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Behavior of hex-1-ene over binary and ternary Cu-Ce-Al oxide catalysts under a hydrogen atmosphere

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Summary — New copper and cerium mixed oxides supported on alumina of a high surface area (prepared by sol-gel method) have been synthesised. Hex-1-ene undergoes both hydrogenation and isomerization reactions over these catalysts under a hydrogen atmosphere. The role of each element (Cu, Ce, Al) was studied as well as the effect of their extent. The activities and the selectivities (more particularly the *cis/trans* ratio of hex-2-ene products) lead us to propose a mechanism via a non-ionic path. This pathway can be considered as a balance between a σ-alkyl semi-hydrogenated intermediate, precursor of the hydrogenated product, and a concerted mechanism (SN'_2) leading meanly to the isomerization.

alkene hydrogenation / alkene isomerization / hex-1-ene / Cu-Ce-Al oxide

Résumé — Transformation de l'hex-1-ène sous atmosphère d'hydrogène en présence de catalyseurs oxydes à base de Cu-Ce-Al. *Différents oxydes à base de cuivre, cérium et aluminium ont été préparés par imprégnation à sec de sels de ces éléments sur une alumine de grande surface spécifique (préparée par la méthode sol-gel). Sur ces catalyseurs une compétition entre hydrogénation et isomérisation de l'hex-1-ène a été entreprise sous une atmosphère d'hydrogène. L'étude comparative de ces solides a permis d'évaluer les effets liés à chaque élément ainsi qu'à sa teneur. Les résultats en termes d'activité et de sélectivité (plus particulièrement le rapport* cis/trans *du produit hex-2-ène) permettent de proposer un mécanisme réactionnel via une voie non-ionique. Ce mécanisme de réaction proposé peut être considéré comme une balance entre le passage par un intermédiaire σ-alkyle semi-hydrogéné, précurseur du produit d'hydrogénation et un mécanisme concerté (SN'_2) menant essentiellement à l'isomérisation.*

hydrogénation / isomérisation / hex-1-ène / oxyde de Cu-Ce-Al

Introduction

The chemical transformation of alkenes in the presence of hydrogen over heterogeneous catalysts is one of the most studied reactions in both academic and industrial laboratories. However, most work has been performed on metals and relatively little on mixed oxides. One of the reasons is the difficulty of the stereochemical approach over this kind of solid. However, such an approach gives interesting data for studying mechanistic processes. Moreover, these oxides present good activities and often better selectivities than metals. A considerable amount of work has been done in our laboratory using a large number of various mixed transition metal oxides leading to active and selective catalysts in the hydrogenation reaction of polyunsaturated organic compounds [1–8]. Copper-based mixed oxides, where copper ions are associated with other cations such as Zn^{2+}, Al^{3+}, Cr^{3+} and Th^{4+}, have an excellent selectivity for the monohydrogenation of conjugated diene [2]. In these cases, the selectivity toward hydrogenation or double-bond migration also depends on the electronic and steric effects related to the reagent [3]. Ceria-based catalysts, such as Ce-Ni-O, are less selective [1] but have an advantage due to the existence of two cerium oxidation states (Ce^{4+}/Ce^{3+}) which avoids nickel poisoning in the presence of small amounts of sulfur [4]. On the other hand, the addition of aluminium to Ce-Ni oxide totally changes the product distribution, because it can prevent the *cis/trans* isomerization as in the linolenic acid hydrogenation [5, 6].

In order to exploit the advantages of each species, we have prepared various binary and ternary copper, cerium and aluminium mixed oxides. The studies performed over these oxides in terms of activities and selectivities in the hydrotreatment of alkene, in addition to the structures which are described elsewhere [8], allow us to propose a mechanistic model.

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Experimental section

Catalysts

Ternary oxide catalysts were obtained by coimpregnation of copper nitrate and cerium nitrate solutions into an alumina support prepared by sol-gel process and precalcined at 773 K under dried air (S = 420 m^2/g). Two solids, with various Cu/Ce atomic ratios (Cu/Ce = 1; Cu/Ce = 5) and the same Ce/Al atomic ratio (Ce/Al = 0.1) were prepared and named 1Cu1Ce10Al and 5Cu1Ce10Al respectively.

