JOURNAL OF CATALYSIS 124, 1–11 (1990)

Surface Mobility and Reactivity of Oxygen Species on a Copper–Zinc Catalyst in Methanol Synthesis

D. DUPREZ,[1,*] Z. FERHAT-HAMIDA,* AND M. M. BETTAHAR†

*Laboratoire de Catalyse en Chimie Organique, 40 Avenue Recteur Pineau, 86022 Poitiers Cedex, France, and †Laboratoire de Chimie du Gaz Naturel, Université des Sciences et Techniques, Boîte Postale 31, El-Alia, Bab-Ezzouar, Algiers, Algeria

Received April 28, 1989; revised October 16, 1989

A coprecipitated $Cu–ZnO/Al_2O_3$ catalyst [Cu/(Cu + Zn) = 0.3] was prepared and characterized by XRD, XPS, N_2O chemisorption, and its activity in methanol synthesis at 220°C, 1 atm. The size of the copper particles deduced from XRD line broadening agreed with that measured by N_2O chemisorption (16–20 nm). Moreover, XPS showed that the composition of the surface, slightly enriched in zinc in the reduced catalyst, was similar to the composition of the bulk in the oxidized catalyst. Catalytic activity was similar to the activity already reported for this type of catalyst under similar conditions. Isotopic exchange of $^{18}O_2$ and of $C^{18}O$ was performed on this catalyst to evaluate the surface mobility as well as the reactivity of the oxygen species on the support. Some experiments were also carried out on a Rh/ZnO catalyst. $Cu^{16}O$ was active in exchange with gaseous $^{18}O_2$ but did not promote exchange with the oxygen of ZnO. By contrast, with Rh/ZnO, $^{18}O_2$ could be exchanged with the ^{16}O of ZnO at a significant rate. These results show that the surface oxygen species are mobile on ZnO but only in the direction ZnO to Cu: once they are bonded on the copper, oxygen atoms can no longer leave the metal particles. Oxygen transfer in both directions (metal to support and vice versa) being possible with rhodium, the rate of oxygen migration on ZnO could be measured by isotopic exchange of $^{18}O_2$ with $Rh/Zn^{16}O$. With $C^{18}O$ the most striking feature was the formation of large amounts of CO_2, first $C^{16}O^{18}O$ and $C^{16}O_2$, then by $C^{18}O_2$. The formation of $C^{16}O$, initially very fast, was interrupted as soon as the partial pressure of CO_2 became significant. These results concerning isotopic exchange, either with $^{18}O_2$ or with $C^{18}O$, show that oxygen species (probably OH groups) can migrate from ZnO to the copper particles during methanol synthesis. This is discussed in the light of the different reaction mechanisms. ZnO can play a role in mechanisms with formate intermediates, especially in the synthesis with CO_2/H_2 mixtures.

INTRODUCTION

The system $Cu–ZnO/Al_2O_3$ is one of the most selective catalyst in the synthesis of methanol from $CO/CO_2/H_2$ mixtures (*1–3*). During the synthesis, three main reactions are possible:

$$CO + 2H_2 \rightarrow CH_3OH \quad (1)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2. \quad (3)$$

Numerous studies have been devoted to determine the reaction intermediates, to characterize the active sites, and to define the role of CO_2 in the synthesis. In particular, many studies quoted by Klier (*1*) and by Bart and Sneeden (*2*) have shown that copper–zinc catalysts were more selective and more stable during methanol synthesis in $CO_2 + H_2$ than in $CO + H_2$. Nevertheless, a significant rate of the water–gas shift reaction [Eq. (3)] is always observed so that, whatever the reactant composition, the catalyst operates in a mixture of carbon oxides, hydrogen, and steam.

The surface species involved in methanol synthesis can be classified as (i) the species bonded to active sites by the carbon, particularly carbonyl O═C═*, formyl O═CH—*, hydroxycarbene OH—CH═*, and hydroxymethylene or "carbinol"

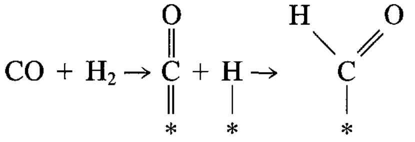
---

[1] To whom correspondence should be addressed.

0021-9517/90 $3.00

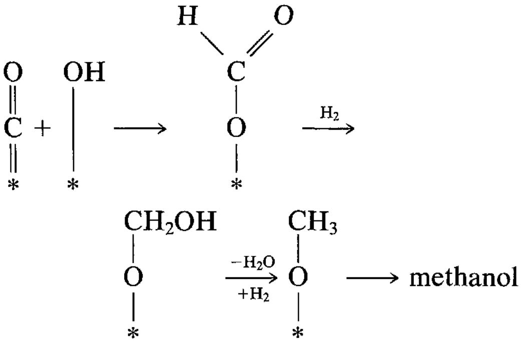
OH—CH_2—*, where the asterisk signifies the surface site; (ii) the species bonded to active sites by the oxygen, such as methoxy CH_3—O—*, oxycarbinol OH—CH_2—O—*, formate O═CH—O—*, and hydroxyl OH—*; and (iii) the hydrogen species H—*. Most of these intermediates have been detected and characterized by IR and UV–visible spectroscopy (*4–7*), by thermodecomposition of adsorbed reactants (*8, 9*), and by use of either labeled molecules (*4, 10*) or a specific reactant during the reaction (*4*) or a specific reactant after the reaction (chemical trapping) (*11, 12*). On the basis of the most probable intermediates, three mechanisms have been proposed:

Mechanism I (Main Intermediate: Formyl Species)



Formyl species are then hydrogenated, step by step, into hydroxycarbene, carbinol, and finally methanol. In this mechanism, originally proposed by Klier (*1*), all the intermediates are bonded to the surface by the carbon.

