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Activity, Selectivity, and XPS Analysis of γ-Alumina-Supported Group VIII Metals Used in 1-Butene Isomerization in the Absence of Molecular Hydrogen

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The isomerization of butene-1 has been studied on γ-alumina-supported Pt, Ir, Rh, and Os in the range 140–240°C and on Ru between 61 and 75°C. Including previously published work on Pd/Al_2O_3 (S. Carrà and V. Ragaini, *J. Catal.*, **10**, 230, 1968), the order of reactivity is $Ru \gg Rh > Os > Pd \simeq Pt > Ir$; the *cis*-2-butene/*trans*-2-butene selectivity ratio (s) varies in the order $Pd > Pt > Ir > Rh \simeq Ru > Os$. An interesting result of this study, and of the earlier work on Pd, is the high selectivity s for Pt and Pd catalyst (s in the range 3 to 6): this is discussed in comparison with the data of other papers. For the ruthenium catalyst coke and/or polymer formation prevents activity of the metal at temperatures above 75°C. X-Ray photoelectron spectroscopy measurements on some of the catalysts employed are discussed in the light of recent results in the literature to clarify the behavior of this catalyst. The γ-alumina used was activated only at 330°C; its inactivity is discussed in relation to the reactivity of pure metals and to the published literature on the activity of alumina-supported metals. A detailed kinetic analysis has not been performed, but the overall kinetic and adsorption constants have been calculated by applying a kinetic equation, based on a Langmuir-type isotherm, with the aim of quantifying the differences in reactivity of the different catalysts.

INTRODUCTION

The isomerization reaction 1-butene $\rightleftarrows$ 2-butenes (*cis* and *trans*) and the catalyst systems employed here have been widely studied in the past. Table 1 summarizes the main results and the experimental conditions of some of these studies (*1–12*), namely the catalyst metal, support, reaction mixture, and the *cis*/*trans* ratio. It is seen that pure (*2, 7, 9, 10*) and supported metals (*3–6, 8, 11*) or complexes (*10, 12*) may be used, in the presence (*1–3, 7, 8, 11*) or in the absence (*3–7, 9, 10*) of molecular hydrogen. Although the literature cited in Table 1 is not comprehensive as a review, it is sufficient to demonstrate the interest in this topic for the study of the mechanism and the influence of the catalytic metal and the support on activity and selectivity. The same reaction on alumina and silica–alumina has been discussed for more than 30 years (*24–35*). Quantum chemical calculations on the topic have also been reported (*13*).

This paper is not concerned with the study of the reaction mechanism, but treats instead a large number of original experimental data for the reaction on Group VIII noble metals, with the aim of comparing the activity and selectivity of the different catalysts. Moreover, using XPS analysis and TPR (Temperature-Programmed Reduction) (*14*), an attempt has been made to clarify the unusual behavior of Ru catalyst.

EXPERIMENTAL

Catalysts. The nonactivated support (Alcoa-Chemical γ-alumina, surface area 169 m^2/g, sieved at 40–60 mesh) was impregnated at room temperature by slow stirring for 2 h with an aqueous solution of the ap-

0021-9517/85 $3.00

TABLE 1

Summary of Published Studies on *n*-Butene Isomerization (Double-Bond Migration) on Supported or Unsupported Metals

Metal	Support	Reaction mixture	T	s and c	Reactor	Reference
Pt, Ir	γ-Al_2O_3	*n*-Butenes + hydrogen	−20/150	Pt: $s = 1.6$ ($T = 15$); $s = 0.7$ ($T = 106$) R(H/B) = 0.72–2.5 Ir: $c = 0$ (T between −20 and 20)	st	*1*
Co	None or γ-Al_2O_3	*n*-Butenes or *n*-butenes + H_2	197	Co wire: $s = 0.56$ ($c = 14$) Co–Al_2O_3: $s = 0.50$ ($c = 18$)	st	*2*
Transition metals	None or alumina or silica or pumice	Olefins or paraffins or aromatics pure or with hydrogen or deuterium				*3*
Ni, Ru, Rh Pd, Os, Ir, Pt	(A) Boehmite and amorphous alumina (B) $\alpha + \kappa$-Al_2O_3 (C) α-Al_2O_3 (D) Pumice	*n*-Butenes (in the absence of molecular hydrogen)	100–150	Pd–A: $s = 0.53$ ($T = 97$; $c = 92$) Pd–A: $s = 0.54$ ($T = 150$; $c = 90$) Pd–C: $s = 0.55$ ($T = 150$; $c = 89$) Ru–A: $s = 0.46$ ($T = 97$; $c = 92$) Ru–A: $s = 0.57$ ($T = 151$; $c = 90$) Os–A: $s = 0.75$ ($T = 97$; $c = 3.5$) Ir: $s = 2.4$ ($T = 100$; $c \rightarrow 0$)	st	(*4b,c*)
Pd	γ-Al_2O_3	1-Butene	160–240	$c_{max} = 1.5$ for all T $T = 160$; $s = 2.5$ ($P = 60$); $s = 6.0$ ($P = 350$); $s = 7.1$ ($P = 600$) $T = 180$; $s = 4.4$ ($P = 130$); $s = 5.0$ ($P = 350$); $s = 6.9$ ($P = 720$) $T = 200$; $s = 3.2$ ($P = 100$); $s = 5.0$ ($P = 320$); $s = 6.4$ ($P = 700$) $T = 240$; $s = 3.9$ ($P = 170$); $s = 5.0$ ($P = 460$); $s = 4.9$ ($P = 590$)	fl (see also Table 4)	*5*