Binary oxides were obtained by impregnation of copper nitrate solution into the above alumina support or a ceria support (S = 116 m^2/g). On alumina, catalysts 1Cu10Al and 5Cu10Al had Cu/Al atomic ratios equal to 0.1 and 0.5, respectively. On ceria support, the Cu/Ce atomic ratio was equal to 1 and the catalyst was named 1Cu1Ce.

The solids were dried for about 20 h in a drying oven (~ 373 K) and then calcined under a flow of dried air. The temperature was raised at a rate of 30 Kh^{-1} from room temperature to 673 K and maintained for about 4 h.

Reactions

The catalytic reactions were carried out in all-glass, grease-free flow apparatus, at atmospheric pressure. Precursor oxides were reduced for 15 h at 403 K under hydrogen (Air Liquide, N 55). Competitive reactions between hydrogenation (HYD) and isomerization (ISOM) were carried out in an isothermal reactor operating at 333 K. The reagent (hex-1-ene; Fluka, 99.8%) was introduced at constant partial pressure (1.3 kPa) in a flow of purified hydrogen (1 atm). Products were analysed with a Varian 3600 CX chromatograph provided with a flame ionization detector and a capillary column (chrompack CP-SIL 5 CB, 50 m x 0.25 mm).

Results and discussion

Role of each component

We should first note the absence of activity over the solids that do not contain copper. In fact, ceria, alumina and binary Ce- Al solids were tested in the same conditions as the copper-containing catalysts and no activities related to these solids were observed. Thus, the copper species are essential to activate molecular hydrogen and/or hex-1-ene. Table I displays the intrinsic activities for various amount of copper in the catalysts. This intrinsic activity increases a little with the copper contents (eg, 1Cu1Ce10Al - 5Cu1Ce10Al and 1Cu10Al - 5Cu10Al).

From physicochemical techniques described elsewhere [7, 8], four different forms of copper species have been identified in the Cu-Ce solids: isolated Cu^{2+} ions called monomers, copper dimers, Cu^{2+} clusters, and small particles or aggregates of CuO. The alumina-based catalysts have, approximately, the same copper species as the Cu-Ce oxides, but most of the CuO is deposited on alumina. The reduction of these precursor oxides under hydrogen atmosphere, at 403 K, leads to the formation of a mixture of Cu^{2+}, Cu^+ and mainly Cu metal. The EPR spectra show a best dispersion of the Cu^{2+} species at lower copper concentration. Indeed, Berger and Roth [9] showed that the EPR intensity only depends on the amount of isolated copper species and the intensity of the copper signal observed is about 1.5 times higher for 1Cu1Ce10Al than for 5Cu1Ce10Al [8]. Thus, assuming that the isolated copper species are the active species, the change of the activity versus copper concentration can be the result of a dispersion phenomenon. Consequently, this large dispersion can explain the higher activity observed for 1Cu1Ce10Al, when this is calculated per copper atom (fig 1).

Table I. Total activity (HYD + ISOM) and hydrogenation selectivity for various mixed oxides.

Catalyst	*Intrinsic activity (10^6 mol.$m^{-2}.h^{-1}$)*	*Hydrogenation selectivity (%)*
5Cu1Ce10Al	38.9	58.7
1Cu1Ce10Al	26.8	58.5
5Cu10Al	28.3	53.8
1Cu10Al	6.6	53.9
1Cu1Ce	122.6	72.6

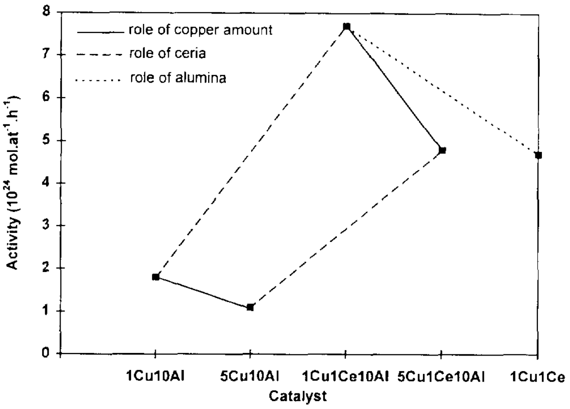

Fig 1. Activity reduced to one copper atom (mol Cu $atom^{-1}$ h^{-1}) for various oxides.

