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Oligomerization of ethylene on platinum by a two-step reaction sequence

L. Lefort, A. Amariglio and H. Amariglio [1]

Laboratoire de Catalyse Hétérogène, Université de Nancy I, BP 239,
54506 Vandoevre Cédex, France

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On Pt, substantial fractions of chemisorbed C_2H_4 can be converted to C_{3+} alkanes by subsequent hydrogenation. The absence of H_2 during chemisorption is considered as the main factor favoring C–C bonding between adsorbed species, whereas its further addition permits higher alkanes to be released.

Keywords: homologation; oligomerization; EUROPT-1; platinum catalyst; ethylene

1. Introduction

We have recently reported that CH_4 can be homologated to higher alkanes on various transition metals when, after chemisorption accompanied by H_2 evolution, the remaining chemisorbed species are submitted to H_2 at ordinary pressure [1–3]. Hydrogen removal from the methyl species accumulating on the surface during chemisorption is a key point because the resulting H-deficient CH_x species can give rise to C–C bonding and to the formation of alkane precursors. Numerous alkane precursors have been identified in the case of Pt, through displacement of alkanes and alkenes by CO pulses [4]. They are efficiently removed as alkanes ranging from C_1 to possibly C_8 by H_2 and the cycle CH_4/H_2 can be repeated several times with no visible deactivation.

Similar processes are obviously expected in the case of other light alkanes and we have recently reported preliminary results concerning ethane [5]. However, this kind of transformation should be even easier when unsaturated hydrocarbons such as ethylene, for example, are involved. This is the more expected as no thermodynamic barrier has then to be overcome. Formation of some C_3 and C_4 olefins was reported to occur upon contact of small Fe clusters with ethylene [6], but more often homologation of ethylene on metal surfaces, as well as that of heavier ole-

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[1] To whom correspondence should be addressed.

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fins, has been only reported in the presence of H_2, so that the homologation (leading mainly to the next higher olefin) was always accompanied by the more favored hydrogenation and also by hydrogenolysis [7]. A more complicated case is afforded by numerous studies devoted to the role of light olefins added to the Fischer–Tropsch reactant mixture [8,9]. They showed that when the olefin pressure was increased the hydrogenation of CO was progressively suppressed, so that the formation of heavier products which continued to be observed resulted from the olefin homologation instead.

The fate of a chemisorbed C_2H_4 molecule may be expected to be very different according to whether foreign adsorbed molecules are present or not as they may impede oligomerization processes. Spectroscopic evidence of oligomers being present on Ni after adsorption of C_2H_4 at room temperature (r.t.) was first reported by Eischens and Pliskin [10]. Similar results were obtained by Morrow and Sheppard on Pt but at 95°C instead of r.t. [11]. Spontaneous evolution of higher olefins in such conditions may not be possible due to the strength of their bonding to the metal. It was therefore in order to use a *two-step sequence* for maximizing chain lengthening of C_2H_4: first, adsorption of C_2H_4 and, second, subjection to H_2 allowing removal of higher alkanes at an extent expected higher than under *co-feed* of the catalyst with C_2H_4 and H_2. This view is substantiated by the results reported here.

2. Experimental

2.1. CATALYST

We used 100 mg of EUROPT-2 (6.3 wt% Pt/SiO_2) [12–14] placed in a continuous flow fixed bed reactor made of a U-shaped quartz tube (4 mm i.d.). The Pt was initially reduced in flowing H_2 (50 cm^3/min) during a slow ramp of temperature (1 K/min) up to 400°C, at which temperature it was maintained in the H_2 flow for 1 h.

Between two experiments the catalyst was first submitted to a flow of H_2 (50 cm^3/min) for 1 h at 400°C in order to remove any carbonaceous residue. It was then fed for 30 min with a flow of Ar (50 cm^3/min) for removing H_2 and finally cooled in the flow of Ar at the desired temperature of experiment.

