JOURNAL OF CATALYSIS **144**, 544–555 (1993)

Hydrogen Species, Vacancies, and Alkadiene Hydrogenation Selectivity on Copper-Based Hydrogen Reservoirs

A. SENE, L. JALOWIECKI-DUHAMEL, G. WROBEL,[1] AND J. P. BONNELLE

Laboratoire de Catalyse Hétérogène et Homogène, U.R.A. C.N.R.S. No. 402,
Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France

Received October 27, 1992; revised March 10, 1993

Hydrogenation of 2-methylbuta-1,3-diene (isoprene) under helium flow in the absence of gaseous hydrogen is used to provide evidence for reactive hydrogen species (H*) present in copper-based oxides (Cu–Cr–O, Cu–Al–O, Cu–Zn–O). These compounds are hydrogen reservoirs with marked diffusion properties for hydrogen species (H*, OH^-). Moreover, analysis of the distribution of hydrogenated products obtained under H_2 + isoprene in relation to the solid structure of the catalyst leads to the proposition of particular active sites, ^XM–$^YM'$. These are constituted of two cations: ^XM is the 3-coordinatively unsaturated Cu^+ ion and $^YM'$ is a second cation (Cr^{3+}, Al^{3+}, Zn^{2+}) with Y unsaturations of coordination. Under H_2 a high degree of unsaturation can exist (^3M–$^3M'$), whereas under helium a change in the selectivity of hydrogenated products is observed that is attributed to the variation of Y (3 down to 0). This phenomenon corresponds to a progressive blocking of the surface unsaturations, probably due to the migration of OH^- groups. © 1993 Academic Press, Inc.

INTRODUCTION

Copper-based mixed oxides are of industrial importance. They are widely used in the selective hydrogenation of organic compounds as well as in the synthesis of methanol from CO and H_2 (*1, 2*). Although it is well known that the presence of copper is the prerequisite condition for obtaining catalytic activity, the oxidation state of the active species remains a controversial question. In the literature, three different active species have been proposed: Cu^+ (*3–5*), Cu^0 (*6, 7*), Cu^0 + Cu^+ (*8, 9*).

On another line of study, the presence of anionic vacancies is seen as necessary to obtain catalytic activity. Evidence has been provided of their role in lattice diffusion phenomena (*10, 11*). By analogy with homogeneous catalysis, Siegel has defined three different coordinatively unsaturated sites (CUS) with 1, 2, or 3 unsaturations on the cation (^1M, ^2M, or ^3M) in chromium and cobalt oxides. The ^3M and ^2M sites have been respectively associated with alkadiene hydrogenation and isomerization reactions (*12, 13*). The concept has been validated and widely used by Tanaka and co-workers (*14–17*). Concerning methanol synthesis, Frost has postulated a direct correlation between the catalytic production of methanol and the concentration of vacancies calculated from the theory of "junction effect interactions" (*18*). Thus it seems from these studies that an important parameter in the constitution of the active site is the number of coordinative unsaturations.

Besides this aspect of characterization of active sites, the behavior of catalysts towards reactive hydrogen species as well as towards hydroxyl groups remains unexplained. Duprez *et al.* have shown for Cu–Zn–Al catalysts by thermodesorption the existence of two peaks (at 480 and 600 K) associated with hydrogen (*19*). The intensity of the low-temperature peak is directly correlated to catalytic activity in methanol synthesis from CO + H_2. In the same way, by thermodesorption, Roberts and Griffin have also shown the presence of

---

[1] To whom correspondence should be addressed.

0021-9517/93 $5.00

two peaks in Cu–Zn systems, at 320 and 450 K (*20*). The high-temperature peak has been attributed by these authors to hydrogen species bonded to isolated copper cations. In addition, Ostrovski and Dyatlov have reported the presence of hydrogen species which are not bonded to oxygen on Cu–Zn–Al systems (*21*).

In our laboratory, several studies dealing with the concept of CUS centres participating in the active site composition, and with hydrogen reservoirs, have been performed on copper-based reduced systems (Cu–Cr–O, Cu–Al–O, Cu–Zn–O) (*22–25*) as well as on sulfide solids (*26, 27*). Evidence has been provided for the existence of particular hydrogen species of the solid (denoted H*, since the exact charge of these species was not the aim of the studies). These H* species are able to hydrogenate alkadienes at 423 K without the presence of gaseous H_2 when the solid has previously been treated under H_2; otherwise no H* species is found (*28*). Hence these reactive H* species are different from those of hydroxyl groups still present on the solid. Moreover, the concentration of the reactive H* species has been found to depend on the creation of anionic vacancies in the catalysts (*22, 26*) and it has been shown for Cu–Cr–O (Cu/Cr = 1) that the first hydrogen species introduced in the alkadiene hydrogenation reaction comes from the solid and is of hydridic nature (*29*). Indeed, it has been verified using the substitution of the reactive hydrogen species by deuterium that the reactive hydrogen species does not come from the reactants (*28*). Moreover, this reactive hydrogen species also participates in the alkadiene isomerization reaction (*28*), which can be seen to be very similar to the hydrogenation reaction: a hydrogen species (H^-) is introduced to the alkadiene but then, before desorption of the isomerized alkadiene, a H^- species is furnished back to the solid.

