

Reactional mechanism of various isomeric C6 alkenes over reduced mixed Cu–Ce–Al oxide catalysts

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Received 20 July 1996; accepted 18 October 1996

Abstract

Hydrogenation and isomerization of many C6 alkenes are studied over reduced Cu–Ce–Al oxide catalysts. Activity and selectivity are strongly dependent on the steric and electronic effects characteristic of the reagent molecule. The less crowded the double bond of the alkene, the more important the activity is. On the other hand, the more polar the reagents are, the more favoured the hydrogenation selectivity is. The proposed reaction mechanism can be considered as a balance between the passage by an intermediary σ -alkyl leading mainly to hydrogenation product, and a concerted mechanism where the resultant is a double bond migration product. The equilibrium of this balance depends essentially on the polarity of the used reagent.

Keywords: Cu–Ce–Al oxides; C6 alkenes; Hydrogenation; Isomerization; Non-ionic mechanism

1. Introduction

The hydrogenation reactions of mono ethylenic compounds are frequently accompanied by double bond migration and/or *cis*–*trans* isomerization [1]. The competition between hydrogenation (HYD) and isomerization (ISOM) is depending on the adsorption–desorption equilibrium: the weaker the bond with the adsorbed intermediate, the higher the extent of isomerization [2]. Thus, the value of HYD/ISOM ratio is related to the reagent structure [3], and the double bond migration only occurs when

favourable conditions are put together [4]. In fact, the allyl hydrogen which has to be removed must be sterically accessible to the active site. For a given catalyst, the use of isomeric ethylenic compounds as reagents must lead to a variation of the HYD/ISOM ratio. On the other hand, many authors propose, on transition metal oxides, a non-ionic intermediate σ -alkyl and (σ - or π -allyl complex) rather than a ionic species [1,5,6].

Recently, we have shown that the value of the HYD/ISOM ratio and the products distribution inside the isomerization reaction obtained from hex-1-ene over binary and ternary Cu–Ce–Al oxides could be explained by such a non-ionic intermediate [7]. To confirm this pro-

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posal, in this work, we have performed the chemical transformation of isomeric C6 alkenes (namely: hex-1-ene (H1), *trans* hex-2-ene (T2), *cis* hex-2-ene (C2), *trans* hex-3-ene (T3), 2-methyl pent-1-ene (M2P1), 3-methyl pent-1-ene (M3P1)) over these catalysts under hydrogen atmosphere.

2. Experimental

2.1. Catalysts

Ternary oxide catalysts were obtained by co-impregnation of copper nitrate and cerium nitrate solutions on alumina support prepared by sol-gel process and precalcined at 773 K under dried air ($S = 420 \text{ m}^2/\text{g}$). Two solids, with various Cu/Ce atomic ratios (Cu/Ce = 1; Cu/Ce = 5) and a same Ce/Al atomic ratio (Ce/Al = 0.1) were synthesised and named 1Cu1Ce10Al and 5Cu1Ce10Al, respectively. Binary oxide was obtained by impregnation of copper nitrate solution on ceria support ($S = 116 \text{ m}^2/\text{g}$). The Cu/Ce atomic ratio was equal to 1 and catalyst was named 1Cu1Ce. The solids were dried for about 20 h in a drying oven ($\sim 373 \text{ K}$) and then calcined under a flow of dried air at 673 K for 4 h. The temperature was raised at a rate of 30 K h^{-1} .

2.2. 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 (C6 alkenes, Fluka) was introduced at constant partial pressure (1.3 kPa) in a flow of purified hydrogen (1 atm). Activity and selectivity were measured at the stationary state, with 5–10% conversion range. Products were analysed with a VARIAN 3600 CX chromato-

graph provided with a flame ionisation detector and a capillary column (chrompack CP-SIL 5 CB, $50 \text{ m} \times 0.25 \text{ mm}$).

3. Results and discussion

Table 1 displays the activities obtained from the various mono ethylenic compounds over 1Cu1Ce10Al catalyst. The highest total activity is observed with H1; it is about four times more important than with T2, C2, T3, M3P1 and ten fold higher than with M2P1. This hierarchy remains true for hydrogenation and isomerization activities, separately. These results are in perfect agreement with the Lebedev rule [8] (the more substituted the olefinic bond, the slower the process of hydrogen addition) and take into account the steric effect of the Csp^2 substituents.

