JOURNAL OF CATALYSIS 37, 339–347 (1975)

Kinetic Study and Catalyst Structural Analysis for the Dehydrogenation–Hydrogenolysis of *n*-Pentane over Ru–Al_2O_3 Catalysts

VITTORIO RAGAINI AND LUCIO FORNI

Istituto di Chimica Fisica e Centro C.N. R.,
Universita di Milano, Milan, Italy

AND

LE VAN MAO

Faculty of Science, University of Saigon, Saigon, Vietnam

Received April 17, 1974; revised July 26, 1974

The reaction of *n*-pentane over Ru–alumina was studied at total pressure 1 atm, 450–490°C, molar feed ratio (H_2/n-C_5) ranging from 5 to 20 and Ru wt% on the support from 0.034 to 1.492. The activity of Ru black was also tested. The kinetics of reaction and the dependence of rates and selectivities upon experimental variables were determined. For the overall reaction the partial orders were 0.4 and −0.7 with respect to *n*-pentane and hydrogen, respectively, and $\Delta E\ddagger = 26.5 \pm 1.9$ kcal/mol.

The catalyst activity was strongly dependent on surface topography and a maximum specific activity was found at 0.085 Ru wt%. The influence of reactant feed ratio on selectivity was also tested.

By applying the Kobozev–Lebedev theory it was possible to determine that the number of Ru atoms which constitute the active center for dehydrogenation is 2–3 and that they are all accessible in each active center for the <0.1 Ru wt% catalysts.

INTRODUCTION

In a previous study (*1*) it was observed that, over finely dispersed Ru on γ-Al_2O_3, in the presence of hydrogen and at temperatures of 450–490°C, the main reactions taking place on *n*-pentane are successive dehydrogenations to 1-pentene, which isomerizes to 2-pentenes, and pentadienes. Small quantities of other substances form from the mono- and di-olefins and from pentane itself by skeletal isomerization (isopentenes and isopentane), cracking and hydrocracking (C_1 to C_4 paraffins and olefins).

In the present work the previous study has been developed with the aim of determining the kinetic parameters of the main reaction taking place on the catalyst and of correlating the catalyst activity with the structure of active centers, evaluated by means of a statistical analysis of the distribution of metallic atoms on the support surface.

EXPERIMENTAL METHODS

Materials. *n*-Pentane was obtained by passing a commercial "pure grade" product (99.74 mol%) over Linde 5A molecular sieve and recovering a practically pure (>99.99 mol%) substance. Hydrogen purity was >99.99 mol%.

Catalysts. The method followed in the preparation of the catalysts from Ru ace-

TABLE 1

PHYSICAL PROPERTIES OF THE CATALYSTS[a]

Ru (wt%)	Total Ru surf. area A_s (m^2/g cat)	Specific Ru surf. area a_s (m^2/g Ru)	(Ru*/Ru)[b]	Mean crystallite diam (d_{av}[c] (Å)
100[d]	7.30	7.30	0.01	—
1.492	2.21	148	0.28	31
0.859	1.54	179	0.33	26
0.523	1.31	251	0.47	18
0.331	0.99	301	0.56	15
0.301[e]	—	—	—	—
0.224	0.66	296	0.55	16
0.152	0.56	373	0.69	12
0.099	0.50	509	0.95	9
0.061	0.32	525	0.97	8–9
0.034	0.19	548	1.00	~8

[a] The BET (nitrogen) total surface area of all catalysts, except Ru black, is 175 ± 10 m^2/g.

[b] The accessibility coefficient is defined (*3*) as (Ru*/Ru), i.e., as the ratio of the number of surface Ru atoms accessible for adsorption to the total number of Ru atoms.

[c] The mean diameter of Ru crystallites is defined (*3*) as $d_{av} = f/\delta\, a_s$, f being a factor depending on the crystallite form and δ the specific density of the metal [for Ru, $f = 5.6$, $\delta = 12.063$ g/cm^3 (*3*)].

[d] Finely dispersed Ru black powder, obtained by reduction of an aqueous $RuCl_3$ solution with sodium borohydride at 25°C.