Mechanism II (Main Intermediate: Formate)



This mechanism, proposed by Kung (*13*), requires the presence at the surface of OH groups probably generated by the water produced in the third step. Recently, Bowker *et al.* (*14*) have proposed, for the synthesis from CO_2/H_2 mixtures, a type II mechanism in which CO_2 and H_2 would be coadsorbed on the copper component of the catalyst, forming a formate species, whose hydrogenation/hydrogenolysis would be the rate-determining step in the synthesis. In the formate mechanisms, the intermediates are bonded to the surface by the oxygen.

Mechanism III (Main Intermediates: Formate and Formyl)

Vedage *et al.* (*4*) have proposed a mechanism which takes into account the water–gas shift reaction in methanol synthesis. The mechanism starts in the same way as mechanisms II but the formates are transformed into methoxy via a series of steps involving the formation and transposition of formyl species. This mechanism explains the promoter effect of water and the formation of methanol CH_2DOH when D_2O is added to the reactant mixture.

In the latter two mechanisms, hydroxyl species play a key role since the synthesis requires continuous insertion of CO in these OH groups and permanent rehydroxylation of the surface by water produced in the reaction (or added to the reactants). In Cu–ZnO/Al_2O_3 catalysts, zinc oxide and alumina could be active in the production of OH species and probably of other oxygen species such as the formates. All these species have to migrate to the copper sites, where most of the reaction steps occur. Most probably, the surface mobility of the oxygen species depends on the mobility of the oxygen atoms (or ions) on the catalyst. We have studied, by exchange of $^{18}O_2$ with the ^{16}O of a Cu–ZnO/Al_2O_3 catalyst in various states (oxidized and reduced), the mobility of these oxygen species. For measuring the intrinsic oxygen mobility on zinc oxide, Rh/ZnO was also studied. Rhodium instead of copper was chosen because it was shown to be the best promoter of the exchange reaction between

$^{18}O_2$ and the ^{16}O of conventional supports, e.g., Al_2O_3 and SiO_2 (*15*).

EXPERIMENTAL

The Cu–ZnO/Al_2O_3 catalyst was prepared by precipitating at 85°C aqueous solutions of copper and zinc nitrates (1 mol Cu + Zn liter^{-1}) with an aqueous solution of disodium carbonate (1 mol liter^{-1}). The support (Oxyd C Degussa alumina) was added at the end of precipitation. After it was carefully washed with twice-distilled water, the precipitate was dried at 100°C and then calcined in a flow of air at 350°C for 3 h. The oxidized catalyst contained 26.2 wt% CuO, 59.4 wt% ZnO and 7.89% Al_2O_3 (the remainder being water held by the solid) and the Cu/(Cu + Zn) atomic ratio was 31.1%. This catalyst is referred to as Cu-30. The same method was used to prepare a pure zinc oxide on which 0.25 wt% Rh was introduced by impregnating the support with an aqueous solution of rhodium nitrate. This metal precursor was chosen because chlorine was shown to be a serious inhibitor of oxygen exchange on alumina (*16*).

Catalysts were characterized by XRD and N_2O decomposition (Cu-30) and by hydrogen chemisorption (Rh/ZnO). XRD measurements were carried out in a powder diffractometer (Co source, $\lambda = 0.179026$ nm) on the copper–zinc catalyst in the oxidized and in the reduced forms (H_2 flow, 4 K min^{-1}, 300°C, 3 h). This showed that copper was present mainly as CuO in the oxidized catalyst and as metallic copper in the reduced catalyst. No trace of Cu_2O was detected. Zinc oxide was the only form of zinc evidenced, even in the reduced catalyst.

The sizes L of the crystallites deduced from XRD line broadening were calculated by the Debye–Scherrer equation with a shape parameter of 0.9 (spherical particles). N_2O decomposition and H_2 chemisorption were carried out in a pulse chromatographic apparatus described elsewhere (*17*). The catalysts were reduced in a hydrogen flow (4 K min^{-1} from 25 to 300°C, 3 h at 300°C), flushed by helium (Cu-30) or by argon (Rh/ZnO), and then cooled to room temperature. Pulses of N_2O or of H_2 (0.288 cm^3) were injected every other minute until saturation. The nitrogen formed by decomposition of N_2O was analyzed on a Porapak T column (1 m). The surface stoichiometries were taken as equal to 1 : 2 for $N_2O : Cu_s$ and to 1 : 1 for $H : Rh_s$. The copper surface area S_{Cu} was calculated on the basis of 1.46×10^{19} atoms m^{-2} (*18, 19*) and the particle size d_{Cu} was obtained from the equation $d_{Cu} = 673/S_{Cu}$ where S_{Cu} was given in m^2 g_{Cu}^{-1} (*19*).