The role of cerium can be deduced by comparing the catalysts in table I and figure 1. For a given copper dispersion (about 3.5 × 10^{18} atoms.m^{-2} for 1Cu1Ce10Al and 1Cu10Al), the activity is higher in the presence of cerium. It is about 4.3 times as active for 1Cu1Ce10Al than for 1Cu10Al. The same remark can be made after comparing 5Cu1Ce10Al and 5Cu10Al activities. Clearly, ceria induces an important synergic effect on copper active sites. This synergic effect appears more significant for the hydrogenation reaction. Indeed, the selectivity of hydrogenation is always greater in the presence of cerium (table I). Several reasons could cause this effect:

- The Ce species can have two oxidation states and consequently allow electron transfer with the copper species, making it less reduced. This will be favorable to an active species that is not totally in a metallic state.
- Cerium dioxide has an oxygen-defective structure, which leads to non-stoichiometric solids (CeO_{2-x}) with anionic vacancies, particularly under a reducing atmosphere [10]. These anionic vacancies can be shared with the nearest copper species in the same manner as copper chromium catalysts [11, 12].

Table II. Product distribution (%) from the isomerization reaction of hex-1-ene over various mixed oxides.

Catalyst	trans-*Hex-2-ene* (T2)	cis-*Hex-2-ene* (C2)	trans-*Hex-3-ene* (T3)	C2/T2 ratio
5Cu1Ce10Al	80.4	19.6	–	0.24
1Cu1Ce10Al	81.5	18.5	–	0.23
5Cu10Al	80.6	19.4	–	0.24
1Cu10Al	80.0	20.0	–	0.25
1Cu1Ce	63.6	16.0	20.4	0.25

– Binary transition metal-cerium oxides are very important hydrogen reservoirs [11]. Hydrogen species and anionic vacancies can be shared with copper. This model is very similar to the proposed active sites in Cu-Cr and Cu-Al oxides, where copper species are surrounded by anionic vacancies and hydride ions [12].

The comparison between 1Cu1Ce and 1Cu1Ce10Al indicates that the presence of aluminium leads to a significant decrease in the intrinsic activity (table I) due to presence of inactive alumina. In agreement with this, an increase in the activity per copper atom is observed (fig 1). This increase can result from the better dispersion of copper species on the alumina surface. However, the most important effect related to the presence of alumina is the drastic change in the selectivity. Indeed, all the alumina-based catalysts lead to an increase in the isomerization process (table I). Thus, if we admit the previous model of an active copper species with a lacunar environment, in agreement with the Siegel's proposals [13], assuming that hydrogenation needs a more lacunar neighborhood than isomerization, alumina must decrease the extent of the anionic vacancies or decrease the reducibility of copper to explain the increase in the selectivity of the isomerization. As a matter of fact, EPR results show that copper strongly interacts with its ligands and the alumina matrix, and becomes less reduced. Obviously, we cannot exclude the participation of aluminium species in the isomerization process in a similar manner to that over Cu-Al-O, in which the copper species activate the molecular hydrogen and supply the reactive hydrogen species to aluminium by a 'spill over' phenomenon [14]. It is important to note again that hydrogen cannot be activated in the absence of copper, since no activity was observed for such solids.

The most interesting result of this section is the isomerization product distribution (table II). *trans*-Hex-2-ene is the preponderant product, irrespective of the catalyst used. Moreover, the *cis*-hex-2-ene/*trans*-hex-2-ene ratio (C2/T2) remains constant (~ 0.25) even in the absence of alumina. This result is very important from a mechanistic point of view, as will be explained below.