The ability to selectively favor one among various competitive chemical reactions is by far the most fascinating characteristic of a catalyst. It seems essential to define the important parameters for the orientation of the catalytic reaction in the surface structure of active sites, the nature and ability of the active species to diffuse through the solid, and the catalytic properties of surface ions coming by diffusion from the bulk to the surface. This phenomenon deals with solid–solid and solid–gas phase interfaces and can be very useful for membrane reactor designs. In particular, membranes having a high permeability to hydrogen while restricting the flow of other gases have important catalytic activity for hydrogenation or dehydrogenation reactions. We propose in this study to analyze the behavior of hydrogen species in copper-based oxides (Cu–Zn–O, Cu–Al–O, and Cu–Cr–O) and to define the alkadiene hydrogenation active sites involving interactions between vacancies and hydrogen species: H* and/or OH^-.

EXPERIMENTAL

The copper–chromium (Cu/Cr = 1) and copper–aluminium (Cu/Al = 0.5) samples were prepared by coprecipitation of the corresponding hydroxides with ammonium hydroxide. The oxide precursors were obtained by decomposition under flowing nitrogen for Cu–Cr–O at 643 K (*22*) and under flowing air at 1083 K for Cu–Al–O. The Cu–Zn–O (Cu/Zn = 0.43) catalyst and pure ZnO were prepared by coprecipitation from the corresponding nitrates and sodium carbonate at 353 K until pH = 7 was reached according to a procedure already published (*25*); the obtained hydroxides were then calcined at 623 K in air.

Finally, the oxides were pretreated under hydrogen for Cu–Cr–O and Cu–Al–O at 423 K and 573 K, respectively, and for Cu–Zn–O at 523 K under a flowing mixture of 50% hydrogen in helium for 16 h.

The pretreatment under H_2–He and catalytic experiments were carried out *in situ* at atmospheric pressure in an all-glass, grease-free flow apparatus previously described (*30*). After each treatment by H_2 or He–H_2, the reactants were introduced at constant pressure (20 or 7 Torr, respectively, with regard to the nature of the gas phase, H_2 or He) in a flow of purified hydrogen or helium (1 atm, 20 ml min^{-1}) in an isothermal reactor. Catalytic tests were carried out at 323 K under hydrogen and the reported hydrogenation activity is that observed at the stationary state.

The dynamic method which allows us to provide evidence for and to determine the concentration of reactive and extractable hydrogen H* species has been previously reported (*28*). The solid was purged under a purified helium flow (2 liter h^{-1}) at 323 K for 17 min and then the temperature was increased to 423 K in 13 min. The total elimination of gaseous hydrogen was followed by the use of a catharometer. After 4 min the concentration of molecular hydrogen in the gas phase was lower than 0.1%. Isoprene was then introduced at constant pressure (6 up to 8 Torr) in a flow of purified helium in an isothermal reactor (423 K). The solid under helium is purged for 30 min. The hydrogenation reaction under He + isoprene involves the participation of reactive hydrogen species H* of the solid which hydrogenate isoprene and are consumed by a diffusion process. In the present study another procedure is also applied corresponding to an initial catalytic test under a mixture H_2 + isoprene at 423 K. Once a steady state of catalytic activity is reached, the mixture H_2 + isoprene is replaced by a mixture of He + isoprene.

Isoprene, purum grade from Fluka, was used after purification by distillation under vacuum. Hydrogen and helium (N-55 grade) came from Air Liquide. The reaction products were analyzed by gas chromatography using a capillary column (squalane, 0.2 mm i.d., 100 m long) operating at 313 K and a flame ionisation detector.

RESULTS

I. Diffusion of the Reactive Hydrogen Species

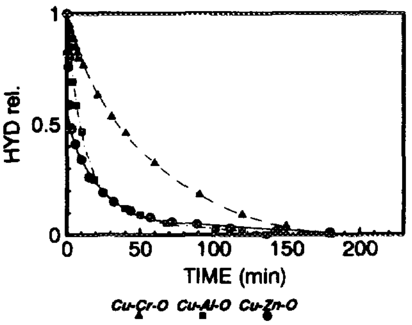


FIG. 1. Relative hydrogenation activity at 423 K under isoprene + helium flow versus time.

In previous studies, we reported that after treatment under H_2, Cu-Cr-O, Cu-Al-O (*22*), and Cu-Zn-O (*25*) catalysts contain anionic vacancies produced by the elimination of H_2O (OH groups) and also some reactive hydrogen species able to hydrogenate alkadienes in the absence of gaseous hydrogen. At 423 K, under a helium + isoprene flow, alkadiene hydrogenation occurs on H_2-treated copper-based oxides as presented in Fig. 1. As a function of time on stream, the isoprene conversion or hydrogenation activity (HYD) is measured. The ratio $\mathrm{HYD_{rel}} = A_{H_t}/A_{H_0}$ (where A_{H_t} and A_{H_0} are the initial hydrogenation and the hydrogenation activity at time t) can be plotted versus time; this relative hydrogenation activity at 423 K under helium + alkadiene feed decreases with time. For each solid a similar curve is obtained and by integrating this curve the extractable reactive hydrogen H* content of the solid can be determined if the product distribution is taken into account (2 H* for monohydrogenation and 4 H* for dihydrogenation).

The extractable H* content found on Cu-Zn-O (30-70) oxide catalyst, previously treated under H_2 at 523 K is 17.9×10^{-3} mol g^{-1}, which is the highest value found in this study, as summarized in Table 1.