The Cu-30 catalyst was also characterized by X-ray photoelectron spectroscopy in a Riber spectrometer using the $K\alpha$ radiation of magnesium at 1253.6 eV. The catalyst sample was analyzed in its oxidized form and in its reduced form. In the latter case, the catalyst was prereduced in a flow reactor (H_2 300°C) and then rereduced in an annex chamber of the spectrometer before transfer into the analysis chamber.

Catalytic activities in methanol synthesis from $CO_2 + H_2$ mixtures (1 : 4) were measured at 220°C in a dynamic reactor at atmospheric pressure. The catalyst was reduced at 300°C in H_2 flow and then cooled to the reaction temperature. Reaction products were analyzed by GC on a Porapak R column at 110°C. Besides methanol, only traces of methane and methyl formate were detected, in agreement with the previous work of Bardet *et al.* (*20*) showing that Cu–ZnO/Al_2O_3 was remarkably selective to methanol in $CO_2 + H_2$ mixtures. After a short period of apparent activation, the catalyst became very stable: it is this steady-state activity that was taken into consideration.

$^{18}O/^{16}O$ exchange reactions were carried out at 350°C in a recycling reactor coupled via a calibrated leak to a mass spectrometer for isotopic analysis (*14*). The reaction volume was 46.9 cm^3 and the recycle flow rate was 170 cm^3 s^{-1}. To avoid fluidization phenomena, the catalysts were pressed so as to obtain wafers of about 25 mg. Experiments were carried out on oxidized and reduced

TABLE 1

Characteristics of the Reduced Cu-30 Catalyst

XRD						N_2O decomposition			Catalytic activity [mmol h^{-1} g^{-1} (220°C)]
Cu metal			ZnO			molec g^{-1}	m^2_{Cu} g^{-1}	d_{Cu} (Å)	
2θ°	d (Å)	L (Å)	2θ°	d (Å)	L (Å)				
50.24	2.115	160	55.53	1.912	204	5.21×10^{19}	7.14	197	1.18

samples. In the latter case the catalysts were reduced *ex situ* at 300°C in a H_2 flow and rereduced *in situ* under 150 mbar H_2 at 300°C for 1 h and then evacuated at 10^{-3} mbar for 15 min. Exchange experiments were carried out either with $^{18}O_2$ to determine oxygen mobility at the catalyst surface or with $C^{18}O$ to characterize the surface reactivity of oxygen-containing species formed on carbon monoxide chemisorption.

RESULTS

The main characteristics of the reduced Cu-30 catalyst are given in Table 1. The average size of the copper particles deduced from XRD spectra is similar to the average size deduced from the amounts of N_2O decomposed. This shows that the copper microcrystals are relatively isolated on the ZnO/Al_2O_3 matrix and that their surface is almost entirely accessible to gases. It can thus be stated that these microcrystals are not agglomerated, each of them constituting a particle of copper. The catalytic activity in methanol formation is similar to that reported by Denise and Sneeden (*21*) under similar conditions: $H_2/CO_2 = 4$, 1 atm. Liu *et al.* (*22*) also found activities of the same order of magnitude (0.4 to 1.6 mmol per gram catalyst and per hour) with $CO/CO_2/H_2$ mixtures at 17 bar and 225°C, whereas Klier *et al.* (*23, 24*) reported, for similar catalysts, activities of about 75 mmol CH_3OH per gram catalyst and per hour at 75 bar and 250°C. This value is very close to those reported by Chinchen *et al.* (*3*) for some recent industrial catalysts. Moreover, the kinetic equation of Szarawara and Reychman (*25*), in the case of synthesis from CO_2 20%/H_2 mixtures, leads to an activity of 45 mmol CH_3OH per gram at 250°C and 75 bar (10% conversion) and predicts that this activity will be reduced by two orders of magnitude if the total pressure is decreased by 10. We can thus conclude that the activity found for the $Cu-ZnO/Al_2O_3$ catalyst is consistent with that of conventional copper–zinc catalysts.

XPS results are given in Table 2. In the oxidized catalyst, a very small peak of carbon 1*s* appears. Oxygen 1*s* appears in the

TABLE 2

XPS Data of the Cu-30 Catalyst

Peak	Oxidized		Reduced	
	Binding energy[a] (eV)	Relative intensity[b]	Binding energy[a] (eV)	Relative intensity[b]
O 1*s*	529.2	11,454	530.4	11,963
	531.3	157,319	532.2	5,850
C 1*s*	285.0	Weak	281.2	960
			285.0	2,191
Cu $2p_{3/2}$	933.3	13,264	931.8	11,599
			933.6	1,508
	941.7(sat)	4,877		
Cu $2p_{1/2}$	953.3	7,776	951.5	5,876
			953.5	970
	961.5(sat)	2,802		
Zn $2p_{3/2}$	1020.4	28,850	1020.1	100,000
	1022.4	71,150	1022.0	
Zn $2p_{1/2}$	1043.6	14,498	1043.4	48,010
	1045.6	31,375	1045.3	

[a] Reference C 1*s* at 285.0 eV.
[b] Based on Zn $2p_{3/2}$ = 100,000.