Mechanism

The hydrogenation and isomerization of alkenes could pass through ionic or non-ionic intermediates. Tanaka and Okuhara [15] treated catalytic hydrogenation and isomerization reactions on oxide catalysts and assumed that reaction via alkyl (or allyl) intermediates requires a specific structure, such as a certain degree of coordinative unsaturation of the active sites, the so-called 'coordinative unsaturated site' (CUS), while reaction through ionic intermediates does not require such specific structures. The reaction via ionic intermediates is controlled rather by the Bronstëd acidity of the surface and mainly occurs on basic or acidic oxides, whereas reaction via non-ionic species is typical of transition metal oxides [16]. Tanaka and Okuhara [15] and Siegel [13] postulated that the structural prerequisite for the hydrogenation reaction was different from that for isomerization, which needs a less lacunar environment. These CUSs have a Lewis acidity character and the ability to coordinate a hydride species to become an active species. Since these reports, many workers have confirmed these hypotheses on transition metal oxides [1] and sulfides [17–19]. Particularly, Choudary and Ravi Kumar [20] show that the clusters of organic complexes of transition metals are only active for hex-1-ene isomerization if they possess coordinative unsaturations. The C2/T2 ratio value obtained from hex-1-ene isomerization is basically different, because of the structural differences between the ionic and non-ionic intermediates.

The basic oxides, such as CdO, MgO and ZnO, favor the formation of *cis*-hex-2-ene leading to a high C2/T2 ratio [16]. In the same manner, the acidic catalysts give an initial ratio C2/T2 $\geqslant$ 1 significantly above the equilibrium value (0.4) [21]. Thus, the preferential formation of the *cis* isomer on basic or acidic oxides is well documented [16, 19–26]. Similarly, when the intensity of Bronstëd sites of the catalyst decreases, such as with a boron substitution in ZSM-5 type zeolites [27], the C2/T2 ratio decreases (0.61), but remains greater than the expected thermodynamic equilibrium value (0.4). In contrast, the non-ionic intermediates give rather small values of the C2/T2 ratio [15]. It should be noted that our data show a quasi-constant C2/T2 ratio of 0.25 (table II). Moreover, the acidic catalysts can lead to skeletal isomerization [28]. This was not observed in our experiments. On the other hand, there is a close similarity between our results and those obtained in heterogeneous metal catalysis on which the hydrogenation reactions of the olefins are frequently accompanied by double bond migration and *cis/trans* isomerization. Most of our results agree with a reaction route via a half-hydrogenated intermediate as described by Bartok [29] on metals, ie, an associative mechanism which well supports the Horiuti–Polanyi mechanism. In this case, as with our own experiments, the isomerization is observed only in the presence of hydrogen. This probably means that the first step is the fixation of a hydrogen species over the substrate for both hydrogenation and isomerization reactions. This reaction is then a hydroisomerization, as claimed previously for a Cu-Cr oxide [30].

All the results for the various binary and ternary oxides indicate that the chemical transformations of hex-1-ene take place through a non-ionic mechanism. This is strengthened by the fact that, according to the hard and soft acid base theory, the Cu(0) and Cu^+ species are softer acids than Cu^{2+}, Al^{3+} and Ce^{4+}. Indeed, the acidity of these species can be estimated by the semi-empirical equation proposed by Tanaka and Ozaki [31], which assimilate acidity and electronegativity:

$$\chi_i = (1 + 2Z)\chi_o$$

where χ_i, χ_o are, respectively, the electronegativity of the metal ion and atom, and Z is the ionic charge. The χ_i values for the Cu(0), Cu^+, Cu^{2+}, Ce^{4+} and Al^{3+} species are 1.9, 5.7, 9.5, 9.9 and 10.5. We have recently shown that soft Lewis acidic centers are hydrogenating, whereas strong Lewis acidic active sites lead mainly to isomerization [30]. As mentioned above, cerium and aluminium are only slightly implicated as direct active sites. Thus, it can be assumed that the reduced copper species are the main active sites and give rise to a preferential non-ionic mechanism. Owing to the results of physicochemical studies [8], the simultaneous presence of the three copper species in the reduced oxides with a very low Cu^+ content, on the one hand, and the numerous results over copper-based catalysts [1] in accordance with Siegel's proposals [13] on the other, we propose that the low positive charge species (strongly reduced) and/or species with a high degree of coordinative unsaturation favor the hydrogenation reaction. Species with a high positive charge (weakly reduced) and/or with a low degree of coordinative unsaturation lead preferentially to isomerization.