Ni and Pt [and their complexes] Co, Pd, Fe	None or quartz or alumina. Also homogeneous phase	1-Butene	40–120	Na_4NiPc ($c \rightarrow 0$); $s = 4.0$ ($T = 45$) $s = 3.5$ ($T = 75$); $s = 2.2$ ($T = 100$) $s = 1.2$ ($T = 125$) $Ni–Al_2O_3$ ($c \rightarrow 0$): $s = 0.57$ ($T = 100$) $Pt–Al_2O_3$ ($c \rightarrow 0$): $s = 1.10$ ($T = 103$) $Pd–Al_2O_3$ ($c \rightarrow 0$): $s = 1.06$ ($T = 100$)	st	*6*
Pd, Au Pd–Au (alloy) Pd–Ag (membrane)	None	Butenes or butenes + hydrogen	300–400	Pd–Au (40/60): $T = 300$; $R(H/B) = 0.4–1.5$ $s = 0.67$; $c = 75–80$ Pd–Ag membrane: $T = 330$ $R(H/B) = 40–50$; $s = 0.70–0.75$; $c = 50–60$ $R(H/B) = 10$; $s = 0.67$; $c = 55$	fl	*7*
Pd	γ-Al_2O_3	1-Butene + hydrogen	50–100	$T = 50$; $R(H/B)_{initial} = 0.33$; $s = 0.89$; $c = 33$ $R(H/B)_{initial} = 0.6$; $s = 0.52$; $c = 95$ $T = 75$; $R(H/B)_{initial} = 0.06$; $s = 0.90$; $c = 42$ $R(H/B)_{initial} = 12$; $s = 0.50$; $c = 94$ $T = 100$;$R(H/B)_{initial} = 0.02$; $s = 0.69$; $c = 43$ $R(H/B)_{initial} = 0.2$; $s = 0.54$; $c = 90$	fl	*8*
Pt	None	Butenes	135–180	$T = 135$; $s = 1.4$; $c = 10$ $s = 0.52$; $c = 82$ $T = 180$; $s = 1.35$; $c = 8$	fl	*9*
Ni, Ag	None	1-Butene	300–375	Ni: $T = 300$, $s = 0.67$, $c = 9.8–17$ Ag: $T = 375$, $s = 1.27$	fl	*10*
Rh	$\frac{Al_2O_3}{SiO_2}$	1-Butene + hydrogen (1 : 1)	−20 to 153 −16 to 75	$Rh–Al_2O_3$; $T = 67$, $s = 2.9$ (c-butene → butane = 75%) $Rh–SiO_2$; $T = 75$, $s = 3.3$ (c-butene → butane = 75%)	st	*11*
Os $(HOs_3(CO)_{10}—O—Si\equiv)$	SiO_2	1-Butene	50–90	No kinetic measurements	fl	*12*

Note. s, molar selectivity ratio *cis*-2-butene/*trans*-2-butene starting from 1-butene; c, molar conversion of 1-butene to 2-butenes; 1-b, 1-butene; P, partial pressure of 1-b (mm Hg); Pc, phthalocyanine; T, temperature (°C); $R(H/B)$, molar ratio H_2/1-butene; st, static reactor (batch type); fl, flux reactor (tubular type).

propriate metal salts. For Pd, Pt, Ir, Rh(I), Rh(II), Os, and Ru the salts used in the impregnation and the weight percentages of metal on the catalysts are, respectively, $PdCl_2$ (0.484), H_2PtCl_6 (0.553), Na_2IrCl_6 (0.681), Na_2IrCl_6 (0.681), Na_2RhCl_6 [(0.407 for Rh(I) and 1.265 for Rh(II)], $(NH_4)_2OsCl_6$ (0.536), and $RuCl_3 \cdot xH_2O$ (0.913). After standing overnight the impregnated materials were washed with cold water, dried at 120°C for 2 h, and reduced in a flow of hydrogen at 330°C for 2 h. The catalysts were again dried and reduced under the same conditions. Quantitative analysis of the catalytic metals was made by means of X-ray fluorescence, after calibration with samples of known metal content.

Apparatus and procedure for catalysis measurements. The reactor employed for the activity tests was of tubular type made of Pyrex glass (height 200 mm; i.d. 5 mm).

The isomerization kinetics were studied by continuous feeding of mixtures of 1-butene and helium to the reactor kept at temperatures between 140 and 240°C (except for the Ru catalyst). For each catalytic metal and temperature 5–7 kinetic runs were performed at different partial pressures of 1-butene. The flux of 1-butene was varied between 600 and 7200 ml (STP)/h, except for the Ru catalyst where it varied from 1200 to 7200 ml (STP)/h; the flux of helium was regulated to give partial pressures of 1-butene ranging from 50 to 700 mm Hg (7–93 kPa). The weight of the catalysts varied from 0.5 to 3 g, except for Ru (7.5 g). Therefore the minimum and the maximum values of the time-factor W/F [g metal (mol 1-butene)$^{-1} \cdot h^{-1}$], where W is the weight of the metal and F the flux of 1-butene, are as follows: Pd 4.6–27.6; Pt 1.8–55; Ir 3.2–68; Rh 0.7–50; Os 0.2–30; and Ru 23–140.

The kinetic runs have been performed in order to give a differential conversion of 1-butene (maximum 5% molar). Therefore the reaction rates r were obtained as the ratio of the conversion of 1-butene to the *cis* or *trans* isomer over the time factor, W/F, to give r_c (reaction rate for the *cis* isomer) and r_t (reaction rate for the *trans* isomer), respectively; the total reaction rate has been considered as $r = r_c + r_t$.