TABLE 3

Characteristics of the Rh/ZnO Catalyst, Reduced (H_2) and Flushed (Ar Flow) at 350°C

Rh (μmol g^{-1})	H_C (μmol H g^{-1})	% *D*
24.3	11.4	47

form of a double peak which can be ascribed to oxygen anions (529.2 eV) and to hydroxyl or residual carbonates (531.3 eV). The Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks are present in the spectrum with their satellites at +8.3 ± 0.1 eV characteristic of the copper in the oxidized form. The surface composition percentage Cu/(Cu + Zn) deduced from the peak intensities of copper and zinc (ratio of the sensitivity factor of zinc to that of copper: 1.24) amounts to 29%, a value close to the atomic ratio in the bulk (31%). Some significant changes are observed on reduction: (i) the C 1*s* peak intensity increases; deconvolution of this peak shows a principal component at 285 eV (elementary carbon), and the presence of a minor component at 281.2 eV could be indicative of a special form of carbon; (ii) the high-energy component of the O 1*s* peak decreases by a factor of 27, suggesting that a significant part of this oxygen was associated with copper in the oxidized catalyst; (iii) the satellites of the Cu 2*p* peaks disappear, but the shapes of the principal peaks prove the presence of a secondary component at +1.8 eV which could correspond to a special form of copper (11–14%); (iv) the percentage of copper atoms on the surface decreases and reaches 19% in the reduced catalyst.

The characteristics of the Rh/ZnO catalyst are given in Table 3. Although the stoichiometry of hydrogen chemisorption has not been definitely established in the case of rhodium deposited on ZnO, it seems that the metal is relatively dispersed.

$^{18}O/^{16}O$ *Exchange on the Oxidized CuO-30 Catalyst*

Prior to exchange experiments, the catalyst was heated from 25 to 350°C and outgassed at this temperature. During this treatment, large amounts of water (820 μmol g^{-1}) and carbon dioxide (160 μmol g^{-1}) were desorbed from the catalyst. However, the rate of desorption rapidly decreased at 350°C and no traces of H_2O and of CO_2 were detected after evacuation for 15 min at 350°C. The carbon dioxide was certainly formed via decomposition of residual carbonates.

Upon admission of $^{18}O_2$ on the degassed catalyst, the most striking reaction was a decarbonation: Fig. 1 shows the change with time of the CO_2 formed during oxidation of the surface carbon. The rate of CO_2

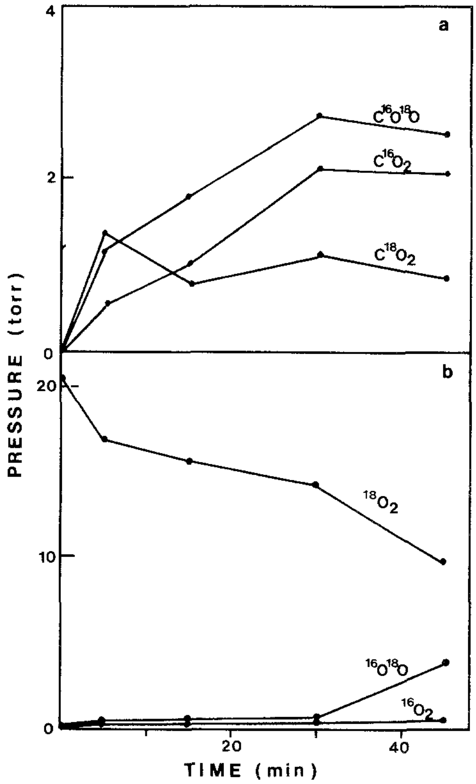


FIG. 1. Changes in the partial pressures of the isotopes of CO_2 (a) and O_2 (b) during exchange and reaction of $^{18}O_2$ at 350°C on the oxidized Cu-30 catalyst.

production, initially very high, decreases with time and drops to zero after 30 min; simultaneously the rate of O_2 exchange starts slowly increasing (appearance of $^{18}O^{16}O$ in the gas phase). It can thus be concluded that the oxygen of oxidized CuO–ZnO/Al_2O_3 catalysts is exchangeable at a very low rate after decarbonation of the solid. During the initial period, the rate of $C^{16}O^{18}O$ formation is almost as high as that of $C^{18}O_2$ although there is practically no ^{16}O in the gas phase. This shows that surface oxygen atoms can participate in carbon oxidation.

The surface carbon leading to CO_2 most probably results from carbonaceous impurities introduced at different stages of the preparation (starting materials, drying, calcination) and not from residual carbonates which could still have been present on the catalyst after outgassing. This is supported by the fact that the initial rate of $C^{18}O_2$ formation is very high and is confirmed by the following experiment: if argon, instead of $^{18}O_2$, is brought into contact with the outgassed catalyst, there is no formation of CO_2. It is interesting that the amount of surface carbon detected by XPS in the oxidized catalyst is very low, which suggests that a large part of the carbon is carbon species desorbable under the UHV conditions prevailing in the photoelectron spectrometer. These carbon species could be elemental carbon or strongly chemisorbed carbon oxides which can desorb under UHV conditions or be displaced by O_2.