In addition, between *t* and t_f (time at which the hydrogenation activity is found to be 0), the percentage of reactive hydrogen still present in the solid can be estimated. $\mathrm{HYD_{rel}}$ versus H* concentration data are

TABLE I

Hydrogen H* Content and Isoprene Hydrogenation Activity (HYD)

Catalyst	H* (10^3 mol g^{-1} h^{-1}	H_s^* (10^3 mol g^{-1})	HYD (10^3 mol g^{-1} h^{-1})
Cu–Cr–O	13.0	1.0	30
Cu–Al–O	7.2	0.2	4
Cu–Zn–O	17.9	0.4	1

presented in Fig. 2 for each solid purged in the same way (30 min in this case). The curves obtained show clearly that there is no proportionality between the relative hydrogenation rate consuming H* and the H* content of the solid. The kinetics of H* consumption by the alkadiene is a complex phenomenon which has been widely studied (*22*, *28*); in particular, a diffusional process of the H* species within the solid must be considered. Among the kinetic models which have been taken into account the most appropriate to the results obtained postulates that the surface hydrogen (H_s^*) is constant as long as bulk hydrogen exists and so permits one to determine the hydrogen H* species concentration present at the surface of the solid (Table 1).

In another experiment,when the alkadiene feed is suppressed in the He + isoprene flow for a time Θ, the consumption of hydrogen species at 423K from the catalyst ceases until the isoprene flow is restored. The results obtained, presented in Fig. 3 for Cu–Cr–O (similar results are observed on Cu–Zn–O and Cu–Al–O), correspond to the diminution of the hydrogenation activity, i.e., the disappearance rate of hydrogen species consumed from the surface by isoprene as a function of time. It also appears that after suppression of alkadiene from the feed during time Θ, the concentration of surface hydrogen species increases. In this way, diffusion of the hydrogen species H* from the bulk to the surface is evidenced again, but the initial activity cannot be restored completely.

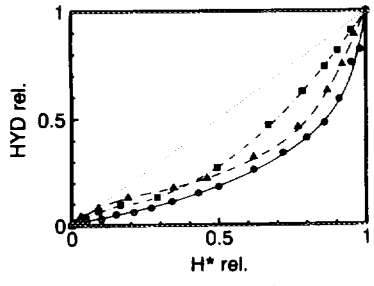


FIG. 2. Relative hydrogenation activity at 423 K under helium + isoprene flow versus the hydrogen H* species concentration.

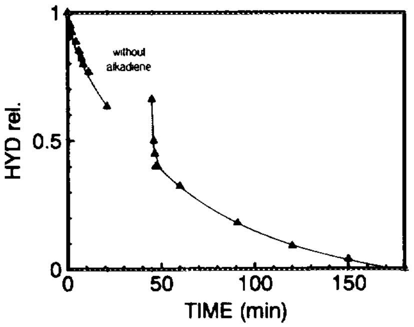


FIG. 3. Hydrogenation activity under a discontinuous isoprene + helium flow (i.e.,during time Θ, isoprene is suppressed from the feed) at 423 K as a function of time on Cu–Cr–O.

On the other hand, after a first consumption of the hydrogen species H* (i.e., the result previously presented in Fig. 1), a short treatment under H_2 (323 K, 15 min) is able to regenerate, at least partially, the hydrogen reservoir, as a second consumption of the H* species by isoprene gives a quite similar experimental result afterwards. Thus the H* species can be replaced easily by diffusion from the surface to the bulk.

The comparison between the results obtained for different times of purging (Fig. 1, Fig. 4, and Table 2) shows that the initial activity, as well as the concentration of extractable hydrogen species H*, decreases when the time of purging under helium increases. The decrease of the extractable H*

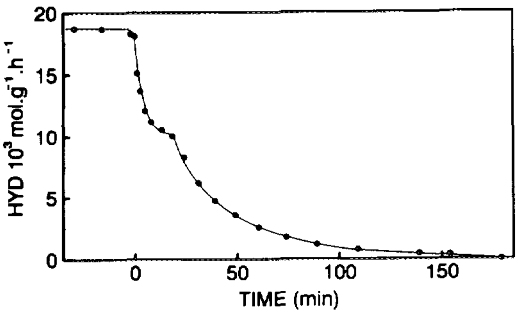


FIG. 4. Hydrogenation activity under a continuous isoprene flow first in H_2 and then in helium at 423 K as a function of time of purge under helium on Cu–Zn–O.

concentration cannot be attributed to a loss of hydrogen in the gas phase, as no loss of weight has been observed by thermogravimetry under pure helium after reduction of the catalysts. Hence, hydrogen H* is maintained in the solid and only a small amount can be extracted. To the contrary, the temperature of purge (chosen between 323 and 423 K) does not change the concentration of extractable hydrogen species.

II. Alkadiene Hydrogenation Selectivity

Under hydrogen. The isoprene hydrogenation activity was measured at 323 K under H_2. The results obtained are presented in Table 1. The highest alkadiene hydrogenation activity (mol g^{-1} h^{-1}) is observed on H_2-treated Cu–Cr–O: the lowest on Cu–Zn–O, even though this solid contains the highest concentration of H* species. This result shows that there is no proportionality between the H* concentration and the alkadiene hydrogenation activity. One must recall that the nature of the information given by the experiments is different:

TABLE 2

Extractable H* Ratio as a Function of Time of Purging under Helium for Catalysts Cu–Cr–O, Cu–Al–O, and Cu–Zn–O

Time of purging (h)	Extractable H* ratio		
	Cu–Cr–O	Cu–Al–O	Cu–Zn–O
0	1	1	1
0.5	0.38	0.29	0.31
1	0.16	0.12	0.18
2	0.08	0.02	0.04
3	<0.01	—	<0.01

(i) the catalytic activity (under H_2) is a surface phenomenon and is proportional to the number of active sites accessible to alkadienes;

(ii) the reactive hydrogen amount is mainly characteristic of the bulk since the reactive hydrogen species are consumed by diffusion from the bulk to the surface and then by surface reaction.