2.2. APPARATUS AND ANALYSIS OF THE PRODUCTS

The apparatus, already described [2], essentially allowed us to feed the catalyst with pure H_2, Ar or C_2H_4 and to analyze the products of C_2H_4/H_2 cycles. To this end a chromatographic analysis was used with a column (1.80 m long and 2.1 mm i.d.) filled with Hayesep Q (90–190°C). As the removal of the hydrocarbons from the Pt surface in the H_2 flow was fast as compared to the duration of their analysis, the products were collected in a large sampling loop (5.2 cm^3) able to accommodate a good part of the total production. Each experiment was repeated five times so that, thanks to samplings shifted by 6 s in two successive experiments, all the products formed during the first 30 s of the hydrogenation step could be recovered. Reasonably reproducible results could so be obtained.

3. Results

The results given below refer to r.t., 100 and 150°C. At each temperature the Pt sample was exposed to a flow of (Ar + 1% C_2H_4) for 1 min. Not any product evolved from the catalyst at r.t., but some C_2H_6 was formed at 100 and 150°C. This was due to self-hydrogenation, a process already reported [15–18] and leading to the release of C_2H_6 with parallel formation of chemisorbed acetylene. Just after exposure to C_2H_4, the catalyst was fed with flowing H_2 and immediate production of alkanes up to C_8 followed. Table 1 gives the quantities of each kind of alkanes produced. Fig. 1 illustrates the product selectivity to C_1, C_2 and C_{3+} and fig. 2 gives the detailed selectivity to each higher alkane.

It must, however, be noticed that the amount of C_2 was indirectly determined in a way explained below. This was due to the impossibility to distinguish the ethane formed at the onset of hydrogenation from that resulting from self-hydrogenation and already present in the reactor when C_2H_4 was switched to H_2.

The main indications we can take out from table 1 can be readily summarized:

(i) sizeable amounts of C_{3+} alkanes can be formed at temperatures sufficiently higher than r.t.;

Table 1

Nature and quantities (10^{-9} molequiv. C_2) of alkanes produced by isothermal hydrogenation of preadsorbed C_2H_4 [a]

T (°C)	C_1	C_2	C_3	C_4		C_5			C_6		ΣC_7	ΣC_8	ΣC_{3+}
				iso	*n*	iso	*n*	cyclo	*n*	cyclo			
25	2.25	1080	0.06	0.01	46.0	–	–	–	–	–	–	–	46.07
100	9.83	927	0.97	0.61	898	0.10	0.24	0.01	54.8	0.32	–	1.81	957
150	51.7	344	5.28	6.53	1240	0.65	2.14	0.57	312	2.65	1.20	106	1677

[a] Conditions: 1 min exposure of 100 mg EUROPT-1 to (Ar + 1% C_2H_4), 100 cm^3/min, followed by 30 s hydrogenation in 50 cm^3/min H_2.

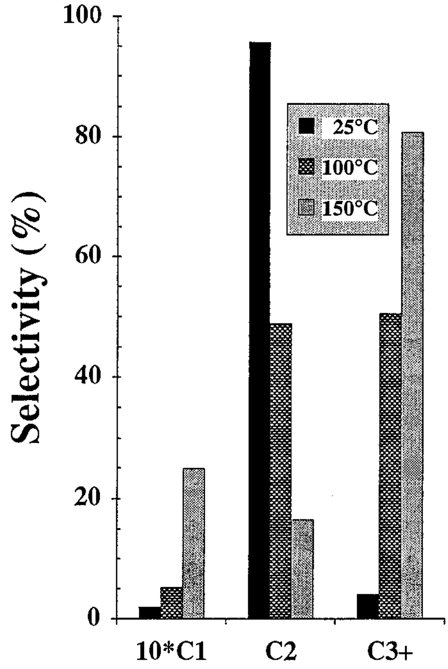

Fig. 1. Selectivity of the hydrogenation to C_1, C_2 and C_{3+} versus temperature.

(ii) alkanes containing an even number of C atoms are strikingly predominant, from which we can infer that they result from oligomerization of C_2 units whereas very little C–C breaking occurs during chemisorption.

(iii) iso/*n* ratio is very small for butanes (even number of C atoms) but much less small for pentanes, whose formation required addition (more or less at random) of C_1 units to C_2 dimers.