$^{18}O/^{16}O$ Exchange on the Reduced Cu-30 Catalyst

Exchange was studied at 350°C on the nondecarboned catalyst. The results are shown in Fig. 2. The main reaction remains the surface carbon oxidation, which implies that the carbon species are not eliminated on reduction. The distributions of the isotopes of CO_2 produced by carbon oxidation are relatively similar for the reduced and the oxidized catalysts. Even so, the isotopic distributions of oxygen on the surface are very different: in particular, whereas copper is in the form of $Cu^{16}O$ in the oxidized catalyst, metallic copper is rapidly reoxidized into $Cu^{18}O$ as soon as the reduced catalyst comes into contact with $^{18}O_2$. This corresponds to the quasi-instantaneous drop in $^{18}O_2$ pressure recorded at zero time (Fig. 2b). As the two solids (oxidized and reduced) have practically the same behavior as far as the isotopic distribution of CO_2 is concerned, it is very likely that the carbon is located on the support and not on the copper. These results can also be explained if a significant source of ^{16}O was in the carbon species as carbon oxides: the CO_2 isotope distribution is then linked to the ratio C : CO : CO_2 of the different carbon species present both on the oxidized and the reduced catalysts. Direct $^{18}O/^{16}O$ exchange does not seem to occur: $^{18}O^{16}O$ appears at a very low rate only after 30 min.

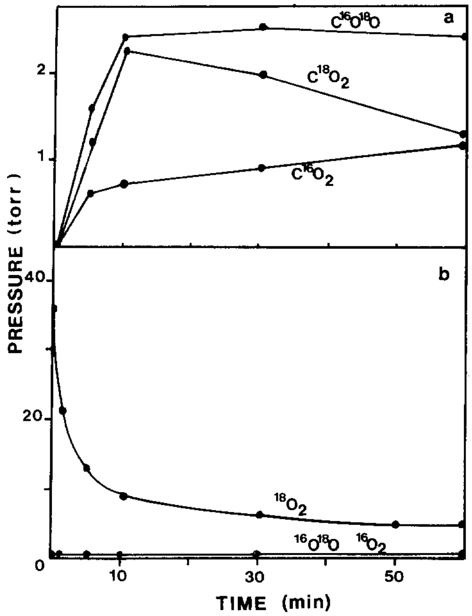


FIG. 2. Changes in the partial pressures of the isotopes of CO_2 (a) and O_2 (b) during exchange and reaction of $^{18}O_2$ at 350°C on the reduced Cu-30 catalyst.

$^{18}O/^{16}O$ Exchange on the Decarboned Catalyst

The carbon was eliminated by successive oxidations ($^{16}O_2$) and outgassing until there were no traces of CO_2. The catalyst was finally reoxidized by $^{16}O_2$, outgassed, and brought into contact with $^{18}O_2$. The results presented in Fig. 3 show that the decarboned oxidized catalyst is able to exchange oxygen at a significant rate at 350°C.

If the decarboned catalyst is first reduced at 350°C, $^{18}O^{16}O$ does not appear in the gas phase. These results prove that only oxygen atoms of CuO are exchangeable with $^{18}O_2$.

Mobility of Oxygen Species on ZnO

Zinc oxide, which is not able to dissociate dioxygen at 350°C, cannot exchange directly with gaseous oxygen. This was confirmed by complementary experiments carried out on a ZnO/Al_2O_3 catalyst prepared in the same way as $CuO–ZnO/Al_2O_3$. Whatever the state of the sample (oxidized or reduced, decarboned or not) the ZnO/Al_2O_3 catalyst cannot exchange with $^{18}O_2$.

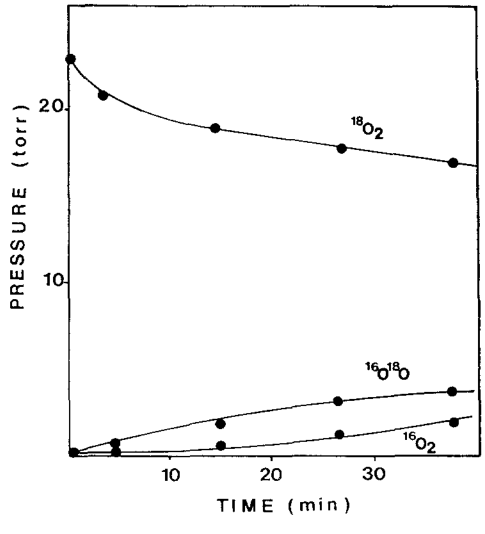


FIG. 3. Changes in the partial pressures of the isotopes of O_2 during exchange of $^{18}O_2$ at 350°C on the decarbonated oxidized Cu-30 catalyst.

As CuO can exchange with O_2 under the same conditions, it could be concluded that oxygen is not mobile on the ZnO surface.

A second hypothesis can be put forward to explain the results of exchange, namely, that surface ^{16}O is mobile on ZnO but the ^{18}O atoms are strongly bonded to copper particles. In this case, ZnO would not be active in exchange because oxygen atoms cannot leave the copper particles to migrate onto the support. To confirm this, similar experiments were carrier out on the Rh/ZnO catalyst. Rhodium was chosen because it is very active in $^{18}O/^{16}O$ exchange: first, interexchange of the oxygen isotopes is extremely fast on rhodium, and, second, oxygen atoms can easily leave the rhodium particles to exchange with oxygen of the support (*15*). The results concerning the reduced Rh/ZnO catalysts are shown in Fig. 4. It is obvious that the solid contains a significant amount of carbon, with probably the same origin as in the Cu-30 catalyst. This carbon is oxidized at a much higher rate than in $Cu–ZnO/Al_2O_3$. Even in the presence of this carbon, the catalyst was able to exchange $^{18}O_2$: a significant increase in the partial pressure of $^{16}O^{18}O$ was observed. The same rate of exchange was measured on the decarboned catalyst. These results show that ZnO possesses some oxygen species having a significant mobility at 350°C.