When surface hydrogen (H_S^*) is considered, the highest alkadiene hydrogenation activity is found for Cu–Cr–O, which contains the highest H_S^* concentration, but such a small hydrogenation activity of Cu–Zn–O cannot be justified. Nevertheless, a good proportionality is obtained between alkadiene hydrogenation activity and the H_S^* concentration within a given series of solids, as for example Cu–Cr–O catalysts with various Cu/Cr ratios (*22*) or the Cu–Zn–Al–O series (*31*). However, one must recall that the participation of H* species in alkadiene hydrogenation and isomerization reactions has been previously noted and so hydrogenation active sites correspond to a fraction of sites involving hydrogen H*.

Hydrogenation activity takes into account all the hydrogenated products, which for isoprene are isopentane (dihydrogenated), 2-methylbut-1-ene (2MB1), 3-methylbut-1-ene (3MB1), and 2-methylbut-2-ene (2MB2) (monohydrogenated). Typical variations in the product distribution are presented in Table 3. All the catalysts exhibit very similar selectivities, somewhat independent of the type of catalyst used, as observed previously (*32*); 2-methylbut-1-ene is always the major product obtained, at about 80%.

Under the same conditions pure Cu^0 and ZnO have been tested under H_2 + isoprene. No activity is observed on reduced ZnO

TABLE 3

Selectivity (%) in Isoprene Hydrogenation

Catalyst	Product[a]		
	3MB1	2MB1	2MB2
Cu–Cr–O	12	79	7
Cu–Al–O	10	82	8
Cu–Zn–O	10	73	17

[a] 3MB1—3-methylbut-1-ene; 2MB1—2-methylbut-1-ene; 2MB2—2-methylbut-2-ene.

even at 423 K, while metallic copper presents a significant activity only at 423 K (*22*).

Under helium. The variation of isoprene hydrogenation activity as a function of time, as well as the corresponding hydrogenated product distribution, is presented in Fig. $5a_1$, b_1, and c_1,obtained after a purge under helium of 0 min. The direct analysis of the curves obtained reveals three different areas, as specified below:

Area I. The steady state observed under a flow of H_2 + isoprene at 423 K is maintained as long as there is enough molecular H_2 in the gas phase. In these conditions the surface state corresponds to a high majority of isopentane formed.

Area II. When molecular hydrogen disappears completely from the gas phase a sharp decrease of activity is observed. At the same time the production of isopentane also decreases drastically, whereas the production of monoenes formed changes. Maxima are reached successively by 2-methylbut-2-ene and the two methylbut-1-enes. Moreover, 3-methylbut-1-ene starts to increase when 2-methylbut-2-ene disappears. However, for Cu–Zn–O the phenomena are shifted to area III and the variations of products are more spread out (isopentane disappears the most slowly), perhaps because of the large hydrogen reservoir. No simple correlation is found between the time of isopentane disappearance or the appearance of the maxima of formation of the various products and either the H* content or the H_s^* content.

Area III. After 22 min under He + isoprene the production of isopentane is almost nil. Similar results are obtained after 30 min of purge under He (Fig. $5a_2$, b_2, c_2) (*28*)).

It can be recalled that similar behaviour (Fig. $5a_1$, b_1, c_1) is also observed on sulfides ($MoS_2/\gamma-Al_2O_3$), for which a good correlation has been obtained between the selectivity (i.e., production of isopentane) and the site structure. Similar variations of isoprene product distribution under helium + isoprene flow as a function of time have also been obtained with various H* species concentrations. It has been shown that a small number of active sites are sufficient to produce a large quantity of isopentane when the hydrogen reservoir is large enough. However, even though the amount of H* hydrogen species in the solid is high, the formation of isopentane is nil when the corresponding active sites do not exist (*33*).

DISCUSSION

1. Active Sites

In almost all cases, the copper-based catalysts employed in this work are biphasic and composed of metallic copper and a residual oxide still containing copper ions, generally in the Cu^+ state (*34*). In our experimental conditions, Cu^0 is shown to be inactive up to 373 K for alkadiene hydrogenation (*22*). Above this temperature it is slightly active but its behaviour is quite different and it cannot store reactive hydrogen. Thus, for Cu–Cr–O and Cu–Al–O spinels, a model of the active sites, derived from the Siegel model (*12*, *13*), has been proposed in order to explain the alkadiene hydrogenation and isomerization reactions. The active sites that have been associated with hydrogenation and isomerization reactions are respectively the three-coordinatively unsaturated (3 CUS) Cu_B^+ ion in an octahedral environment and the 2 CUS Cr^{3+} or Al^{3+} ions of the spinel network, one unsaturation being filled by a hydrogen species, H^- (*22*, *29*,