On the other hand, this can also be a good argument in favour of the previous proposed mechanism in which hydrogenation and isomerization start, in an identical step, by the addition of a hydrogen species [7]. Indeed, the hierarchy of the activities is the same for the two reactions, even though, hydrogenation appears much more dependent upon the reagent structure (Table 1). Moreover, generally the *cis* isomer is more reactive than the *trans* isomer, because the former may be adsorbed on the catalyst surface via three sides but the latter via only two. The small difference between the respective total activities of C2 and T2, in our experi-

Table 1
Intrinsic and total activities (hydrogenation and isomerization) reduced to one Cu atom over 1Cu1Ce10Al

Reagent	H1	C2	T2	T3	M3P1	M2P1
Intrinsic activity ($10^6 \text{ mol m}^{-2} \text{ h}^{-1}$)	26.8	8.5	6.6	6.2	5.4	2.5
Total activity per Cu atom ($10^{24} \text{ mol Cu at}^{-1} \text{ h}^{-1}$)	7.7	2.4	1.9	1.8	1.5	0.71
HYD activity ($10^{24} \text{ mol Cu at}^{-1} \text{ h}^{-1}$)	4.5	0.3	0.2	0.1	1.05	0.7
ISOM activity ($10^{24} \text{ mol Cu at}^{-1} \text{ h}^{-1}$)	3.2	2.1	1.7	1.7	0.45	0.01

ments (Table 1), allows to think that the molecules must rather be adsorbed in a flat position (parallel to the catalyst surface) which leads to the same number of adsorption possibilities for the two geometric isomers.

Concerning the isomerization reaction of alkene, Resofszki et al. [9] have performed an interesting study on acidic and basic metal oxides. The experiments were carried out with hex-1-ene, 2-methyl pent-1-ene and 3-methyl pent-1-ene. Over basic oxides, the first step of the mechanism is the abstraction of an acidic allyl hydrogen by the basic O^{2-} of the surface, to form allyl anions as intermediate. This latter is stabilised on the metal cations of the surface. Under allyl anion form, the *cis* configuration is more stable than the *trans* one and, in this case, hex-1-ene leads preferentially to *cis* hex-2-ene [10]. Moreover, in this type of oxides, a methyl substituent on the third carbon (3C) — which decreases the acidic nature of the allyl hydrogen — makes the loosening and bond splitting more difficult; whereas, a methyl substituent on the second carbon (2C), has only a slight steric effect without electronic influence on the reaction rate. Thus, the order of the relative activities over basic oxides is: $H1 > M2P1 > M3P1$. Over acidic and amphoteric oxides, an electrophilic addition of the acidic proton of the hydroxyl groups of the catalyst surface, can be initially observed [9]. This process occurs over reduced metal oxides, under hydrogen atmosphere, in accordance with the Markovnikov rule, leading to the more substituted carbon (second carbon over H1, M2P1 and M3P1) having a cationic character. In fact, the coordination of the double bond on the metal ion leads to the development of a positive charge on the two sp^2 carbons. In this case, methyl groups

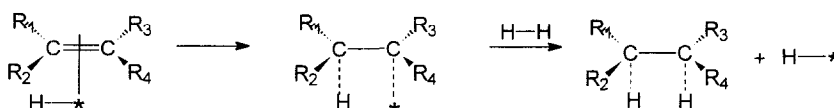
Table 2

Relative total intrinsic activities ($\text{mol m}^{-2} \text{ h}^{-1}$) over various catalysts for the reaction of H1, M2P1 and M3P1

Catalyst	1Cu1Ce	1Cu1Ce10Al	5Cu1Ce10Al
a_{H1} / a_{M2P1}	1.9	10.7	14.6
a_{H1} / a_{M3P1}	1.2	5.0	9.7
a_{M3P1} / a_{M2P1}	1.6	2.2	1.5

on second carbon stabilise these carbocations by electron-donor effects; whereas, a methyl group in the allyl position now has about the same steric effect as the 2-methyl had for basic oxides. The order of the relative activities, on this acidic oxides, becomes: $M2P1 > H1 > M3P1$. Any of these hierarchies, characteristic of an ionic process, is observed in our experiment as the order is $H1 > M3P1 > M2P1$. This order remains true independently of the catalyst (Table 2). Owing to the results obtained previously over numerous mixed transition metal oxides [3,11], it seems to be a general feature of this kind of catalysts.