Conversion on the alumina. Before the runs with the supported metal catalysts the activity of the alumina (treated 2 h at 330°C under helium flux) was carefully checked. No conversion of 1-butene took place up to 220°C at the lowest flux of 1-butene among the ones indicated. At 240°C the ratio between the reaction rates on alumina and on the supported metal catalysts at the same partial pressures of 1-butene averaged at 6 : 100 for the Pd catalyst and 4 : 100 for the others. Therefore only at 240°C has the reactivity of the catalysts been corrected on this basis.

X-Ray photoelectron spectroscopy (XPS). XPS analyses were carried out in a modified ESCA III (Vacuum Generators) apparatus. The metal concentration, c_{S_i}, is normally evaluated by means of the formula

$$c_{S_i} = \frac{S_i}{\Sigma_i S_i} \quad (1)$$

where

$$S_i = \frac{A_i}{q_i} \quad (2)$$

and A_i is the area of the peak relative to a chosen level of the species i, q_i is the photoionization cross section of the atomic level concerned (*15*). The summation in the denominator is extended over all species present on the surface.

In order to avoid the analysis being affected by the presence of adsorbed oxygen or carbon species, the concentration of the metal was referred to the signal generated by the Al $2s_{1/2}$ peak:

$$c_{S_i} = \frac{S_i}{S_{Al}} \quad (3)$$

c_{S_i} gives the number of atoms of metal ratioed to the number of Al atoms, as determined by XPS analysis.

Al$K\alpha$ radiation (1487 eV) was used as incident radiation. From the curve of the escape depth as a function of the kinetic energy of the electrons (*16*), it is evident that the electrons contributing to the signal come from a surface layer of less than 20 Å.

The Binding Energy (B.E.) of an atomic level in a solid sample is given by

$$\mathrm{B.E.} = E_{\mathrm{inc}} - E_{\mathrm{kin}} - \varphi_{\mathrm{s}}, \qquad (4)$$

where E_{inc} is the energy of the incident radiation (1487 eV), E_{kin} the kinetic energy of the emitted electron, and φ_{s} the work function of the spectrometer. The energy scale was obtained using the Au $4f_{7/2}$ (83.8 eV) as a reference. From the chemical shift with respect to the energy of the free atom, information about the valence state is obtained. For poorly conducting solids, the assignment of the binding energy is complicated by the charging effect.

To separate this effect from the chemical shift, a value of 120.5 ± 0.5 eV was attributed to the measured Al $2s_{1/2}$ level in Al_2O_3 (see values of the chemical shifts for other oxides in Ref. (*16*)). The difference in energy between this value and the experimental one,

$$\delta = E_{\mathrm{Expt}\ 2s_{1/2}(\mathrm{Al})} - 120.5\ (\mathrm{eV}) \qquad (5)$$

was attributed to the charging effect. If the same value, δ, is considered to affect the energy of the electrons coming from the metal, we obtain the corrected energy by means of the formula

$$E_{\mathrm{corr}} = E_{\mathrm{Expt}} - \delta. \qquad (6)$$

Coke deposition. The Ru catalyst cannot be used above 75°C due to coke deposition and/or polymer formation (see under Discussion). A systematic analysis of this phenomenon has been made by flushing the catalyst for 14 h (corresponding to the average conditioning time of the catalysts), with an equimolar mixture of helium and 1-butene at different temperatures. The catalyst was then flushed with nitrogen and the temperature raised, always under nitrogen flux, at 200°C for 2 h; finally, the total carbon content of the catalyst has been determined by elemental analysis.

RESULTS

Molar ratios *cis*-2-butene/*trans*-2-butene at equilibrium at the reaction temperatures used in this work, calculated according to Golden *et al.* (*18*), are: 0.3166 (61); 0.3259 (67); 0.3384 (75); 0.4618 (160); 0.4885 (180); 0.5143 (200); 0.5392 (220); 0.5633 (240), where the figures in parentheses show the temperature in °C.

In order to compare the reactivity of the different catalysts at the same temperature and partial pressure of 1-butene, the results have been expressed in terms of the reaction rates r_c and r_t, at 100 and 400 mm Hg (13 and 52 kPa) partial pressure of 1-butene. These results are collected in Table 2, together with the average molar selectivities $\bar{s}$ = *cis*-2-butene/*trans*-2-butene, in the range 50–700 mm Hg partial pressure of 1-butene. One example of full results, i.e., reaction rate r_c and r_t vs partial pressure of 1-butene, has been reported for Pt catalyst in Fig. 1. Table 3 shows the values of metal concentration in the bulk (c_B) and at the surface (c_S) for some catalysts, as derived by XPS analysis, applying Eq. (3) for calculation of c_S. Table 4 reports the values of the binding energy calculated by Eq. (6), together with the values of the relevant peak of the metals under examination in the atomic state (*17*). Finally, in Fig. 2 the weight percentage of carbon on the ruthenium catalyst is shown as a function of the temperature treatment, according to the procedure previously described.

Kinetic calculations. As mentioned above, kinetic calculations have been performed only in order to compare the reactivities of the different supported metals, and were not aimed at finding the detailed rate equations for the formation of the *cis* and *trans* isomers, as reported in a previous paper (*5*). Two alternative procedures have been used for the evaluation of the overall rate constants. In the first procedure a linear regression has been adopted for $1/r$ vs $1/$