$C^{18}O/^{16}O$ Exchange and Reaction on $Cu–ZnO/Al_2O_3$

In this experiment, $C^{18}O$ was substituted for $^{18}O_2$ to evaluate the rate of $^{18}O/^{16}O$ exchange with a carbon-containing molecule and the reactivity of the adsorbed species. The catalyst was reduced and outgassed at 300°C, then decarboned by successive $^{16}O_2$ treatments and outgassing until there were no traces of CO_2, and finally reduced. Exchange and reaction with 50 mbar $C^{18}O$ were carried out at 200°C. The results (Fig. 5) show that there was formation of $C^{16}O$ and of different molecules of labeled carbon

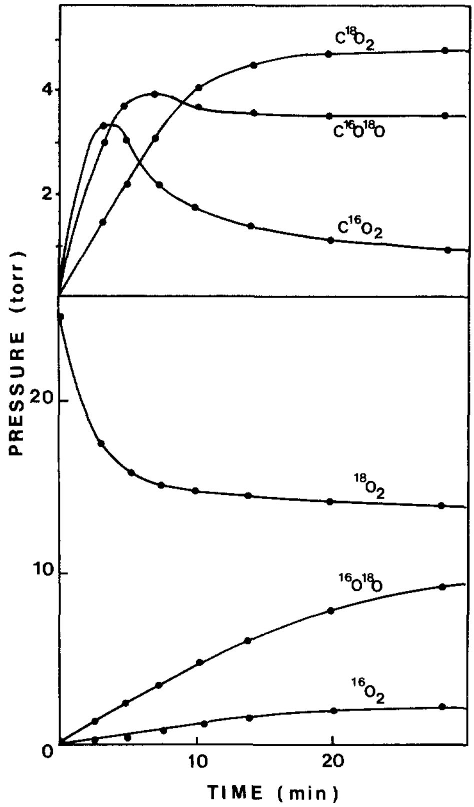


FIG. 4. Changes in the partial pressures of the isotopes of O_2 during exchange of $^{18}O_2$ at 350°C on the Rh/ZnO catalyst.

dioxide. This implies the following reactions at the catalyst surface:

exchange of CO

$$C^{18}O + {}^{16}O \rightarrow C^{16}O + {}^{18}O \quad (4)$$

oxidation of CO

$$C^{18}O + {}^{16}O \rightarrow C^{18}O^{16}O \quad (5)$$

$$C^{18}O + {}^{18}O \rightarrow C^{18}O_2 \quad (6)$$

$$C^{16}O + {}^{16}O \rightarrow C^{16}O_2 \quad (7)$$

$$C^{16}O + {}^{18}O \rightarrow C^{16}O^{18}O \quad (8)$$

We note that the initial formation of $C^{16}O$ was extremely fast, which shows that exchange of ^{16}O was more rapid with $C^{18}O$ than with $^{18}O_2$. This is consistent with the previous results of Vedage *et al.* (*4*) who showed that equilibration of $^{13}C^{16}O$ with $^{12}C^{18}O$ could be carried out at 25°C on similar catalysts.

Nevertheless, in our case, $C^{18}O/C^{16}O$ exchange was interrupted after 2 min, whereas oxidation of CO continued. The reactive oxygen involved in this exchange and in the oxidation of CO could be either oxygen or hydroxide ions of ZnO (and Al_2O_3) or oxygen atoms resulting from the dissociation of CO on copper. Participation of surface oxygen ions of ZnO in the oxidation of CO is relatively unlikely at 200°C; but the high activity of copper–zinc catalysts in water–gas shift reactions suggests that the hydroxyl groups of ZnO are extremely reactive. Nevertheless, no desorption of $H_2{}^{18}O$ was observed, whereas slow desorption of $H_2{}^{16}O$ occurred during the experiment (about 2 Torr after 30 min). This proves that the number of ^{18}OH remains relatively small and that a significant part of reactive ^{18}O results from the dissociation of $C^{18}O$. However, the mere dissociation into carbon and oxygen has never been observed on copper, and the molecule of $C^{18}O_2$, for instance, could be formed via an

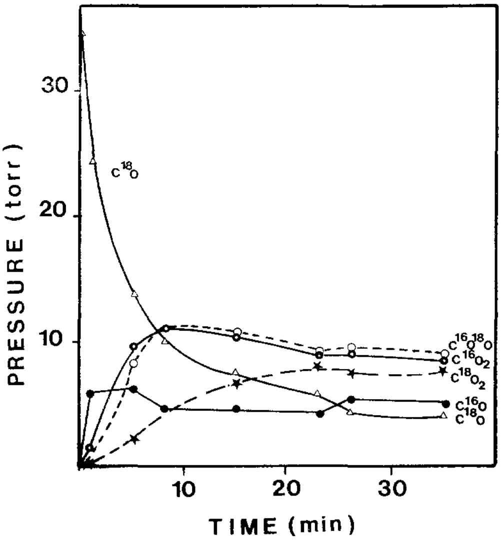


FIG. 5. Changes in the partial pressures of the isotopes of CO and of CO_2 during exchange and reaction of $C^{18}O$ at 200°C on the decarboned reduced Cu-30 catalyst.

interexchange between molecules of CO_2 already formed and molecules of CO:

$$C^{18}O^{16}O + C^{18}O \rightarrow C^{18}O_2 + C^{16}O. \quad (9)$$

Another explanation suggested by Jackson (*26*) would be the scrambling of the isotopes of CO_2 via the formation of an intermediate CO_3(ads). However, this hypothesis implies that a significant fraction of the catalyst has been exchanged to enable the formation of $C^{18}O^{18}O$ to occur.