Thus, the hypothesis of a non-ionic intermediate as previously proposed for the chemical transformation of hex-1-ene from physicochemical results [12] and indirect examinations [7], appears at present very probable. Tables 1 and 2 confirm the weak participation of the amphoteric oxide Al_2O_3 and the only synergetic effect of CeO_2 because it is well known that the rare earth oxides which are stable at higher oxidation states of metal cations show weak basic properties [13]. Concerning the hydrogenation reaction, for which the active sites are assumed to be reduced copper species in a lacunar environment shared with the cerium species [7], the proposed mechanism starts by the addition of a hydrogen species to the associatively adsorbed substrate; the σ -adsorbed



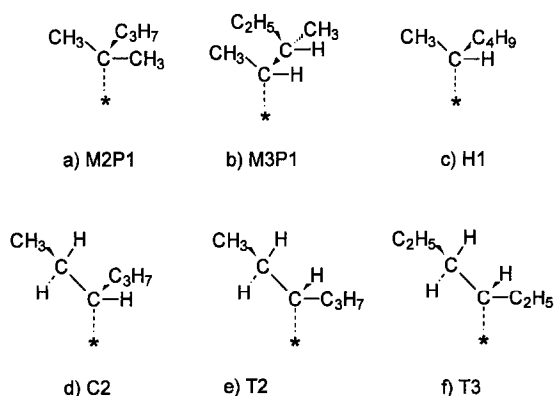
Scheme 1. Hydrogenation mechanism of alkene via a non-ionic σ -alkyl intermediate.

Table 3
Hydrogenation selectivity from various isomeric C6 alkenes over 1Cu1Ce10Al

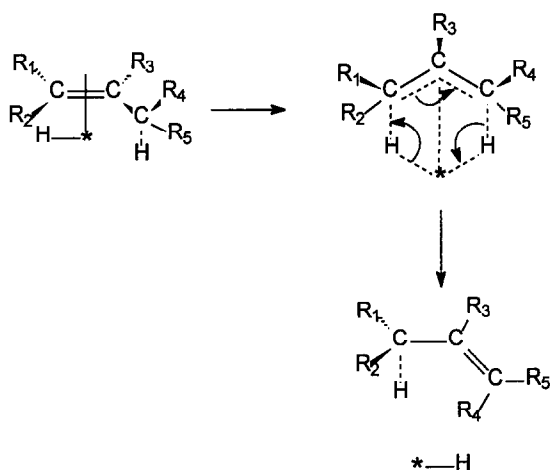
Reagent	M2P1	M3P1	H1	C2	T2	T3
S_{HYD} (%)	98.5	70	58.5	13.5	9	7

half-hydrogenated product further undergoes the transformation up to alkane compound (Scheme 1).

The σ -adsorbed intermediate is more or less stable depending on the electronic effects of the carbon three substituents. It is noteworthy, that the stability of this intermediate is directly related to the hydrogenation selectivity (Table 3,



Scheme 2. σ -alkyl intermediates in the hydrogenation process of the various isomeric C6 alkenes.



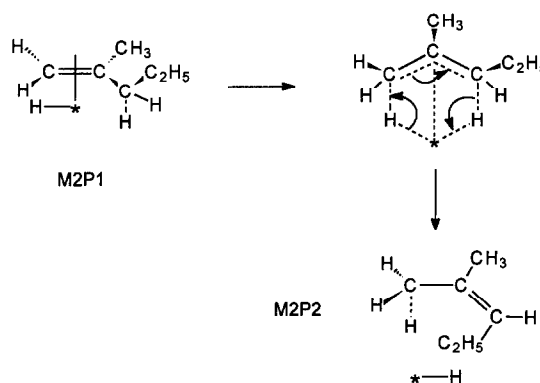
Scheme 3. Full concerted mechanism for the double bond isomerization.