Not all the chemisorbed species were removed from the surface during the hydrogenation limited to 30 s (see section 2.2). This was apparent from the small concentrations of products continuing to be present in the H_2 flow, but this residual production was neglected. The total amount of adsorbed matter which escaped from hydrogenation could, however, be determined thanks to a TPSR (temperature programmed surface reaction) with H_2 from the temperature of experiment up to 450°C. Mainly CH_4 and C_2H_6 were formed during the heating to 450°C and their total amounts could easily be determined. The amount of the residue (in equivalent molar C_2 units) is given in table 2.

As already mentioned, the ethane produced during the hydrogenation step could not be directly measured so that the total quantity of chemisorbed C_2H_4 had to be determined in separate experiments. After exposure to C_2H_4 and cooling at r.t., a TPD (temperature programmed desorption) in a flow of Ar was conducted up to 300°C. Only CH_4, C_2H_4 and C_2H_6 were formed and monitored. Fast cooling of the catalyst followed and a TPSR with H_2 up to 450°C was then conducted with

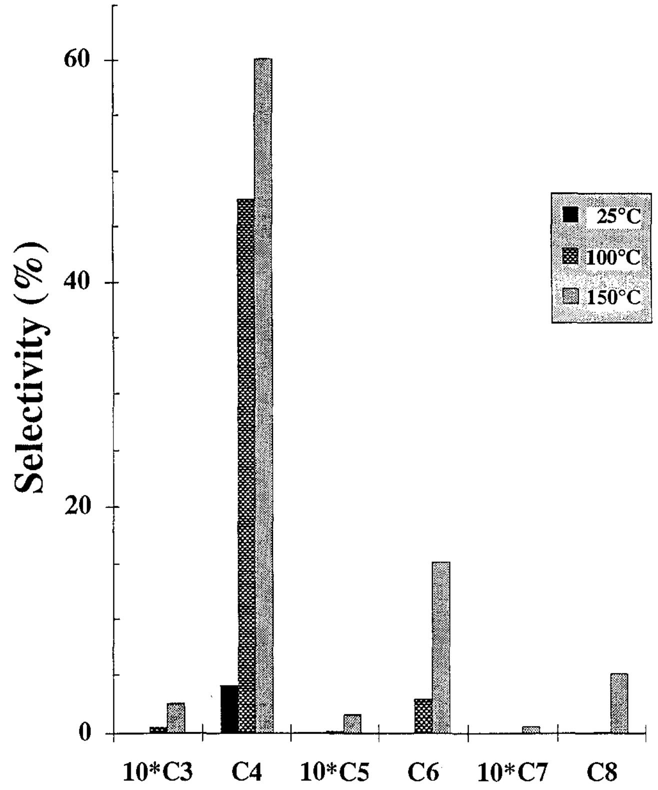

Fig. 2. Selectivity of the hydrogenation to the higher alkanes versus temperature.

CH_4 and C_2H_6 as only products. The total amounts of C_2H_4 chemisorbed during the exposures referred to in table 1 are displayed in table 2. The quantity of C_2 evolved during hydrogenation and given in table 1 was derived from the amount of C_2H_4 chemisorbed, the amounts of C_1 and C_{3+} released during the hydrogenation step and that of the residue.

Table 2

Quantities of C_2H_4 initially adsorbed, of C_2H_4 remaining after incomplete hydrogenation and fractions of C_2H_4 converted to C_{3+} [a]

T (°C)	C_2H_4 ads. (μmol)	Residue (μmol)	C_{3+} (1) (%)	C_{3+} (2) (%)
25	1.61	0.480	2.86	4.08
100	2.30	0.406	41.6	50.5
150	2.64	0.567	63.5	80.9

[a] The exposures to C_2H_4 are those referred to in table 1. C_{3+} (1): percentage of the adsorbed C_2 converted to C_{3+}. C_{3+} (2): percentage of C_{3+} in the products of the hydrogenation.

4. Discussion

The preceding results clearly show that C–C bonding between C_2 species can proceed upon C_2H_4 adsorption on a Pt surface as it proceeds between CH_x species upon CH_4 chemisorption [1–3]. Therefore these results confirm the possible extension of the early IR observations of Eischens and Pliskin on Ni [10] to the case of Pt [11]. Formation of higher alkanes by hydrogenation of surface complexes formed upon preliminary adsorption of C_2H_4 had already been mentioned briefly by Beeck [15,16] in the case of Ni: 90% of C_4–C_8 alkanes and 10% only of C_2H_6 were formed at r.t. Contrasting with Ni, Rh led to ethane mainly with only little polymerization.