[e] The parameters relative to the 0.301 Ru wt% catalyst have not been determined.

tate and 40–60 mesh F-110 ALCOA γ-Al_2O_3 is reported in our previous paper (*1*). The Ru concentration in the catalysts was determined spectrophotometrically (*2*) and checked by X-ray fluorescence spectrometry. The total surface area of the metal alone was evaluated by a pulse chromatographic adsorption method with oxygen (*3*). The physical properties and the chemical composition of the catalysts employed are reported in Table 1, where A_s and a_s are the surface areas of Ru per gram of catalyst and per gram of Ru, respectively.

Apparatus and procedure. The reaction system employed and the procedure followed in the correlation of experimental data were as previously described (*1*). The range of reaction parameters was carefully chosen so that: (a) reproducible steady state conditions were attained, with respect to the small initial catalyst activity decay, and (b) neither external, nor internal diffusion would determine the kinetic results. Feed rates of *n*-pentane ranged from 1.65×10^{-3} to 168×10^{-3} mol/hr and the hydrogen/*n*-pentane molar ratio in the feed (FR) varied from 5 to 20.

Analysis. Details of the reactor effluent analysis were published elsewhere (*4*).

RESULTS AND DISCUSSION

All the experimental runs were performed at a total pressure of 1 atm. The ranges within which the various reaction parameters were changed are: temperature, 450–490°C; Ru wt% in the catalyst, 0.034–100 (see Table 1); FR, 5–20; catalyst conditioning temperature, 500–800°C; catalyst conditioning time, 2–48 hr; reaction time, 0.25–7 hr.

The experimental results are collected in Tables 2–9.

Initial reaction rate. The total conversion C of *n*-pentane is given by:

$$C = \frac{(\Sigma N_j Y_j) - 5Y_{n\text{-}C_5}}{\Sigma N_j Y_j}, \qquad (1)$$

TABLE 2

Total Conversion vs Time Factor. FR = 5, Different Temperatures (°C)

τ = ghr/mol	C
Ru = 0.301 wt%, T = 490	
88.2	0.184
58.8	0.145
28.6	0.081
14.9	0.071
12.8	0.064
9.5	0.046
5.9	0.045
5.7	0.035
3.0	0.027
2.5	0.021
1.7	0.021
0.9	0.014
Ru = 0.301 wt%, T = 470	
58.8	0.078
29.4	0.059
17.2	0.056
14.9	0.047
12.8	0.041
8.6	0.040
5.9	0.029
5.7	0.028
4.3	0.029
3.0	0.021
2.5	0.018
Ru = 0.301 wt%, T = 450	
88.2	0.057
58.8	0.040
28.6	0.028
9.5	0.015
5.7	0.014
2.5	0.011
Ru = 0.331 wt%, T = 490	
12.8	0.077
6.4	0.063
4.7	0.054
3.1	0.038
1.8	0.028
1.2	0.023
0.9	0.023
0.6	0.019
Ru = 0.331 wt%, T = 470	
12.8	0.053
6.4	0.043
4.7	0.046
3.1	0.025
1.2	0.023
0.6	0.016
Ru = 0.331 wt%, T = 450	
12.8	0.041
6.4	0.026
4.7	0.025
3.1	0.019
1.2	0.010
0.6	0.007

where Y_j are the molar fractions of the various hydrocarbons in the reactor effluent and N_j the number of carbon atoms in each hydrocarbon. The time factor is defined as $\tau = W/F$, W being the catalyst (Ru + alumina) weight (g) and F the n-pentane feeding rate (mol/hr).

The conversion C_{tc}, due to thermal cracking alone, was determined by substituting the catalyst with an equal volume of quartz sand, crushed and sieved to obtain a 40–60 mesh fraction and performing the reaction in the same conditions. The conversions in presence of quartz sand were about the same as with pure alumina and in any case they were very low, reaching

TABLE 3

Total Conversion vs Time Factor. Same Catalyst (Ru = 0.331 wt%) and Different FR Values