Table 4
Isomerization products distribution over 1Cu1Ce10Al

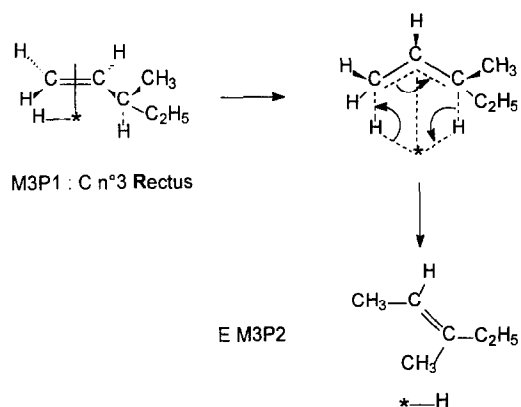
Reagent	S_{ISOM} (%)	Product distribution (%)	<i>Cis-trans</i> ISOM extent (%)	C2/T2	
T3	93.0	T2	84	0	0.18
		C2	15		
		H1	1		
T2	91	T3	62	34	—
		C2	34		
		H1	4		
C2	86.5	T3	18	80	—
		T2	80		
		H1	2		
H1	41.5	T2	81.6	—	0.22
		C2	18.4		
		T3	0		
M3P1	30	<i>E</i> M3P2	60	—	0.67
		<i>Z</i> M3P2	40		
M2P1	1.5	M2P2	100	—	—

Scheme 2): the more important the electron donor effects, the higher the selectivity in hydrogenation. These results are in agreement with the fact that the intermediate strongly bound to the catalyst, leads mainly to hydrogenation [2].

About the product distribution within the isomerization reaction, we have previously proposed a balancing mechanism between a σ -alkyl intermediate and a full concerted mechanism (SN'_2) [7]. It is obvious that the concerted mechanism can explain the double bond migration (Scheme 3), but not the *cis-trans* iso-

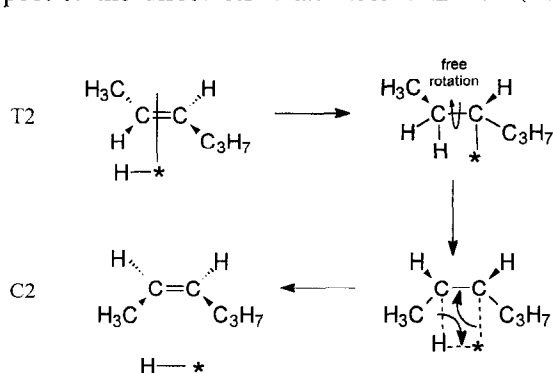


Scheme 4. Formation mechanism of M2P2 from M2P1.

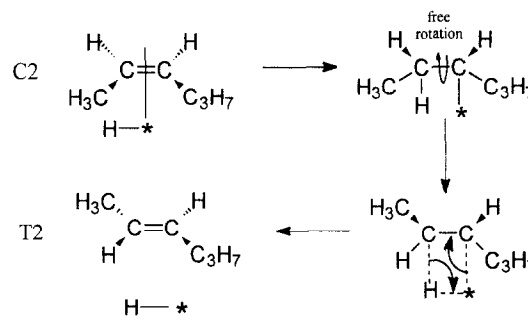


Scheme 5. Formation mechanism of *E* and *Z* M3P2 from respectively *R* and *S* M3P1.

merization which needs either a combination with double bond migration and a σ -alkyl intermediate. Table 4 shows the product distribution obtained over 1Cu1Ce10Al. It is worthy to note, that the double bond migration extent, by respect to the direct *cis*–*trans* isomerization (T3,



Scheme 6. Formation mechanism of C2 from T2.



Scheme 7. Formation mechanism of T2 from C2.