TABLE 2

Activity, r^a, and Average Selectivity, $\bar{s}$,[b] of γ-Alumina-Supported Metals at 100 mm Hg (13 kPa), and at 400 mm Hg (52 kPa), or Otherwise Indicated Partial Pressure (p) of 1-Butene

r and $\bar{s}$	p (mm Hg)	Temperature (°C)						Metal
		140	160	180	200	220	240	
$r_c \times 10^2$	100		0.872	2.10	4.09	8.61	11.0[c]	Palladium (see Ref. (5))
							24.5 (p = 200)	
	400		1.26	4.91	12.1	26.0	49.3	
$r_t \times 10^2$	100		0.260	0.517	1.23	3.59	3.60[c]	
							6.35 (p = 200)	
	400		0.178	0.969	2.19	5.57	10.2	
$\bar{s}$ = c/t			5.60	5.06	5.09	4.36	4.44	
$r_c \times 10^2$	100		1.170	2.17	3.80	7.31	13.1	Platinum
	400		0.886	4.53	12.9	25.1	44.5	
$r_t \times 10^2$	100		0.602	0.674	0.963	1.98	2.83	
	400		0.234	1.26	2.65	6.27	9.35	
$\bar{s}$ = c/t			2.76	3.36	4.30	3.83	4.67	
$r_c \times 10^2$	100		0.528	1.03	1.20	2.47	5.11	Iridium
	400		0.642	1.61	2.67	5.21	13.7	
$r_t \times 10^2$	100		0.330	1.20	1.38	2.60	4.10	
	400		0.427	1.88	3.90	6.74	13.8	
$\bar{s}$ = c/t			1.51	0.80	0.75	0.85	1.11	

$r_c \times 10^2$	100	1.49	4.39	14.9	20.5	45.3		Rhodium
	400	2.11	6.28	26.0	59.8	123		
$r_t \times 10^2$	100	2.08	6.56	22.2	30.4	74.4		
	400	4.92	13.8	55.1	124	254		
$\bar{s}$ = c/t		0.47	0.54	0.44	0.52	0.51		
	100		0.856	—	—	—	12.3	
$r_c \times 10^2$				6.75 (p = 200)	7.22 (p = 200)	12.9 (p = 200)[c]		
	400		4.89	10.1	14.1	44.6	52.9	Osmium
	100		14.7	—	—	—	20.7	
$r_t \times 10$				45.1 (p = 200)	48.6 (p = 200)	46.7 (p = 200)[c]		
	400		76.2	84.2	91.4	134	134	
$\bar{s}$ = c/t			0.07	0.14	0.16	0.32	0.67	
		Temperature (°C)						
		61	67	75				
	100	<0.05[c]	0.101	—				
$r_c \times 10^2$		0.089 (p = 200)		0.150 (p = 200)				
	400	0.300	0.503	0.824				Ruthenium
	100	0.433	0.213	—				
$r_t \times 10^2$				0.488 (p = 200)				
	400	0.985	1.05	1.47				
$\bar{s}$ = c/t		0.29	0.49	0.56				

[a] Activity, r, as moles of isomers *cis* (r_c) or *trans* (r_t) formed × h^{-1} × (g metal)$^{-1}$ at differential conversion of 1-butene.

[b] Average selectivity, $\bar{s}$, as molar ratio *cis*-2-butene(c)/*trans*-2-butene(t) in the range $50 < p < 700$ mm Hg.

[c] Value extrapolated.

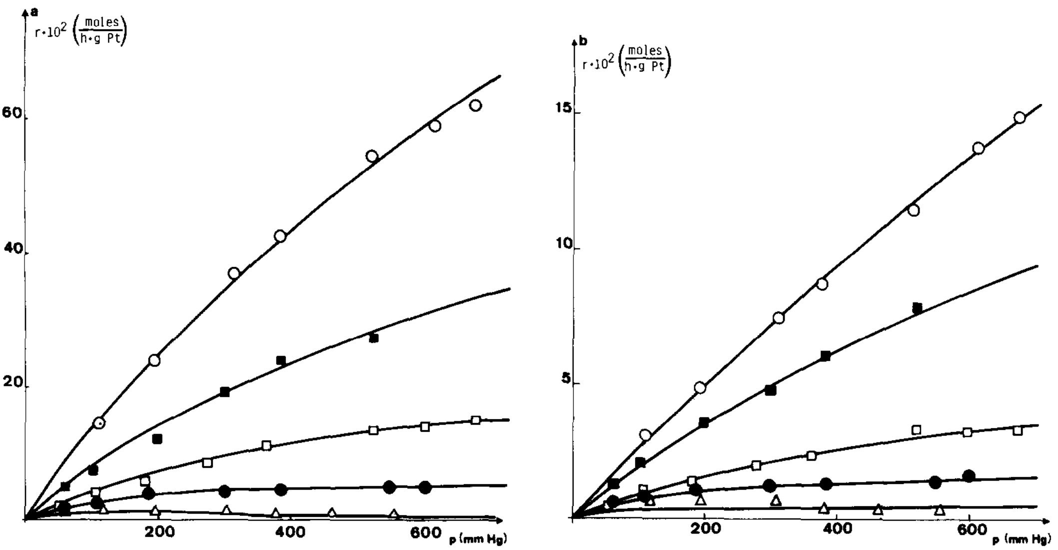

FIG. 1. Reaction rate (r) vs 1-butene partial pressure p (1 mm Hg = 133.3 Pa) Pt–Al_2O_3 [0.553% (w/w)] at different temperatures: (a) r_{cis}; (b) r_{trans}. Temperatures in °C: ○ (240); ■ (220); □ (200); ● (180); △ (160).