τ = ghr/mol	C
T = 490°C, FR = 7.75	
12.8	0.102
6.4	0.055
4.7	0.053
3.1	0.032
1.8	0.026
1.2	0.023
0.9	0.020
0.6	0.015
T = 490°C, FR = 10	
12.8	0.116
6.4	0.064
4.7	0.053
3.1	0.040
1.2	0.026
0.6	0.015
T = 490°C, FR = 12	
12.8	0.230
6.4	0.061
4.7	0.057
3.1	0.038
1.8	0.028
1.2	0.020
0.9	0.018
0.6	0.013
T = 490°C, FR = 15	
12.8	0.088
6.4	0.052
4.7	0.043
3.1	0.031
1.8	0.024
1.2	0.020
T = 490°C, FR = 17.5	
6.4	0.061
3.1	0.054
1.8	0.031
1.2	0.021
0.6	0.010
T = 490°C, FR = 20	
6.4	0.089
3.1	0.042
1.8	0.030
1.2	0.020
T = 470°C, FR = 7.75	
12.8	0.079
6.4	
4.7	0.047
3.1	0.032
1.2	0.019
0.6	0.011
T = 470°C, FR = 12.25	
12.8	0.087
6.4	0.061
3.1	0.048
1.8	0.034
1.2	0.018

TABLE 4

TOTAL CONVERSION VS TIME FACTOR. T = 490°C, FR = 5, DIFFERENT CATALYSTS

τ = g hr/mol	C
Ru = 0.859 wt%	
19.7	0.120
12.8	0.105
6.4	0.058
3.1	0.044
1.8	0.029
1.2	0.023
Ru = 0.523 wt%	
12.8	0.066
6.4	0.048
4.7	0.039
3.1	0.035
1.8	0.027
1.2	0.021
Ru = 0.224 wt%	
12.8	0.062
6.4	0.042
4.7	0.037
3.1	0.032
1.8	0.019
1.2	0.018
Ru = 0.152 wt%	
6.4	0.055
4.7	0.054
3.1	0.040
1.8	0.027
1.2	0.023
Ru = 0.099 wt%	
12.8	0.073
6.4	0.055
4.7	0.040
3.1	0.034
1.8	0.028
1.2	0.024
Ru = 0.061 wt%	
12.8	0.066
6.4	0.053
4.7	0.039
3.1	0.031
1.8	0.020
1.2	0.016
Ru = 0.034 wt%	
12.8	0.053
6.4	0.032
4.7	0.019
3.1	0.017
1.8	0.009
1.2	0.008

only a small fraction (1-3%) of those obtained in presence of Ru-alumina catalysts.

The conversion C_c, due to the catalytic reaction, can be written as:

$$C_c = C - C_{\mathrm{tc}} \tag{2}$$

so that, since the catalytic reaction rate r_c (mol/hr g cat) is given by:

$$r_c = \frac{\partial C_c}{\partial \tau}, \tag{3}$$

we can write:

$$r_c = \frac{\partial (C - C_{\mathrm{tc}})}{\partial \tau} \tag{4}$$

TABLE 5

TOTAL CONVERSION VS TIME FACTOR. DIFFERENT CONDITIONING TEMPERATURES[a]

τ = g hr/mol	C	Cond. temp, 700°C		Cond. temp, 800°C	
Cond. temp, 600°C					
19.7	0.112	19.7	0.082	19.7	0.090
12.8	0.089	12.8	0.066	12.8	0.069
6.4	0.053	6.4	0.040	6.4	0.044
3.1	0.044	3.1	0.029	3.1	0.035
1.8	0.036	1.8	0.023	1.2	0.022
1.2	0.027	1.2	0.018		

[a] T = 490°C, FR = 5, Ru = 0.859 wt%.

and, when working at W = const:

$$r_c = \frac{1}{W} \frac{\partial (C - C_{\mathrm{tc}})}{\partial (1/F)}. \tag{5}$$

The initial catalytic reaction rate can then be defined as:

$$r_0 = \lim_{\tau \to 0} \left[\frac{\partial (C - C_{\mathrm{tc}})}{\partial \tau} \right]. \tag{6}$$

For the determination of r_0 the catalytic conversion C_c was expressed by means of the polynomial:

$$(C - C_{\mathrm{tc}}) = \alpha\tau + \beta\tau^2 + \gamma\tau^3 + \cdots \tag{7}$$

so that:

$$r_0 = \lim_{\tau \to 0} (\alpha + 2\beta\tau + 3\gamma\tau^2 + \cdots). \tag{8}$$

In our calculations the polynomial (7) was

TABLE 6

INITIAL REACTION RATE r_0 (mol/hr g cat)

	Ru (wt%)	
T(°C)	0.301	0.331
490	0.014	0.027
470	0.010	0.018
450	0.006	0.010

TABLE 7

EFFECT OF $H_2/n-C_5$ FEED RATIO ON REACTION SELECTIVITY[a]

FR	S_D[b]	S_C	S_M	S_D/S_C	S_M/S_C
5	74	26	8.6	2.8	0.33
8	72	28	9.0	2.6	0.32
10	70.5	29.5	10.6	2.4	0.36
12	57.5	42.5	25.2	1.4	0.59
15	56.6	43.5	27.0	1.3	0.62
17.5	47.5	52.5	32.6	0.9	0.62
20	50.5	49.5	37.5	1.0	0.76

[a] Total conversion = 0.03, T = 490°C, Ru = 0.331 wt%.