In our case, the fraction of the adsorbed C_2H_4 being hydrogenated off as higher hydrocarbons increases fast with temperature and the C_{3+} alkanes become more abundant than C_2H_6 at 100°C and much more abundant at 150°C (at 100°C, 40.3% of adsorbed C_2H_4 reacted off as C_2H_6 versus 41.6% as C_{3+} and at 150°C, 13.0% of adsorbed C_2H_4 reacted off as C_2H_6 versus 63.5% as C_{3+}). This strongly contrasts with what is observed upon continuous feeding of the catalyst with C_2H_4/H_2 mixtures.

The obtaining of higher coverages of the surface with C_2H_4 when H_2 is absent does not seem a sufficient explanation of these results. We suggest that the key factor here is the self-hydrogenation of C_2H_4, a process occurring in the absence of H_2 and disappearing when H_2 is present. This process results in the release of C_2H_6 with parallel formation of adsorbed C_2H_2 exhibiting more tendency toward association than saturated adspecies. In the case of C_2H_2 instead of C_2H_4, chemisorbed acetylenic complexes are formed directly and no inhibition of their formation by H_2 can therefore take place. The result is that even a *co-feed* of the surface by C_2H_2 and H_2 would not prevent the chemisorbed C_2H_2 from being involved in the association processes leading to higher hydrocarbons as in the hydrogenation processes leading to C_2H_4 and C_2H_6. That is just what Sheridan observed in the mid-forties [20], in the case of a Ni catalyst with which he obtained substantial homologation of C_2H_2 in C_2H_2/H_2 *mixtures*.

In conclusion, our contribution shows that *sequential feed* of a catalyst surface with each reactant can result in responses significantly different from what is obtained through *co-feed*, especially with regard to the product distribution. Such behavior is of course expected to hold in many other situations.

References

[1] M. Belgued, P. Paréja, A. Amariglio and H. Amariglio, Nature 352 (1991) 789.
[2] M. Belgued, H. Amariglio, P. Paréja, A. Amariglio and J. Saint-Just, Catal. Today 13 (1992) 437.
[3] E. Mielczarski, S. Monteverdi, A. Amariglio and H. Amariglio, Appl. Catal. A 104 (1993) 215.

[4] M. Belgued, A. Amariglio, P. Paréja and H. Amariglio, J. Am. Chem. Soc., submitted.
[5] A. Amariglio, L. Lefort, M. Belgued and H. Amariglio, Preprints EUROPACAT-1, Montpellier 1993, p. 564.
[6] F. Hughes, B. Besson, P. Bussière, J.A. Dalmon, J.M. Basset and D. Olivier, Nouv. J. Chim. 5 (1981) 207.
[7] M. Leconte, J. Mol. Catal. 86 (1994) 205, and references therein.
[8] D.S. Jordan and A.T. Bell, J. Phys. Chem. 90 (1986) 4797, and references therein.
[9] D.S. Jordan and A.T. Bell, J. Catal. 108 (1987) 63, and references therein.
[10] R.P. Eischens and W.A. Pliskin, Adv. Catal. 10 (1958) 1.
[11] B.A. Morrow and N. Sheppard, J. Phys. Chem. 70 (1966) 2406.
[12] G.C. Bond and P.B. Wells, Appl. Catal. 18 (1985) 225.
[13] P.B. Wells, Faraday Discussions Chem. Soc. 87 (1989) 1.
[14] G.C. Bond and Z. Paál, Appl. Catal. A 86 (1992) 1.
[15] O. Beeck, Rev. Mod. Phys. 17 (1945) 61.
[16] O. Beeck, Discussions Faraday Soc. 8 (1950) 118.
[17] B.M.W. Trapnell, Trans. Faraday Soc. 48 (1952) 160.
[18] G.I. Jenkins and E.K. Rideal, J. Chem. Soc. (1955) 2490.
[19] R. Komers, Y. Amenomiya and R.J. Cvetanovic, J. Catal. 15 (1969) 293.
[20] J. Sheridan, J. Chem. Soc. (1945) 133.