p where r is the total rate calculated as the sum of the rates toward the *cis* (r_c) and the *trans* (r_t) isomers (i.e., $r = r_c + r_t$) and p is the partial pressure of 1-butene in the feed. This procedure refers therefore to a rate equation based on a Langmuir-type isotherm: $r = k_T\ [bp/(1 + bp)]$, k_T being the overall rate constant and b the adsorption constant for 1-butene. From the slope (S) and intercept (I) of $1/r$ vs $1/p$ it is possible to calculate $k_T = 1/I$ and $b = I/S$. The procedure is the same as that adopted by McMunn *et al.* (*6*). Some examples of the plots of $1/r$ vs $1/p$ are reported in Fig. 3. The results are given in Table 5 together with the activation energies ($\Delta E^{\neq}$) and standard heat of adsorption (ΔH_a°). In the second evaluation procedure the values of the rate constants for the formation of the *cis* (k_c) and *trans* (k_t) isomers have been calculated by a least-squares procedure minimizing the sum of the squares $(r_c)_{\text{Calcd}} - (r_c)_{\text{Expt}}$ or $(r_t)_{\text{Calcd}} - (r_t)_{\text{Expt}}$ where $(r_c)_{\text{Calcd}} = k_c\ [bp/(1 + bp)]$ and $(r_t)_{\text{Calcd}} = k_t\ [bp/(1 + bp)]$. For the parameter b the values from the first method have been assumed at the same temperature. Finally, the overall rate con-

TABLE 3

Atom of Metal/Atom of Al Percentage in the Bulk (c_B) and on the Surface (c_S)

Catalyst	Percentage (Weight)	c_B	c_S	c_S/c_B
1 Ru	0.913	0.45	0.42	0.93
2 Ir	0.681	0.42	1.46	8.11
3 Rh	0.407	0.20	1.06	5.30
4 Rh	1.265	0.63	2.72	4.32

TABLE 4

Binding Energies (B.E.) for Al $2s_{1/2}$ and for the Catalyst Metals M[a]

Catalyst M–Al_2O_3 No.	M	Expt B.E. of Al $2s_{1/2}$ (±0.2)	Atomic level of M	B.E. Expt of M (±0.2)	B.E. corrected[b] (±0.9)	B.E. atomic state
1	Ru	122.6	$3p_{3/2}$	465.0	462.9	461
				466.8	464.7	
2	Ir	122.5	$4p_{3/2}$	497.5	495.5	495
				501.1	499.1 *w*	
3	Rh	122.9	$3p_{3/2}$	497.6	495.2	496
4	Rh	122.4	$3p_{3/2}$	497.2	495.3	496
				500.4	498.5 *w*	
				502.6	500.7 *w*	

[a] B.E. for metals in the atomic state taken from Ref. (*15*). All energies are in eV.

[b] See text. *w*, weak.

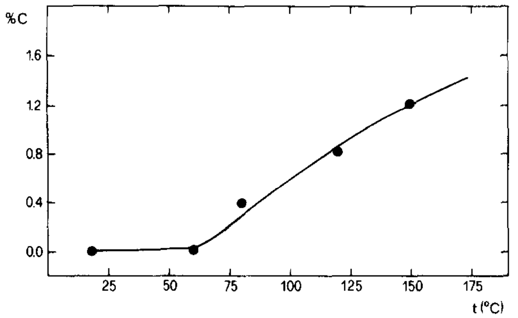

FIG. 2. Carbon deposited (wt%) vs temperature on Ru catalyst.

stant, k'_T, has been calculated as $k'_T = k_c + k_t$. The values of k'_T and the corresponding activation energies $(\Delta E^{\neq})'$, have been reported in Table 5. For the Ru catalyst linearization $1/r$ vs $1/p$ gives poor results; therefore for this catalyst the parameters b and k_T have been found by applying a nonlinear regressive analysis minimizing $(r_{\mathrm{Calcd}} - r_{\mathrm{Expt}})^2$ where r_{Calcd} is taken from the above-mentioned equation based on the Langmuir-type isotherm. The results are reported in Table 5.

DISCUSSION

Reactivity and selectivity. Data reported in Tables 2 and 5 show that the orders of reactivity (r) and selectivity ($\bar{s}$ = *cis*/*trans*) are

$$\text{for } r\text{: Ru} \gg \text{Rh} > \text{Os} > \text{Pd} \simeq \text{Pt} > \text{Ir} \quad (7)$$

$$\text{for } \bar{s}\text{: Pd} > \text{Pt} > \text{Ir} > \text{Rh} \simeq \text{Ru} > \text{Os}. \quad (8)$$

Due to the particular nature of the Ru catalyst the reactivity of this catalyst cannot be considered as being due only to the metal.

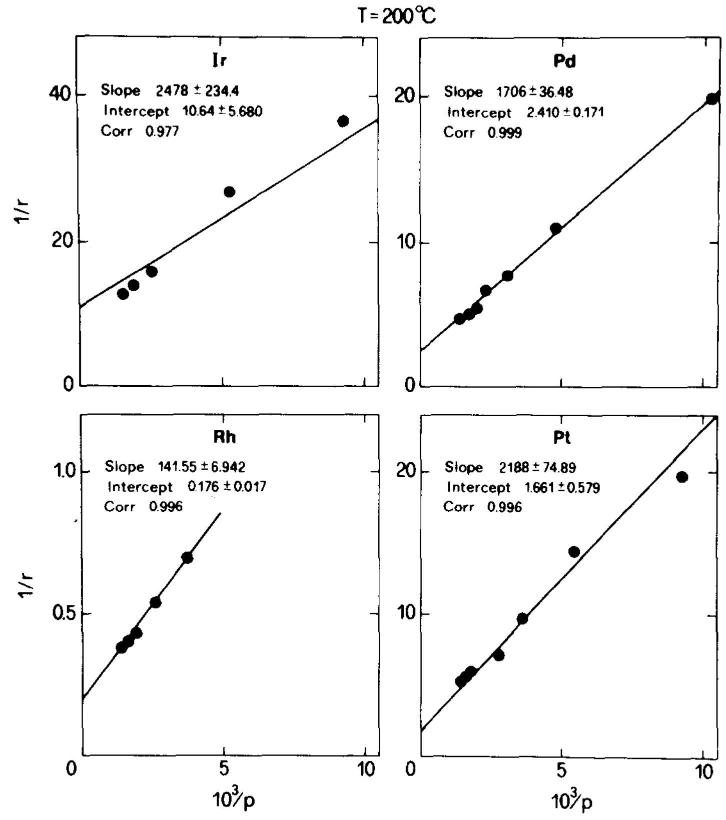

FIG. 3. Examples of $1/r$ vs $1/p$ linearization. (for iridium the point $1/r = 51.4$ and $(1/p) \times 10^3 = 17.5$ is not represented).