DISCUSSION

The results of $^{18}O_2/^{16}O$ exchange, summarized in Table 4, show that oxygen species are mobile on ZnO but only in the direction ZnO → Cu crystallites. Once it is bonded to copper, oxygen can no longer leave the particles: no exchange was observed in the $Cu^{18}O/Zn^{16}O$ system. The mobility of oxygen on ZnO was shown by substituting, for copper, a metal (rhodium) which allows the transfer of oxygen from the metal to the support.

A similar study carried out with deuterium (*27*) showed that hydrogen transfer is possible in both directions: ZnO → Cu and Cu → ZnO. Moreover, a strong synergy was found between copper and ZnO which can store considerable amounts of hydrogen as well as hydroxyl or hydride species (*14, 28*). It is interesting that the rate of D_2 exchange with the hydrogen of the catalyst at 220°C was found to be close to 2×10^{20} atoms H per minute and per gram, a value eight times higher than the rate of oxygen exchange on ZnO at 350°C. Assuming that the activation energy for oxygen migration is 20–25 kJ mol^{-1}, the rate of hydrogen migration would be about 25 times more rapid than that of oxygen under the conditions of methanol synthesis (220°C) on copper/zinc oxide catalysts. These results contrast with those obtained on γ-alumina (*29*): for this support, in a hydroxylation state representative of what is currently encountered in catalysis (one to three OH groups per square nanometer), similar rates of H and O migration were obtained.

Possible role of oxygen species migration in methanol synthesis. First we can remark that the rate of reaction (1.2×10^{19} molecules CH_3OH per minute and per gram) is quite close to the rate of oxygen migration: this is a kinetic argument in favor of the occurrence of oxygen species migration in the mechanism of the reaction. Moreover, hydrogen and probably oxycarbon species can migrate at a much higher rate. Kinnaird *et al.* (*30, 31*) have recently proposed models of adsorption for CO and CO_2 on ternary copper–zinc–alumina catalysts: according to these authors, copper is the main center for the catalytic steps because it can adsorb *and* desorb CO *and* CO_2 at relatively high rates. Moreover, only copper can dissociate CO_2 into CO and adsorbed oxygen. However, the results of Kinnaird *et al.* suggest that ZnO can promote the activation of CO_2 (and this molecule only: CO is practically not chemisorbed on ZnO). This is cor-

TABLE 4

Summary of the Experiments on Exchange with $^{18}O_2$ at 350°C

Catalyst	State of catalyst after contact with $^{18}O_2$	Exchange $^{18}O/^{16}O$
Cu/Zn oxidized	$Cu^{16}O/Zn^{16}O/Al_2{}^{16}O_3$ + carbon	Slow only after decarbonation
Cu/Zn reduced	$Cu^{18}O/Zn^{16}O/Al_2{}^{16}O_3$ + carbon	Very slow only after decarbonation
Cu/Zn decarboned and oxidized	$Cu^{16}O/Zn^{16}O/Al_2{}^{16}O_3$	Rapid (4×10^{19} at. 0 min^{-1} g^{-1})
Cu/Zn decarboned	$Cu^{18}O/Zn^{16}O/Al_2{}^{16}O_3$	Very slow
Rh/ZnO	$Rh_2{}^{18}O_3/Zn^{16}O$	Rapid (2.5×10^{19} at. 0 min^{-1} g^{-1})

roborated by the results of Chaumette *et al.* (*32*) and Burch *et al.* (*33*), who showed that the synergetic role of ZnO, i.e., the increase in the intrinsic rate of methanol synthesis on copper when ZnO is added to the catalyst, was observed only when CO_2 was present in the synthesis gas. The key role of CO_2 was also established by Bowker *et al.* (*34*), who showed that polycrystalline ZnO, prereduced in H_2, was active in methanol synthesis only with CO_2/H_2; methanol is not formed by interaction of CO with H_2 on ZnO. Another synergetic effect between copper and zinc oxide concerns hydrogen storage: in the presence of copper, zinc oxide can store considerable amounts of hydrogen which become quite mobile under the reaction conditions (*27, 28*). Finally, we have shown here that oxygen species can migrate from zinc oxide to copper at a rate close to that of the methanol synthesis. All these results suggest that zinc oxide can participate in the generation or storage of hydroxyl, hydrogen, and certain oxycarbon species created by CO_2. Zinc oxide thus appears as an active support which can intervene directly in the mechanisms of methanol synthesis and particularly in formate mechanisms (referred to as types II and III in the Introduction), which require the presence of OH groups on the reaction centers. Nevertheless, even in the formyl mechanism, which requires hydrogen species, ZnO can play an active role in storing and providing large amounts of these species. Accordingly, the role of ZnO would be to stabilize ionic species of copper at the 1+ valence, particularly in the presence of CO_2, and to bring to the copper particles a continuous flow of OH and H species created by water and hydrogen and most probably certain oxycarbon species created by CO_2.