[b] S_D, S_C and S_M are the selectivities towards olefins, cracking by-products and methane, respectively.

truncated after the second, third and fourth term, respectively, and the results were compared. It was observed that, by passing from a second order to more complex equations, the value of the first parameter α did not vary appreciably. In addition, the criterion followed in choosing among the various order polynomials was that of the best fitting of the calculated curve to the points relating to the conversions less than 0.05. From the data of Table 2 the values of r_0 ($= \alpha$), reported in Table 6, were obtained. The graphical methods involving the extrapolation to $\tau \rightarrow 0$ of the $(C - C_{tc})/\tau$ vs τ curve or the graphical derivation of the $(C - C_{tc})$ vs τ curve, employed as a check, gave results very close (within 5%) to the analytical ones.

Apparent activation energy. The initial reaction rate can be written (*5*) as:

$$r_0 = k_0(p_{H_2})^n(p_{n-C_5})^m \, e^{-\Delta E\ddagger/RT}, \qquad (9)$$

p_i being the partial pressures (atm) of the substances and n,m the partial reaction orders. For low conversions and for constant values of FR, the partial pressures of the various substances can be considered constant, so that Eq. (9) can be rewritten as

$$\log r_0 = -\frac{\Delta E\ddagger}{2.303\ RT} + B. \qquad (10)$$

From the data of Table 6 the following values for $\Delta E\ddagger$ were obtained: 26.6 ± 1.8 kcal/mol (Ru = 0.301 wt%) and 26.4 ± 0.7 kcal/mol (Ru = 0.331 wt%), which were averaged to 26.5 ± 1.9 kcal/mol.

Preexponential factor and partial reaction orders. The preexponential factor and the partial reaction orders have been evaluated by a nonlinear regression analysis on the basis of Eq. (9), i.e., by minimizing the following objective function:

$$\phi(k_0,m,n) = \sum_{T} \sum_{\text{data}} (r_{0,\text{exptl}} - k_0 p_{H_2}^n P_{n-C_5}^m \, e^{-\Delta E\ddagger/RT}), \qquad (11)$$

in which the data of Tables 2 and 3 and the previously obtained values of $\Delta E\ddagger$ were introduced. The results of such calculations are: $k_0 = 1.91 \times 10^6$ mol hr^{-1} g^{-1} atm$^{-(m+n)}$, $m = 0.4$, $n = -0.7$.

Effect of hydrogen partial pressure on selectivity. The reaction selectivity S_i to a given product i was defined as percentage

TABLE 8

EFFECT OF CONDITIONING TEMPERATURE (Ru = 0.859 wt%, FR = 5)

T (°C)	r_0 (mol/hr g cat)	at C = 0.03		S_D/S_C	a_s (m^2/g Ru)	Ru*/Ru[a]	d_{av} (Å)[a]
		S_D	S_C				
500	0.028	64.5	35.5	1.8	179	0.33	26
600	0.027	93.5	6.5	14.4	151	0.29	31
700	0.021	88.0	12.0	7.3	126	0.25	37
800	0.021	89.0	11.0	8.1	104	0.20	45

[a] See footnotes *a* and *b* of Table 1.

TABLE 9

EFFECT OF CONDITIONING TIME ON CONVERSION AND SELECTIVITY[a]

Conditioning time[b] (hr)	Reaction time (hr)	Total conversion (C)	Dehydrogenation selectivity (S_D)
2 at 500°C)	0.25	0.063	56.5
	2	0.053	57.2
	4	0.051	62.5
	5.5	0.052	63.5
	7	0.050	62.2
2 (at 500°C)	0.5	0.059	59.2
+ 7 (at 490°C)	0.5	0.056	65.1
+24 (at 490°C)	0.5	0.059	73.3
+48 (at 490°C)	0.5	0.062	80.5

[a] Ru = 0.331 wt%; FR = 5; τ = 4.72 (g hr/mol); reaction temp, 490°C.