TABLE 5

Overall Rate Constants, k_T or k'_T (mol · h^{-1} · g $metal^{-1}$); Adsorption Constants, b [mm Hg^{-1} (1 mm Hg = 133.3 Pa)]; Activation Energies, $\Delta E^{\neq}$ or $(\Delta E^{\neq})'$ (kcal/mol); Standard Heat of Adsorption, ΔH°_a (kcal/mol); and Preexponential Factors, A or A', for 1-butene Isomerization on γ-Alumina-Supported Group VIII Metals (See Text for Explanations)

Metal	T (°C)	k_T	k'_T	$b \times 10^2$	$\Delta E^{\neq}$ / $(\Delta E^{\neq})'$	$-\Delta H^\circ_a$	ln(A) / ln(A')
Pd	180	0.053	0.052	54.2			
	190	0.110	0.111	0.478	31.6 ± 5.7	57.8 ± 32	32.2
	200	0.415	0.428	0.141	32.3 ± 5.8		33.1
	220	0.836	0.882	0.155			
Pt	180	0.090	0.087	0.477			
	200	0.602	0.576	0.076	25.1 ± 4.1	13.7 ± 6.6	25.7
	220	0.988	1.022	0.107	25.5 ± 3.9		26.1
	240	2.770	2.763	0.061			
Ir	180	0.040	0.040	1.32			
	200	0.094	0.101	0.426	18.8 ± 1.2	14.7 ± 4.2	17.5
	220	0.170	0.178	0.483	19.4 ± 1.2		18.2
	240	0.369	0.410	0.407			
Rh	160	0.268	0.281	0.751			
	180	1.60	1.34	0.277	26.3 ± 1.5	14.1 ± 4.0	29.5
	200	5.67	10.37	0.052	27.4 ± 2.9		27.3
	220	13.04	13.06	0.102			
Os	180	1.50	1.49	0.411			
	200	2.39	2.40	0.223	13.2 ± 1.6	13.6 ± 1.7	15.2
	220	5.38	5.39	0.123	13.2 ± 1.6		15.1
	240	11.21	11.11	0.048			
Ru[a]	61	4.84		0.087			
	67	9.67		0.065	22.8 ± 1.7	18.1 ± 2.4	35.9
	75	19.37		0.029			

[a] For this catalyst a nonlinear procedure has been adopted to optimize the parameters (see text).

The reactivity sequence Rh, Pt, Ir is the same as that found by Wells and Wilson (*4*b) on different supports (Table 1) at 100–150°C for butene isomerization in the absence of molecular hydrogen. In our opinion the results reported in Tables 2 and 5 give a more precise definition of the sequence of reactivity of the Group VIII noble metals; in fact only for Ir (*4*c) and Pd (*5*) are detailed kinetic data available.

The most surprising results obtained in this work and in the previous study (*5*), in comparison with the other data reported in Table 1, are the very high selectivities (*s*) of Pd and Pt catalysts. In fact the highest values of *s* previously obtained are 1.06, 1.10, 2.4, 3.3, and 1.27 for Pd (*6*), Pt (*6*), Ir (*4*c), Rh (*11*), and Ag (*10*), respectively, in comparison with values ranging from 3 to over 6 obtained in the previous (*5*) or in the present work. The absolute maximum of *s* previously obtained is 4.0, and this was for a very congested catalyst, viz. Na_4NiPc (Table 1, Ref. (*6*)).

As the data of Table 1 show, the selectivity *s* is influenced by many parameters (apart from the nature of the catalyst): these include the temperature, the degree of conversion, the partial pressure of the reactant, the congestion of the catalyst site, the ratio between hydrogen (if present), and the butene. Undoubtedly, as the coordination of the double bond of the butenes to the Group VIII metal center is an important step in the isomerization reaction (*19*), also the oxidation state of the catalytic metal, influencing its coordinative capacity, could be relevant.

The abnormal molecular congestion at the surface sites was invoked (*6*) to explain the very high value of s for Na_4NiPc (s = 4.0 for 2-butenes) and for $Pt{-}H(SnCl_3)(PPh_3)_2$ (s = 3 for 2-pentenes). The anomalous value of s for iridium (*4c*) was also attributed to unknown geometrical reasons rather than to energetic factors.

We do not rule out the influence of the geometrical shape of the catalytic center on the selectivity and/or the activity, and in the past we have verified this fact in the disproportionation of cyclohexene over supported palladium (*20*) and in the dehydrogenation–hydrogenolysis of *n*-pentane on supported ruthenium (*21*). Nevertheless, we think that other factors, especially in relation to the experimental conditions, must also be considered, viz. electronic, diffusive, and kinetic factors. Thus:

(i) The influence of the geometric factor can be fully appreciated if the electronic state of the catalytic metal center is the same, comparing its behavior in different catalysts, for the reasons previously indicated; besides, it seems to us that the influence of the geometric factor, for the supported metal catalysts, is more important with small crystallites, where the shape factor influences the behavior of demanding reactions. With supported metal catalysts having more than about 0.5–0.8% (w/w) of metal, and not subjected to a sintering process, it is very difficult to observe the influence of the geometric factor, as the crystallites are larger than 25–30 Å.