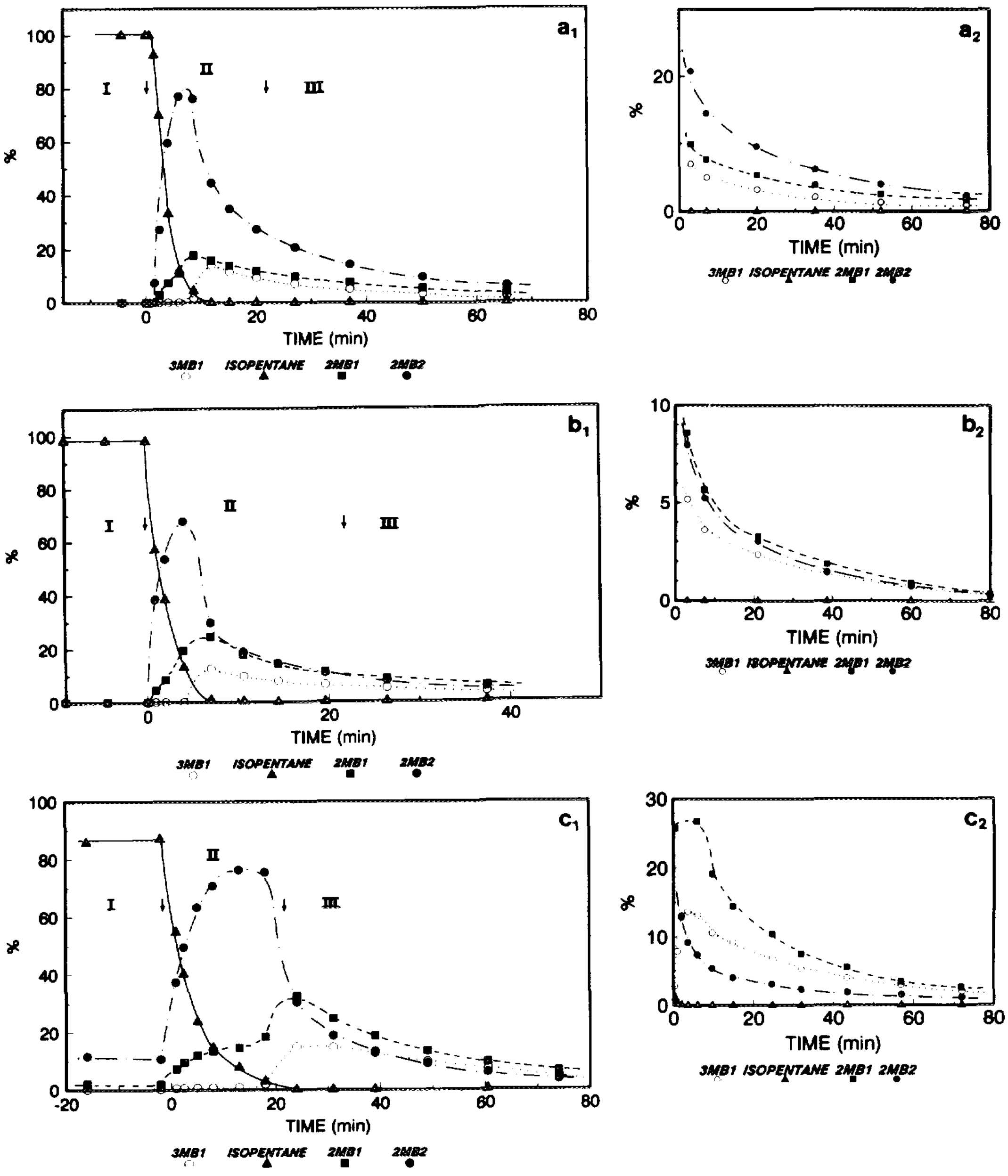
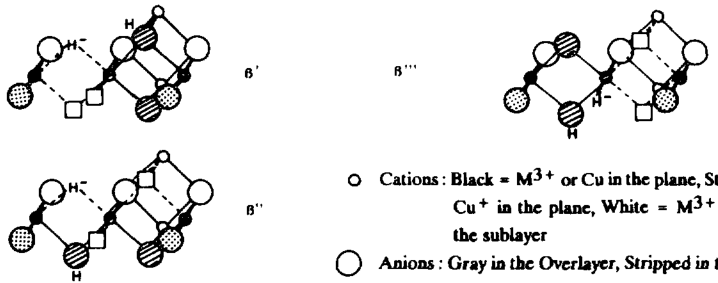


FIG. 5. Isoprene hydrogenated products distribution at 423 K as a function of time for various purge times under helium: (a_1) 0 min, (a_2) 30 min on Cu–Cr–O; (b_1) 0 min, (b_2) 30 min on Cu–Al–O; (c_1) 0 min, (b_2) 30 min on Cu–Zn–O.

35). Moreover, some studies on the same catalysts, using appropriate model molecules (2-butene-1-ol), have shown that several other reactions, exist such as the dehydrogenation reaction associated with Cr^{3+} ions and the hydrodehydroxylation reactions on Cr^{3+}–H^- pairs (*36*).

These reactions require the existence of anionic vacancies which can be occupied by H^- or mobile OH^- species. For Cu–Cr–O



○ Cations : Black = M^{3+} or Cu in the plane, Stripped = Cu^{+} in the plane, White = M^{3+} or Cu in the sublayer
◯ Anions : Gray in the Overlayer, Stripped in the plane, White in the Sublayer
☐ Vacancy

Environment of octahedral cations in the (100) plane - Structures of β sites.

○ Octahedral Cations : Black = M^{3+} or Cu in the plane, Stripped = Cu^{+} in the plane, White M^{3+} or Cu in the Sublayer
◯ Anions : Stripped in the plane, White in the Sublayer
☐ Vacancy

Environment of octahedral cations in the (110) plane - Structure of α sites.

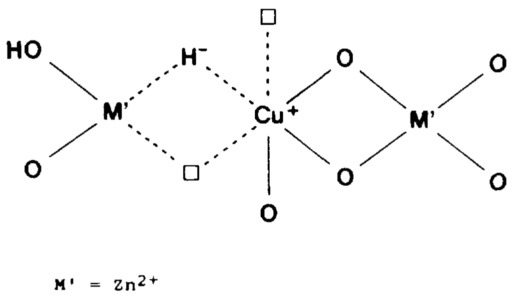
○ Octahedral Cations : Black = M^{3+} or Cu in the plane, Stripped = Cu^{+} in the plane
◯ Anions : Gray in the Overlayer, White in the Sublayer
☐ Vacancy

Environment of octahedral cations in the (111) plane - Structure of γ sites.