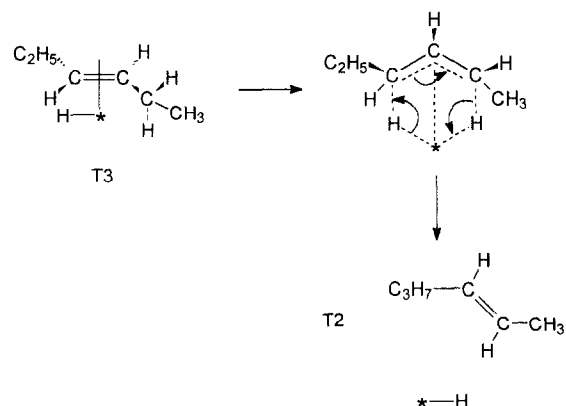
T2 and C2 from respectively C3, C2 and T2) increases when the polarity of the reagent decreases. Thus, two major results can be related to the dipolar moment (polarity) of the reagent:

(i) The hydrogenation extent is much large as the polarity is high.

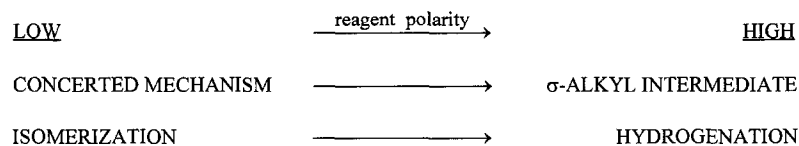
(ii) The double bond migration, within isomerization, is much large as the polarity is lower.

This is in total agreement with the proposed mechanism which is a balance between a σ -alkyl half-hydrogenated intermediate, leading mainly to alkane (and in a weaker proportion to the *cis*–*trans* isomerization product), and a full concerted mechanism (SN_2') responsible of the double bond migration.

The mechanisms for the various alkenes are represented on the Schemes 4–8. From M2P1, the weak amount of 2-methyl pent-2-ene (M2P2) (Table 4) comes from the very stable σ -alkyl



Scheme 8. Formation mechanism of T2 from T3.



Scheme 9. Dependence of the selectivity and the reaction mechanism on the reagent polarity.

intermediate (Scheme 2a), but we cannot exclude the formation of a minor part by the concerted mechanism (Scheme 4). Moreover, the proposed concerted mechanism can lead, in this case, to the initial reagent (M2P1). This possibility can mask more important activity and isomerization selectivity. To clarify this point, it will be important to use marked carbon in the M2P1 reagent.

As it can be seen on Scheme 5, the double bond migration in the enantiomeric *R* and *S* reagent of M3P1 leads respectively to the *Z* and *E* 3-methyl pent-2-ene (M3P2). Thus, the initial racemic mixture used in our experiments, might lead to an equal quantity of stereoisomeric products, that is approximately what we obtain (Table 4).

From H1 and more from C2, T2 and T3, comparing to M2P1, the polarity of the reagent decreases and the process in favour of the concerted mechanism becomes more important (Table 4). Nevertheless, the sp^3 nature of the second carbon allows to obtain C2 from T2 (Scheme 6) in the same manner as C2 leads to T2 (Scheme 7), but the extent of these direct geometric isomerizations, which need σ -alkyl intermediates, drastically increases from 34% to 80% (Table 4). At last, we can see on Scheme 8 that the apolar T3 gives 100% (Table 4) of isomerization (double bond migration) by a full concerted mechanism.

4. Conclusion

To summarise the results obtained in the catalytic transformations of various isomeric C6 alkenes over binary and ternary Cu–Ce–Al oxides, we have seen that activity and selectivity

are strongly dependent on the steric and electronic effects characteristic of the reagent molecule. The less crowded the double bond of the alkene is, the more important the activity is. On the other hand, we can assume that the mechanism of these transformations, is mainly a non-ionic process, which leads to an intermediate with a more or less σ -alkyl nature. The importance of the σ -alkyl character strongly depends on the polarity of the initial reagent (Scheme 9). The higher the polarity is, the more important the σ -alkyl nature of the intermediate and consequently, the higher the extent of hydrogenation; conversely, the lower the polarity, the more concerted the mechanism (SN_2') and the larger the extent of the double bond migration.

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