(ii) As for the diffusive factor, it has been proved (*22*) that at high temperature ($T \geq$ 500°C), internal diffusion may be rate limiting in 1-butene isomerization over alumina with particle dimensions greater than 40 mesh (diameter 0.5 mm). If the isomerization reaction of 1-butene is carried out in the internal diffusion regime the *trans*-2-butene isomer could be the favored one, as its diffusion coefficient in narrow pores may be 200 times greater than that of *cis*-2-butene (*23*); in this case the selectivity will be less than 1. Diffusion processes may be evidenced depending on whether the activation energy is dependent or not on the pressure of the reagent (*22*).

(iii) Concerning the kinetic factor, we have listed in Table 1 the types of experimental devices employed; they are both static, with the catalytic granules resting on the bottom of the reaction vessel and the stagnant gas above, and flux reactors. A static reactor has also been used by Hall and co-workers (Ref. 22 quoted in Ref. (*24b*)) for butene isomerization on different supports, to avoid some inherent uncertainties of the flux microreactor, but in this case the gas was stirred. With completely static devices some doubt may arise as to whether one is really in the regime of surface reaction control. Many studies have been made in the past with catalyst particles greater than 40 mesh and completely static devices. The doubts indicated may be supported considering, for instance, activation energies depending on the pressure of the reactant (1-butene), as for Na_4NiPc (*6*). This fact does not exclude the importance of the congestion of the catalytic center, but uncertainties are present.

(iv) Finally, it has been shown that the hydrogen availability increases considerably the *cis*/*trans* ratio (*4c*). We note that with the original catalyst, not treated with hydrogen, the *cis*/*trans* ratio for 2-butenes is less than 1 also for iridium employing a static apparatus and large catalyst particles (8–16 mesh).

Thus, if the surface reaction controls the rate and the metal catalyst particles are large enough, the most energetically favored path will decide, for low conversions, the value of the *cis*/*trans* selectivity. It seems that for Pt and Pd the favored path is lying between 1-butene and *cis*-2-butene, as for alumina (Ref. (*21*) quoted in Ref. (*24b*)), and this may cause the high selectivity reported in Tables 1 and 4.

Role of the metal. Considering the results of Table 2, it may be deduced that, by changing the metal on the same support (γ-Al_2O_3), the selectivity ($\bar{s}$) toward *cis* and *trans* isomers changes more than one order of magnitude, being on average for T between 140 and 200°C: 5 (Pd), 3.3 (Pt), 1 (Ir), 0.5 (Rh), and 0.1 (Os). This means that the metal is the main factor influencing the selectivity of the reaction 1-butene $\rightleftarrows$ 2-butenes (*cis* and *trans*). Moreover, the pure metals Co, Pd, Au, Pd–Au alloys, and Pt (Table 1) can isomerize *n*-butenes in the absence of molecular hydrogen. This means that many metals *per se* promote the double-bond isomerization in mild enough conditions ($T < 200$°C).

Role of the support. Discussion about the reactivity on supported metals cannot be separated from the role of the support on the reactivity and on the mechanism of the isomerization reaction. It is not the aim of this paper to delve into this subject, but some points should be considered. The literature on this topic is extremely wide, from the early paper of Turkevich and Smith in 1948 (*25*) to those of Haag and Pines (*26*), Foster and Cvetanovic (*10*), Peri (*27*), and the series of papers by Hall and co-workers (*24*), and others specifically referenced earlier in this paper. Therefore we recall here only the cases or the literature in which the presence and the nature of the support gives a different reactivity and/or selectivity for the reaction under discussion (*4*b) and the cases in which the support is active or inactive in relation to its treatment for the same reaction (*24–35*).

As to the first aspect (presence and nature of the support) Wells and Wilson (Table 1 and Ref. (*4*b)) have shown that the same noble metal on different supports gives very different activities; however, the surface area of these supports differs more than one order of magnitude and so it is difficult to compare the results. In this study the A, B, and C supports (namely, a mixture of bohemite and amorphous alumina, a 1 : 1 mixture α- and κ-Al_2O_3, and α-Al_2O_3, respectively) are inactive both for butene isomerization and for deuterium exchange with the support at 152°C, but both reactions take place at 100°C on the system metal–support. The 1-butene isomerization reaction over Pd–A and Pd–C at 150°C (*4*b) and over Pt black at 135°C (*9*) and Pt–Al_2O_3 at 160°C (this paper) at about the same conversion, shows different values of the selectivity *cis/trans*, namely 0.54 and 0.55 for Pd–A and Pd–C, respectively, and 1.3 and 2.8 for Pt and Pt–Al_2O_3, respectively. This may indicate a cooperation between metal and support in the isomerization reaction.

As far as the present study is concerned, it has been shown experimentally (see the results on the conversion on the alumina and also Ref. *34*) that our non-activated γ-alumina is catalytically inactive in 1-butene isomerization up to 220°C, for our time factors; this result led us to think that the reactivity of our metal–Al_2O_3 systems may be regarded as being largely due only to the metal, but we do not rule out the hypothesis that the potential defects (holes) on the surface of alumina can accommodate the different metals in different energetic and topographical ways. Such different metal–support interaction has recently been proposed for Pt and Rh on γ-Al_2O_3 and TiO_2 (*36*). It is clear that the adsorption of the butenes may be influenced in this respect by the presence of the support.

The influence of the support in the Ru catalysts will be discussed in a later section.