SCHEME 1

and Cu–Al–O systems, as the concentration of Cu^{+} or Cu^{2+} ions in octahedral sites, as well as the concentration of anionic vacancies, is low, one could expect that a large majority of anionic vacancies associated with Cu^{+} are shared with an Al^{3+} or Cr^{3+} ion (*22*). This is apparent for the α, β, and γ sites in Scheme 1 for the most common crystallographic planes of defect spinels, which are the (111), (110), and (100) planes (*22*). These bimetallic vacancies (BMV) have been justified by a statistical distribution of the different cations (Cr^{3+}, Al^{3+}) around the central Cu^{+} ion for Cu–Cr–O and Cu–Al–O spinels. It has been calculated, previously, that the probability of having one BMV per site is higher than 97.5% and higher than 72.7% for two BMV. In addition, at least 44% of the ^{3}M sites in the (100) and (111) planes will be composed only of BMV (*22*). Hence, a modeling considering only isolated sites leads to a relatively poor description of the active sites. Moreover, it is important to note that the corresponding probabilities are almost independant of the crystallographic plane. Consequently, the crystal shape has very little influence on the catalytic properties.

The systems based on ZnO differ essentially from the spinel network by the O^{2-} stacking. The same types of cationic sites exist and a priori it must be possible to incor-



SCHEME 2

porate copper ions in the ZnO matrix in tetrahedral or octahedral sites. Besides, Klier *et al.* (*2*a) have reported that

—For global CuO content lower that 30%, from 4% up to 6% of CuO can be dissolved in the ZnO network in the calcined state.

—In the reduced state, up to 12% of copper remains dissolved in ZnO lattice as Cu^+ ions.

More recently, from electron spectroscopic studies of analogous oxides, Yureva *et al.* have shown the existence of Cu^{2+} ions in a slightly distorted octahedral coordination stabilized by ZnO (*37, 38*) and they attribute the high activity of these systems to unsaturated Cu^+ ions present in the reduced state (*39*). Then the situation of copper becomes very similar to those observed with a spinel structure and the transposition of the Cu–Zn–O system of the modeling proposed previously is reasonable (Scheme 2).

The notion of an active site constituted by an ensemble of cations with a specific coordinative unsaturation has previously been suggested for other systems such as sulfur catalysts (bulk MoS_2 and MoS_2/γ-Al_2O_3) where the edge Mo ions with 2, 3, or 4 CUS (the active site) are not isolated (*40*). Thus, different ensembles ^XM–^YM (where X and Y are the number of unsaturations on each cation, varying from 0 up to 4) have been proposed to be the active sites, each elementary ensemble being associated with a particular reaction as proposed in Table 4. Transposed to our binary copper-based systems, different ensembles can be proposed corresponding to ^XM–$^YM'$, where

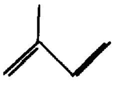
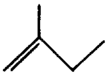
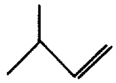
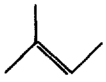
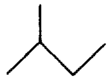
—^3M = Cu^+ with 3 CUS correlated with hydrogenation reaction.

—$^YM'$ = Zn^{2+} or Al^{3+} or Cr^{3+} (or even Cu^+, if the lattice can contain enough ions of this kind) with Y unsaturations of coordination varying from 0 up to 3.

Thus if the hydrogenation reaction is associated with ^3M sites, it appears reasonable to correlate isopentane coming from a double hydrogenation of isoprene with a ^3M–$^3M'$ ensemble where each cation is 3 CUS. In fact the ^XM–$^YM'$ ensemble composed of two cations is correlated with the combination of the corresponding reactions

TABLE 4

Products Associated with Different Active Sites in the Reaction of Isoprene

Sites	^2M-$^0M'$ ^2M-$^1M'$ ^2M-$^2M'$	^3M-$^0M'$ ^3M-$^1M'$	^3M-$^2M'$	^3M-$^3M'$
Products		 		

(hydrogenation, isomerization) occurring on each cation.

Moreover, in view of the catalytic site structures (Scheme 1), as the highest degree of unsaturation will be on copper due to the affinity of the other cations to OH groups, it is highly probable that the $^3Cu^+$ ion neighbour is $^1M'$, at least for α sites located in the (110) plane and for the (111) plane γ sites as well as for the (100) plane β'' sites, which explains the high selectivity of copper-based oxides for monohydrogenation observed at 323 K. For β' and β''' sites located in the (100) plane, when Cu^+ is 3CUS the neighbour will be 2CUS. On the other hand, at 423 K under H_2, much higher degrees of unsaturation can be obtained and the major product observed is isopentane.

II. Active Site Environment and Selectivity

The hydrogen reservoir properties, as presented previously, largely involve diffusion processes of reactive hydrogen species H*. Also, the concentration of extractable hydrogen species H* decreases as the time of purging under helium increases (Fig. 1, Fig. 4, and Table 2). Moreover, Fig. 4 shows that the copper-based catalysts studied here present a very high isoprene hydrogenation activity at 423 K under H_2. Nevertheless, the change of gas phase to a helilum + isoprene mixture involves a decrease of the activity, which reaches 0 in a time dependent on the reservoir capacity. This variation of activity is accompanied by a particular variation of the product distribution (Fig. $5a_1$, b_1, c_1).