The mechanisms of the hydrogenation and isomerization reactions, in agreement with all the results above and in the literature, are represented in figures 2 and 3. These processes always start with π-olefin adsorption, which is more probable on reduced transition metal oxides because of the size of the back donation of the electrons from the filled d orbitals of adsorption centers to the π^* orbital of olefins. Moreover, Efremov et al [32] demonstrated that when an active center can be bound to the substrate by both a π-bond and a σ-bond (from the bonding π orbital of the olefin to the vacant orbitals of adsorption centers), the σ-bond is always weak.

For the hydrogenation process (fig 2), the addition of a hydrogen species leads to a σ-adsorbed half-hydrogenated product. This then undergoes transformation to an alkane.

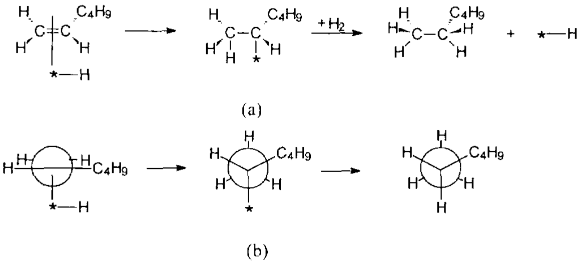

Fig 2. Hydrogenation process of hex-1-ene: a) planar representation; b) Newman representation.

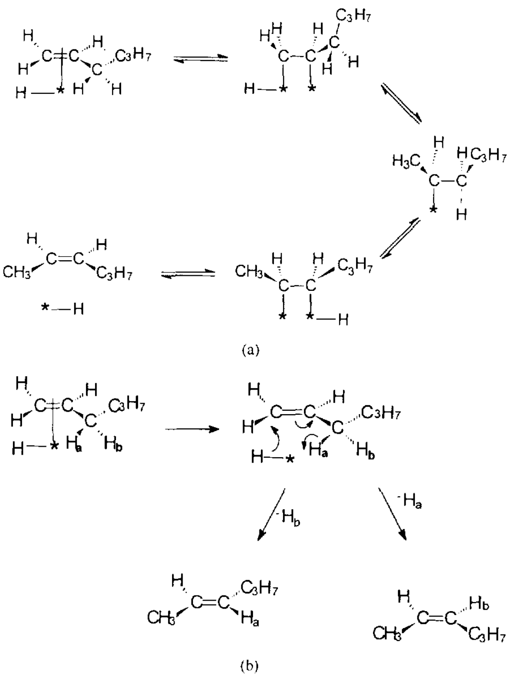

Fig 3. Isomerization process of hex-1-ene: a) Horiuti–Polanyi mechanism; b) concerted mechanism.

In the isomerization process (fig 3), the result can be explained by the formation of the same half-hydrogenated intermediate and the continuity of the Horiuti–Polanyi mechanism. The formation of a new di-adsorbed species thus occurs either by the abstraction of hydrogen from the third carbon atom and formation of the isomeric alkene (fig 3a), or by a concerted mechanism, in which the allylic hydrogen participates in the formation of the adsorbed complex in the same manner as the corresponding pentacoordinate intermediate for the classical S_N2 process (fig 3b). Here, this would be a nucleophilic substitution with an allylic rearrangement (the so-called S_N2' process), a mechanism which has previously been proposed to explain the allylic alcohol isomerization over copper chromium oxide [33]. In this mechanism, the removal of the allylic H_a or H_b lead to the isomeric C2 and T2, respectively.

The Newman representation (fig 4) clearly shows the relative stability of each conformation and could explain the larger amount of T2 obtained in the isomerization products (table II). In contrast, the Horiuti–Polanyi process cannot explain the observed C2/T2 ratio (0.25), since skeletal constraints are small in this mechanism.

Fig 4. Newman's representation of hex-1-ene.

Conclusion

In this work, we present data on the activities and selectivities related to each component of the catalysts (Cu-Ce-Al). In fact, reduced copper species are the only species that can activate both molecular hydrogen and hex-1-ene. The increase in the copper content in the solid is favorable to the formation of a large amount of CuO aggregates, which have a negative effect on the copper dispersion and, consequently, on the activity per copper atom. As regards the role of cerium, a synergic effect of this element on the copper active sites seems to be very beneficial to the activity and hydrogenation selectivity. Alumina, like ceria, does not have any activity when tested in the absence of copper. However, weak isomerization activity can be attributed to this element (Al) via a spill-over reactive hydrogen formed on the copper active sites.

