exchange in CO.

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