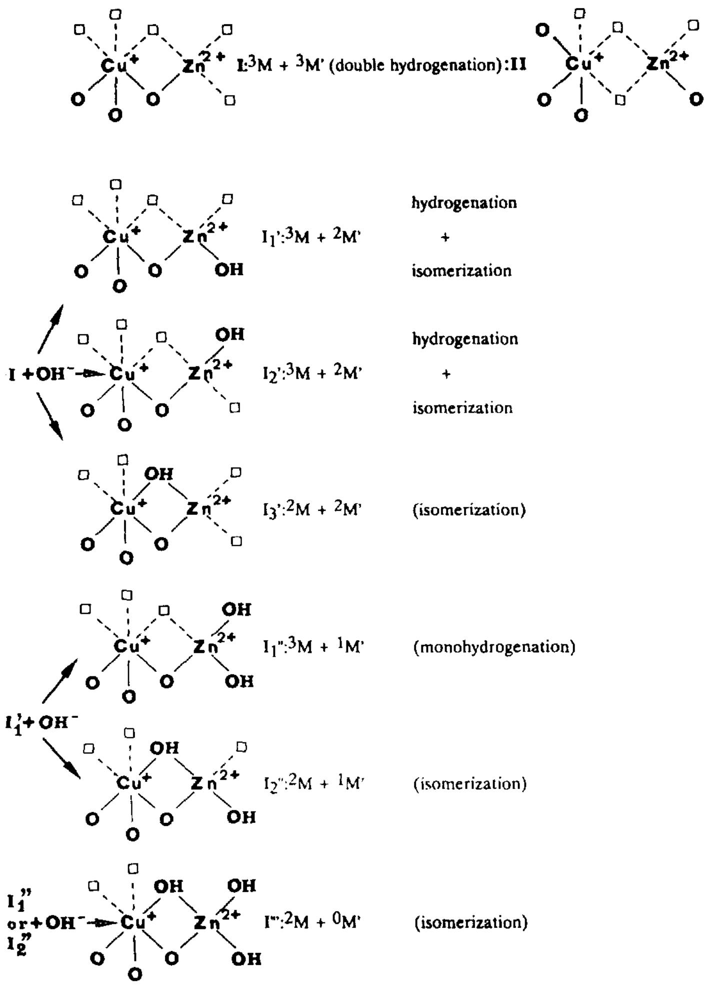
The ^3M–$^3M'$ ensembles are stable under a flow of H_2 + isoprene at 423 K, as the reactive hydrogen species H* consumed by the hydrogenation reaction can be regenerated by heterolytic rupture of molecular hydrogen (*28, 29*). However, it is highly probable that the elementary ensemble sites with some high degree of unsaturation are unstable in the absence of gaseous hydrogen; therefore the substitution of H_2 by He leads to a sharp decrease of isopentane formation which rapidly reaches zero.

The result obtained is a blocking of the sites associated with the production of isopentane (^3M–$^3M'$) simultaneously with the creation of ^3M–$^2M'$ sites correlated with 2-methylbut-2-ene formation resulting from a hydrogenation + isomerization reaction. The concentration of 2-methylbut-2-ene attains a maximum corresponding to a maximum of ^3M–$^2M'$ sites, which become ^3M–$^1M'$ sites before a final transformation to ^3M–$^0M'$ ensembles.

This phenomenon, also observed on intermetallic systems (*Tr*–Ni oxhydride systems, *Tr* = rare earth element) (*41*), has been detailed in a Cu–Zn–(Al)–O catalyst study (*31*) and related to a OH group migration. Indeed from *in situ* XPS and Auger spectroscopic experiments, production of characteristic $Zn2p_{3/2}$ Zn $L_3M_{4.5}M_{4.5}$, and O1*s* peaks has been observed at different reduction steps. After treatment under H_2–N_2 flow (523 K, 16 h), the OH species are largely in the majority in the first layers. In the same way, the energy shifts of the Zn peaks are consistent with a progressive hydroxylation of zinc, which indicates the diffusion of hydroxyl groups from the bulk to the surface. Moreover, the well known affinity of Zn^{2+}, Cr^{3+}, and Al^{3+} for OH^- makes the hydroxyl group located in priority in the anionic vacancy of the $^3M'$, site which becomes $^2M'$.

In Scheme 3, different structural changes under either helium or helium + isoprene mixture are proposed. One must note that the ^3M site is a prerequisite condition for continued hydrogenation activity and if some other transformations exist involving a lower degree of unsaturation of the Cu^+ cation they could only be analyzed by the use of other model reactions.

All the results obtained lead to the conclusion that different structures of active sites occur on copper-based systems. These active sites are composed of elementary ensembles $^3Cu^+$–$^YM'$, where the value of *y* unsaturations of coordination leads to vari-



SCHEME 3

ous selectivities in alkadiene hydrogenated products. Moreover, the $^3Cu^+-^YM'$ active site modeling suggested to explain the well-known synergism effect on Cu–Al–O, Cu–Cr–O, and Cu–Zn–O catalysts could be certainly generalized and applied to most oxide systems.