[b] In hydrogen before the reaction.

molar conversion of n-pentane to the i-th product over total conversion, i.e., $S_i = (C_i/C)100$, where $C_i = (N_iY_i/\Sigma N_jY_j)$. As a consequence the maximum possible selectivity $(S_i)_{\max}$ is given by $(S_i)_{\max} = [(N_i/5)(5/N_i)_{\text{integer}}]100$. In our case we determined a dehydrogenation selectivity, S_D, as the sum of the selectivities towards pentenes and pentadienes, a cracking selectivity, S_C, as the sum of the selectivities towards $\leq C_4$ hydrocarbons and a selectivity S_M to methane. All the values of S_D, S_C and S_M have been determined at constant total conversion $C = 0.03$.

The effect of hydrogen partial pressure on selectivity has been studied by performing a series of runs at 490°C, on Ru = 0.331 wt% catalyst and at constant total conversion $C = 0.03$. The results are given in Table 7. It can be observed that, although FR could only be changed from 5 to 20, due to the analytical difficulties, the S_D/S_C ratio decreases about three times. This confirms, for the dehydrogenation reaction, the negative value of the partial reaction order with respect to hydrogen. The increase in the selectivity for methane formation, and mainly of the S_M/S_C ratio with FR, at constant total conversion, seems to confirm also the findings of Kikuchi *et al.* (*5*), who suggested that, over supported Ru catalysts at 300°C, the hydrogenolysis of n-pentane is unselective with respect to the position of the C–C bond along the chain. Such findings are also in agreement with the observations of Kempling and Anderson (*6*) for the hydrogenolysis of n-butane over Ru–alumina.

Effect of thermal conditioning of the catalyst on r_0 and on reaction selectivity. The study of the effect of the conditioning temperature on initial reaction rate and on selectivity has been made with the 0.859 Ru wt% catalyst. Some different samples of the catalyst have been conditioned at temperatures ranging from 500 to 800°C in a nitrogen atmosphere for 2 hr. All the catalyst samples were then tested at 490°C and FR = 5. The results are reported in Table 8. It can be observed that the initial reaction rate r_0 falls to about 3/4 the value at 500°C as the conditioning temperature rises, due to partial sintering of the metal over the catalyst surface. The dehydrogenation selectivity S_D passes through a very sharp maximum at 600°C, then remaining quite constant at about 88%; the S_D/S_C ratio reaches a very high value at 600°C, and thereafter (700 and 800°C) falls to about four times its value at 500°C.

Correlation between surface structure and catalyst reactivity. Three different measurements have been made on our Ru–Al_2O_3 catalysts. These are:

i. Determination of total (A) and specific (a) activity, that is per unit mass of catalyst and per unit mass of dispersed metal, respectively. These results are reported in Fig. 1 and were obtained at 490°C and FR = 5 (see also Table 4);

ii. Titration of surface Ru atoms by the gas chromatographic pulse technique with oxygen (*3*). The chemisorption of oxygen was made at 25°C on the catalysts conditioned at 500°C. The results are given in Table 1 as total (A_s) and specific (a_s) Ru surface area, respectively;

iii. Measurement of the change in surface area with conditioning temperature. The catalyst employed for this measure-

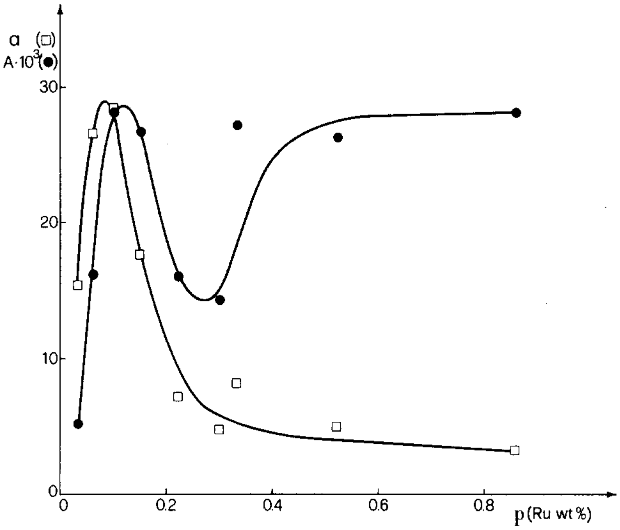

FIG. 1. Total (A) and specific (a) activity vs Ru weight percentage (p). $T = 490°C$, FR = 5.

ment was the 0.859 Ru wt% (see Table 8).