XPS measurements. From Table 3 it may be seen that the surface concentration, c_S, is slightly less than the bulk concentration, c_B, only in the case of Ru. In all other cases, $c_S > c_B$. As far as the valence state of the metal is concerned, it is possible to see from Table 4 that only in the case of the low-concentration Rh is one peak observed; in the spectra of the other catalysts more peaks are present. In the case of Ir and Rh catalysts the high-energy peaks are present as a shoulder, while for the Ru the two peaks are present in a 1 : 1 ratio. For the cases other than Ru, the only peak present (or the main peak) was attributed to atoms present in the metallic state, with the others attributed to higher oxidation states (probably deriving from an incomplete reduction). In the case of Ru, on the other hand, neither of the peaks observed can be assigned to atoms in the metallic state.

Two features discriminate the Ru catalyst from the others: (i) no atoms in the metallic state are present, and (ii) nearly equal distribution of the metal between the bulk and the surface. On the other hand, for Ir and Rh no presence of oxidized states has been detected and moreover the metals are mainly on the surface. These two types of catalyst have comparable selectivities (Table 2).

Experiments with Ru. As shown under Experimental the runs with Ru catalyst have been made at temperatures below 75°C due to coke and/or polymer deposition; this phenomenon is shown quantitatively in Fig. 2. The behavior of Ru catalyst has not been easy to justify, but recently a paper by Blanchard and Charcosset (*14*) supported by another recent paper by Bossi *et al.* (*37*) and by our XPS measurements give a reasonable explanation. Blanchard and Charcosset (*14*) have proved that, in contrast to a Pt/Al_2O_3 catalyst (Pt 1.88 wt%), a Ru/Al_2O_3 catalyst (Ru 0.88 wt%) near to our composition, prepared by impregnation with H_2RuCl_6 and reduced in a flux of hydrogen (2 h, 500°C), shows only 55% of Ru^{4+} reduced to Ru^0, with an increase to 75% in the temperature range 500–800°C. Moreover, the authors found by TPR (Temperature-Programmed Reduction) a maximum of hydrogen consumption at 270°C and a hydrogen desorption at 450°C; these results have been confirmed by Bossi *et al.* (*37*) for a catalyst Ru/Al_2O_3 prepared using $RuCl_3$.

The reduction temperature of all our catalysts in a flux of hydrogen has been 330°C for 2 h. Such conditions are milder than those of the paper previously referenced (*14*); moreover, our XPS measurements show the absence of metallic ruthenium. Our experimental results seem to indicate that our Ru catalyst should be regarded as a system Ru–Cl–Al_2O_3, with the chlorine ions bound to Ru^n ($0 \leq n \leq 3$) or/and to Al^{3+} ions; the chlorine ions should be strongly bonded as the catalyst does not lose Cl^- ions on exhaustive washing with hot distilled water, as described in detail in the experimental section. Such a bifunctional catalyst has acid centers and therefore can produce typical reactions of this kind of catalyst, such as those of cracking, polymerization, and coke deposition. Acid catalysts such as silica–alumina are able to form polymeric complexes rapidly at 25°C with 1-butene, such complexes being the seat of activity of 1-butene isomerization at 25°C (*38*); carbon black, if formed, can isomerize olefins at low temperature (about 50°C), as proved by Meier and Hill (*39*).

On Pt–Al_2O_3–Cl catalyst coke deposition has been recently studied by Figoli *et al.* (*40*), also at low temperatures (123°C), during naphtha reforming. Retention of hydrocarbons (alkanes < cyclopropane < alkenes < acetylene) in an unreactive form has been studied by Taylor *et al.* (*41*) on Pd/Al_2O_3 at temperatures between 20 and 200°C.

On the basis of the above-reported discussion and references, it can be supposed that below 75°C 1-butene isomerization is produced by Ru–Cl–Al_2O_3 catalyst and above this temperature also by carbonaceous residues.

Penetration depth of the metal complexes after reduction. The XPS results in Table 3 show that only in the case of Ru catalyst is the distribution between the surface and the bulk of the catalyst sensibly uniform. In the impregnation of the support we have not used the technique of coprecipitation, usually employed to give a radial profile of metal inside the support (*42*); therefore, since the nature of the support and the treatment of the impregnated catalysts was the same for all of them, the difference between Ru/Al_2O_3 and the other catalysts are due, very probably, to different metal complexes employed, as studied in detail by Summers *et al.* (*43*) and recently reviewed (*44*).

We have not studied in detail the phenomenon of depth profiling, but we may briefly discuss our results with reference to the literature and the unusual reactivity of Ru catalyst. The results in Table 3 on Rh catalyst produced using Na_2RhCl_6 are different (i.e., uniform impregnation; in fact the Ir catalyst gives the maximum surface concentration of the metal among the catalysts studied in this paper). It should be observed, however, that in Ref. (*43*) ammonium salts have been used both for Rh and Ir catalysts, respectively, $(NH_4)_3RhCl_6$ and $(NH_4)_2IrCl_6$, and that the result on Ru/Al_2O_3 shows surface impregnation using $(NH_4)_4RuCl_6$ (*36b*) and uniform impregnation by means of H_2RuCl_6 (*14*). Our XPS results on Ru/Al_2O_3 agree with the recent paper by Blanchard and Charcosset (*14*), and logically are due to the acid nature of our salt ($RuCl_3 \cdot H_2O$).

As for the influence of the uniform distribution of the metal in the Ru catalyst and its unusual activity, besides the hypothesis previously given, it can be argued that Ru atoms (whose quantity is not very different from that of the other catalytic metal here employed) can distribute on a larger surface, being uniformly spread over all the support surface. This will produce smaller catalytic clusters which could have an intrinsically higher activity.

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