REFERENCES

1. Mounts, T. L., and Dulton, H. J., *J. Am. Oil Chem. Soc.* **44**, 67 (1967).
2. (a) Klier, K., *in* "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.), Vol. 31, p. 243. Academic Press, New York, 1982; (b) Mehta, S., Simmons, G. W., Klier, K., and Herman, R. G., *J. Catal.* **57**, 339 (1979).
3. Herman, R. G., Klier, K., Simmons, G. W., Finn, B. P., Bulko, J. B., and Kobylinski, T. P., *J. Catal.* **56**, 407 (1979).
4. Baetzold, R. C., *J. Phys. Chem.* **89**, 4150 (1985).
5. Kuznetsova, L. I., Yurieva, T. M., Minyukova, T. P., Ketchik, S. V., Plyasova, L. M., and Boreskov, G. K., *React. Kinet. Catal. Lett.* **19**, 355 (1982).
6. Fleish, T. H., Mieville, R. L., *J. Catal.* **90**, 165 (1985).
7. Friedrich, J. B., Wainwright, M. S., Young, D. J., *J. Catal.* **80**, 1 (1983).
8. Okamoto, Y., Fukino, K., Imanaka, T., Teranishi, S., *J. Phys. Chem.* **87**, 3747 (1983).

9. Cunningham, J., Al Sagged, G. H., Cronin, J. A., Fierro, J. L. G., Healy, C., Hirschwald, W., Ilyas, M., Tobin, J. P., *J. Catal.* **102,** 160 (1986).

10. Murch, G. E., and Nowick, A. S. (Eds.), "Diffusion in Crystalline Solids," Chap. 3. Academic Press, Orlando, FL, 1984.

11. Sanchez, M. G., and Gazquez, J. L., *J. Catal.* **104,** 120 (1987).

12. Siegel, S., *J. Catal.* **30,** 139 (1973).

13. Siegel, S., Outlaw, J., and Garti, N., *J. Catal.* **52,** 102 (1978).

14. Takeuchi, A. Tanaka, K. I., and Miyahara, K., *Chem. Lett.*, 171 and 411 (1974).

15. Tanaka, K. I., and Okuhara, T., *Catal. Rev. Sci. Eng.* **15,** 24 (1977).

16. Tanaka, K. I., *Adv. Catal.* **33,** 99 (1985).

17. Tanaka, K. I., and Okuhara, T., *in* "Proceedings, 3rd International Conference on the Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 170. Climax Molybdenum Company, Ann Arbor, MI, 1980.

18. Frost, J. C., *Nature (London)* **334,** 577 (1988).

19. Duprez, D., Barbier, J., Fehrat, Z., Bettahar, A., Tchen, A. H., *Appl. Catal.* **16,** 1 (1985).

20. Roberts, D. L., and Griffin, G. L., *Appl. Surf. Sci.* **19,** 298 (1984).

21. Ostrovski, V. E., and Dyatlov, A. A., *Kinet. Catal.* **26,** 838 (1985).

22. Jalowiecki, L., Wrobel, G., Daage, M., and Bonnelle, J. P., *J. Catal.* **107,** 375 (1987).

23. Aïssi, C. F., Daage, M., Wrobel, G., Guelton, M., and Bonnelle, J. P., *Appl. Catal.* **3,** 187 (1982).

24. Aïssi, C. F., Daage, M., Guelton, M., Bonnelle, J. P., B. Nagy, J., and Derouane, E. G., *J. Catal.* **76,** 231 (1982).

25. Wrobel, G., Jalowiecki, L., Bonnelle, J. P., Bali, F., and Bettahar, A., *New J. Chem.* **11,** 715 (1987).

26. Jalowiecki, L., Grimblot, J., and Bonnelle, J. P., *J. Catal.* **126,** 101 (1990).

27. Jalowiecki-Duhamel, L., Grimblot, J., and Bonnelle, J. P., *J. Catal.* **129,** 511 (1991).

28. Jalowiecki, L., Daage, M., Bonnelle, J. P., and Tchen, A. H., *Appl. Catal.* **16,** 1 (1985).

29. Daage, M., and Bonnelle, J. P., *Appl. Catal.* **16,** 355 (1985).

30. Garin, F., Gault, F. G., *J. Am. Chem. Soc.* **97,** 4466 (1975).

31. Sene, A., Ph.D. Thesis, Lille, France (1990).

32. Okkerse, C., Dejonge, A., Coenen, J. W. E., and Rozendahl, A., *Am. Oil Chem. Soc.* **44,** 152 (1967).

33. Duhamel-Jalowiecki, L., Sene, A., Wrobel, G.,and Grimblot, J., *in* "Proceedings of the 9th World Hydrogen Energy Conference, Paris, France, 1992 (T. N. Veziroglu, C. Derive, and J. Pottier, Eds.), Vol. 1, p. 261.

34. Wrobel, G., D'Huysser, A., and Bonnelle, J. P., *Nouv. J. Chim.* **8,** 291 (1984).

35. Bechara, R., Wrobel, G., Daage, M. and Bonnelle, J. P., *Appl. Catal.* **16,** 15 (1985).

36. Hubaut, R., Daage, M., and Bonnelle, J. P., *Appl. Catal.* **22,** 243 (1986).

37. Anufrienko, V. F., Yurieva, T. M., Hadzieva, F. S., Minyukova, T. P., Burglin, S. Yu., *React. Kinet. Catal.* **27,** 201 (1985).

38. Hadzieva, F. S., Anufrienko, V. F., Yurieva, T. M., Vorobiev, V. N., Minyukova, T. P., *React. Kinet. Catal.* **30,** 85 (1986).

39. Yurieva, T. M., Minyukova, T. P., *React. Kinet. Lett.* **29,** 55 (1985).

40. Kasztelan, S., Wambeke, A., Jalowiecki, L., Grimblot, J., and Bonnelle, J. P., *J. Catal.* **124,** 12 (1990).

41. Pinabiau, M., Ph.D. Thesis, Lille, France (1987).