Finally, the proposed non-ionic mechanism can be considered as a balance between a σ-alkyl semi-hydrogenated intermediate, precursor of the hydrogenated product, and a concerted mechanism (SN'_2) leading meanly to the isomerization. Consequently, the more conjugated the double bond, the more concerted the mechanism. Thus, the use of various reagents may lighten the isomerization mechanism. Work is in progress with substituted hexenes and pentenes to confirm our proposals.

References

1 Hubaut R, Bouraada A, Bonnelle JP, In: *Catalysis in Organic Reactions*, Scarros M, Prunier ML, eds, Dekker, New York, 1994, p 445

2 Daage M, Bonnelle JP, *Appl Catal* (1985) 16, 355

3 Hubaut R, Daage M, Bonnelle JP, *Stud Surf Sci Catal* (1988) 41, 131

4 Kherbeche A, Benharref A, Hubaut R, *React Kinet Catal Lett* (1996) 57, 13

5 Alouche A, Hubaut R, Bonnelle JP, Davies P, Lambert D, *Stud Surf Sci Catal* (1993) 78, 235

6 Alouche A, Lambert D, Hubaut R, Davies P, Hertoghe P, French Patent to BP France (1990) 9108893

7 Lammonier C, Bennani A, D'Huysser A, Wrobel G, Aboukaïs A, *J Chem Soc Faraday Trans* (1996) in press

8 Abi Aad E, Rives A, Hubaut R, Aboukaïs A, unpublished results

9 Berger PA, Roth JF, *J Phys Chem* (1967) 71, 4307

10 Fierro JLG, Soria J, Sanz J, Rojo JM, *J Solid State Chem* (1987) 66, 154

11 Pinabiau M, PhD Lille (1987)

12 Daage M, Bonnelle JP, *Stud Surf Sci Catal* (1987) 17, 261

13 Siegel S, *J Catal* (1973) 30, 139

14 Hubaut R, Bonnelle JP, *React Kinet Catal Lett* (1992) 47, 73

15 Tanaka K, Okuhara T, *J Catal* (1980) 65, 1

16 Tanaka K, Okuhara T, *J Catal* (1980) 61, 135

17 Hubaut R, Bonnelle JP, Grimblot J, In: *Trends in Physical Chemistry*, CSRI, Research Trends, India, 1991, Vol 2, p 277

18 Wambeke A, Jalowiecki L, Kasztellan S, Grimblot J, Bonnelle JP, *J Catal* (1988) 109, 320

19 Miciukiewicz J, Massoth FE, *J Catal* (1989) 119, 531

20 Choudary BM, Ravi Kumar K, *Appl Catal* (1987) 35, 177

21 Abbot J, Wojciechowski BW, *J Catal* (1984) 90, 270

22 Rosynek MP, Fox JS, *J Catal* (1977) 49, 285

23 Abott J, Corma A, Wojciechowski BW, *J Catal* (1985) 92, 398

24 Ko AN, Wojciechowski BW, *Int J Chem Kinet* (1983) 15, 1249

25 Sissitoyna A, Mokovokaya IF, Topchieva KV, *Kinet Katal* (1980) 21, 728

26 Brouwers DM, *J Catal* (1962) 12, 22

27 Choung SJ, Butt JB, *Appl Catal* (1990) 64, 173

28 Coranaro U, Wojciechowski BW, *J Catal* (1989) 120, 182

29 Bartok M, In: *Stereochemistry of Heterogeneous Metal Catalysis*, Wiley, New York, 1985, p 53

30 Hubaut R, Daage M, Bonnelle JP, *J Mol Catal* (1989) 55, 170

31 Tanaka K, Ozaki A, *J Catal* (1967) 8, 1

32 Efremov AA, Lokhov YA, Davydov AA, *React Kinet Catal Lett* (1980) 14, 21

33 Hubaut R, Daage M, Bonnelle JP, *Appl Catal* (1986) 22, 243