The data concerning total and specific activity can be employed to calculate the number (n) of atoms constituting the active centers showing the maximum specific activity, according to the Kobozev and Lebedev theory (*7–10*). When the crystallization degree (γ) of the dispersed metal tends to zero, the equations:

$$n = \frac{(N/Z_0)^A_{\max}}{(N/Z_0)^A_{\max} - (N/Z_0)^a_{\max}} \quad (12)$$

or (*11*):

$$n = \frac{p^A_{\max}}{p^A_{\max} - p^a_{\max}} \quad (13)$$

can be employed; when $\gamma > 0$ the following equation holds:

$$n = (N/Z_0)^a_{\max}\,(1 - \gamma) + 1. \quad (14)$$

In Eqs. (12–14) N and Z_0 are the number of metallic atoms and of irreversible adsorption centers (potential holes), respectively, per unit mass of catalyst. The subscript "max" means that N corresponds to the metal percentage p [see also Eq. (13)] in the catalyst, which gives the maximum total (superscript A) or specific (superscript a) activity (see Fig. 1 plots).

The criterion suggested by Lebedev (*8*) about the applicability of Eq. (12–14) is $\alpha = (\sigma N/S) < 0.05$, σ and S being the area occupied by a catalyst metallic atom and of the carrier surface, respectively. In our case, for the catalyst showing the highest specific activity a, $\sigma = 9.04$ Å^2 (*3*), $N = 5.12 \times 10^{19}$, $S = 175$ m^2/g, so that $\alpha = 0.026$. From Fig. 1 plots and by applying Eq. (13) we have:

$$n = \frac{0.125}{0.125 - 0.085} = 3.1.$$

On the other hand, from the knowledge of the crystallization degree γ, it is also possible to evaluate n by means of Eq. (14). The parameter γ can be calculated by applying the following equation (*12*):

$$\gamma = \frac{1 - (a_s A_{\text{cat}}/6.02 \times 10^{23}\,\sigma)}{1 - (5/a_1) + (12/a_1^2) - (8/a_1^3)}, \quad (15)$$

A_{cat} being the atomic mass of the catalytic metal and a_1 the number of metallic atoms in a linear element of the crystallite. From Eq. (15):

$$a_s = \frac{6.02 \times 10^{23}\,\sigma}{A_{\text{cat}}} \left[(1 - \gamma) + \gamma\left(\frac{5}{a_1} - \frac{12}{a_1^2} + \frac{8}{a_1^3}\right)\right]. \quad (16)$$

When $a_1 = 1$, a_s becomes independent of γ and from Eq. (16) one obtains $a_s = 550$ m^2/g. The experimental value for the catalyst showing the maximum for a (see Fig. 1) is $a_{s,\mathrm{exptl}} = 517$ m^2/g. Therefore the value for a must be an integer larger than unity but very close to this value. Then, putting $a_1 = 2$ in Eq. (15) ($a_s = 517$ m^2/g) one derives $\gamma = 0.08$, so that, from Eq. (14), by assuming $Z_0 = 0.4 \times 10^{19}$ (*9,13,14*) and evaluating, for the Ru = 0.085 wt% catalyst (max specific activity), $N = 0.51 \times 10^{19}$, one obtains $n = 2.26$. The proposed value for a_1 (=2) is also confirmed by a simple calculation starting from the experimental datum $d_{\mathrm{av}} \simeq 8$ Å (see Table 1 and Fig. 1) and assuming a close triangular array for spherical particles, each occupying an area of 9.04 Å^2 (*3*).