ACKNOWLEDGMENT

Z.F.-H. thanks the Algerian Ministry of Higher Education for a leave of absence from the University of Science and Technology (Algiers).

REFERENCES

1. Klier, K., *Adv. Catal. Relat. Subj.* **31,** 242 (1982).

2. Bart, J. C. J., and Sneeden, R. P. A., *Catal. Today* **2,** 1 (1987).

3. Chinchen, G. C., Denny, P. J., Jennings, J. R., Spencer, M. S., and Waugh, K. C., *Appl. Cata.* **36** 1 (1988).

4. Vedage, G. A., Pitchai, R., Herman, R. G., and Klier, K., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984" (G. Ertl *et al.*, Eds.), Vol. 2, p. 47. Dechema, Frankfurt-am-Main, 1984.

5. Saussey, J., Lavalley, J. C., Lamotte, J., and Rais, T., *J. Chem. Soc. Chem. Commun.*, 278 (1982).

6. Amenomiya, Y., and Tagawa, T., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984" (G. Ertl *et al.*, Eds.), Vol. 2, p. 557. Dechema, Frankfurt-am-Main, 1984.

7. Edwards, J. F., and Schrader, G. L., *J. Phys. Chem.* **89,** 782 (1985).

8. Tagawa, T., Pleizer, G., and Amenomiya, Y., *Appl. Catal.* **18,** 285 (1985).

9. Bowker, M., Houghton, H., and Waugh, K. C., *J. Chem. Soc. Faraday Trans. 1* **77,** 3023 (1981).

10. Liu, G., Willcox, D., Garland, M., and Kung, H. H., *J. Catal.* **96,** 251 (1985).

11. Deluzarche, A., Kieffer, R., and Muth, A., *Tetrahedron Lett.* **38,** 3357 (1977).

12. Deluzarche, A., Hindermann, J. P., and Kieffer, R., *J. Chem. Res.* **72,** 934 (1981).

13. Kung, H. H., *Catal. Rev. Sci. Eng.* **22,** 235 (1985).

14. Bowker, M., Hadden, R. A., Houghton, H., Hyland, J. N. K., and Waugh, K. C., *J. Catal.* **109,** 263 (1988).

15. Abderrahim, H., and Duprez, D., *in* "Proceedings, 1st International Symposium on Catalysis and Automotive Pollution Control (CAPOC 1), Brussels 1986" (A. Crucq and A. Frennet, Eds.), Studies in Surface Science Catalysis, Vol. 30, p. 359. Elsevier, Amsterdam, 1987.

16. Abderrahim, H., and Duprez, D., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 3, p. 1246. Chem. Institute of Canada, Ottawa, 1988.

17. Duprez, D., *J. Chim. Phys.* **80,** 487 (1983).

18. Evans, J. W., Wainwright, M. S., Bridgewater, A. J., and Young, D. J., *Appl. Catal.* **7,** 75 (1983).

19. Bartley, G. J. J., Burch, R., and Chappell, R. J., *Appl. Catal.* **43,** 91 (1988).

20. Bardet, R., Thivolle-Cazat, J., and Trambouze, Y., *Cl Mol. Chem.* **1,** 201 (1985).

21. Denise, B., and Sneeden, R. P. A., *Appl. Catal.* **28,** 235 (1986).

22. Liu, C., Willcox, D., Garland, M., and Kung, H. H., *J. Catal.* **90,** 139 (1984).

23. Klier, K., Chatikavanij, V., Herman, R. G., and Simmons, G. W., *J. Catal.* **74,** 343 (1982).
24. Herman, R. G., Simmons, G. W., and Klier, K., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), p. 475. Kodansha/Elsevier, Tokyo/Amsterdam, 1981.
25. Szarawara, J., and Reychman, K., *Int. Chem. Proc.* **1,** 331 (1980).
26. Jackson, S. D., *J. Catal.* **115,** 247 (1989).
27. Ferhat-Hamida, Z., Ph.D. dissertation, Poitiers, 1987.
28. Duprez, D., Barbier, J., Ferhat-Hamida, Z., and Bettahar, M., *Appl. Catal.* **12,** 219 (1984).
29. Duprez, D., Abderrahim, H., Kacimi, S., and Rivièѐve, J., *in* "Proceedings, 2nd International Conference on Spillover, Leipzig, 1989" (K.-H. Steinberg, Ed.), p. 127. Karl-Marx Universität Publ., Leipzig, 1989.
30. Kinnaird, S., Webb, G., and Chinchen, G. C., *J. Chem. Soc. Faraday Trans. 1* **83,** 3399 (1987).
31. Kinnaird, S., Webb, G., and Chinchen, G. C., *J. Chem. Soc. Faraday Trans. 1* **84,** 2135 (1988).
32. Chaumette, P., Courty, Ph., Barbier, J., Fortin, T., Lavalley, J. C. Chauvin, C., Kiennemann, A., Idriss, H., Sneeden, R. P. A., and Denise, B., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 2, p. 585. Chem. Institute of Canada, Ottawa, 1988.
33. Burch, R., Chappell, R. J., and Golunski, S. E., *Catal. Lett.* **1,** 439 (1988).
34. Bowker, M., Hyland, J. N. K., Vandervell, H. D., and Waugh, K. C., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984" (G. Ertl *et al.*, Eds.), Vol. 2, p. 35. Dechema, Frankfurt-am-Main, 1984.