Thus the maximum activity for the main reaction (dehydrogenation), observed in such conditions on our catalyst, seems to be connected with active centers containing 2–3 metallic atoms. However, an important question is still open in order to elucidate the reaction mechanism, i.e., how many atoms are really accessible in each active center. The data reported in Table 1 show that the specific surface area a_s grows monotonically when the Ru percentage decreases. Therefore the maximum for the specific activity a does not correspond to the highest value of a_s (Fig. 1). A similar behavior can be observed for the total activity r_0 with respect to total surface area A_s. The accessibility coefficient (Ru*/Ru) of the supported metal can be expressed as (*3*):

$$(\mathrm{Ru}^*/\mathrm{Ru}) = \frac{(\mathrm{O/Ru})}{(\mathrm{O/Ru}^*)},$$

Ru* and Ru being the number of exposed and of total metallic atoms, respectively, and (O/Ru) and (O/Ru*) the ratios of the chemisorbed oxygen atoms over total and exposed metallic atoms, respectively. By assuming a stoichiometric ratio for the chemisorption of oxygen (O/Ru*) = 1.1 (*3*), the (Ru*/Ru) ratio may be evaluated. It is observed that, for the catalysts showing an activity close to the maximum (see Fig. 1 and Table 1), the accessibility coefficient is ≃ 1. Therefore each of the two or three atoms of the active center could be considered as directly connected with the activity of the site.

On the other hand, at temperatures exceeding 450°C, Ru atoms become quite mobile on the support surface and a sintering effect, increasing with temperature (see Table 8), can be observed. A comparison was then made by performing two runs under the conditions reported in Table 9, always starting with fresh catalyst (Ru = 0.331 wt%). From the data of total conversion (C) and dehydrogenation selectivity (S_D) relative to such runs, it can be deduced that, if the temperature does not exceed 500°C, the conversion seems to be affected only by the fouling and not by the sintering effect due to the migration of the metallic atoms. Moreover, some analyses on the fouled catalyst, performed with a secondary ion mass spectrometer (SIMS) (*15*), seem to indicate that such a fouling is due more to relatively light hydrocarbons than to coke residues. Finally, as regards the increase in selectivity with time, it should be remembered that the dehydrogenation reaction is connected, as previously reported, with the centers containing 2–3 atoms. Hence it can be deduced that the surface migration of metallic atoms, at least during the first reaction hours, leads to an increase in the concentration of active sites with 2–3 atoms.

ACKNOWLEDGMENTS

We thank the Italian Ministero degli Affari Esteri for the grant provided to one of us (L.V.M.) and the Italian Consiglio Nazionale delle Ricerche for financial aid.

REFERENCES

1. Forni, L., Ragaini, V., and Mao, L. V., *J. Catal.* **33**, 153 (1974).

2. Marshall, E. D., and Rickard, R. R., *Anal. Chem.* **22,** 6795 (1950).

3. Buyanova, N. E., Karnaukhov, A. P., Koroleva, N. G., Ratner, I. D., and Chernyavskaya, O. N., *Kinet. Katal.* **13,** 1533 (1972).

4. Forni, L., Zanderighi, L., and Carrá, S., *J. Catal.* **12,** 298 (1968).

5. Kikuchi, E., Tsurumi, M., and Morita, Y., *J. Catal.* **22,** 226 (1971).

6. Kempling, J. C., and Anderson, R. B., *Ind. Eng. Chem., Process Des. Develop.* **9,** 116 (1970).

7. Kobozev, N. I., Lebedev, V. P., and Malzev, A. N., *Z. Phys. Chem.* (*Leipzig*) **217,** 1 (1961).

8. Lebedev, V. P., *Russ. J. Phys. Chem.* **38,** 1191 (1964).

9. Strakhov, B. V., and Lebedev, V. P., *Russ. J. Phys. Chem.* **38,** 1206 (1964).

10. Kobozev, N. I., and Reshetovskaya, N. A., *Zh. Fiz. Khim.* **23,** 288 (1949).

11. Carrá, S., Ragaini, V., and Guella, F., *J. Catal.* **8,** 261 (1967).

12. Emel'yanova, G. I., and Lebedev, V. P., *Russ. J. Phys. Chem.* **38,** 1240 (1964).

13. Mal'tsev, A. N., and Kobozev, N. I., *Zh. Fiz. Khim.* **29,** 142, 291 (1955).

14. Dobychin, D. P., and Tsellinskaya, T. F., *Zh. Fiz. Khim.* **33,** 2498 (1959); and *Russ. J. Phys. Chem.* **33,** 492 (1959).

15. Benninghoven, A., *Z. Phys.* **230,** 403 (1970).