Bimetallic Catalysts. V. Kinetics of the Hydrogenolysis of Butane over Pt–Mo/SiO₂ Catalysts

G. LECLERCQ,[1] A. EL GHARBI, AND S. PIETRZYK

Laboratoire de Catalyse Hétérogène et Homogène, U.R.A. C.N.R.S. no. 402, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France

The kinetics of the hydrogenolysis of butane on various Pt–Mo catalysts deposited on silica with the same metal content but with various Mo/(Mo + Pt) ratios has been studied. The hydrogenolysis of the two different kinds of C–C bonds has been distinguished. It is shown that the addition of Mo to Pt drastically changes the selectivity of the reaction, but that this selectivity is approximately the same for all the bimetallic Pt–Mo catalysts. Using a rate equation that had already been used for the hydrogenolysis of alkanes (Maurel, R., Leclercq, G., and Leclercq, L., *J. Catal.* **44**, 68 (1975)), calculation has been made of the values of the equilibrium adsorption constants (λ) and those of the rate constants of the C–C bond splitting steps (k) for the hydrogenolysis of the terminal C–C bonds (λ_1 and k_1) and of the middle C–C bond (λ_2 and k_2). In this way it has been shown that on Pt alone, two different intermediaries with high λ values are formed in which the C–C bonds will be broken further with different selectivities but with low rate constants. On the contrary, on all Pt–Mo catalysts, butane is adsorbed as a single intermediate adsorbed species with a much lower adsorption equilibrium constant than on Pt alone, but this adsorbed species is much more reactive (k_1 and k_2).

The adsorption equilibrium constants are the same for all Pt–Mo taking into account the margin of error, which shows that, on all Pt–Mo, butane is adsorbed on the same mixed Pt–Mo site of constant composition whatever the catalyst composition. The number of these active sites (proportional to k_1 and k_2) increases as Mo/(Mo + Pt) increases up to 25–30%, then it decreases. © 1993 Academic Press, Inc.

INTRODUCTION

The hydrogenolysis of alkanes and cycloalkanes is an interesting reaction that has been extensively studied and used for the characterization of metal catalysts (see, for example, Refs. (*1–11*)). The reaction of butane with hydrogen is particularly useful and interesting, since it gives a simple mixture of products which are easy to analyze but can lead to various reactions: (i) two "single hydrogenolysis" reactions (that is, the rupture of only one C–C bond): $C_4H_{10} + H_2 = CH_4 + C_3H_8$ and $C_4H_{10} + H_2 = 2C_2H_6$; (ii) multiple hydrogenolysis reactions: $C_4H_{10} + 2H_2 = 2CH_4 + C_2H_6$ or $C_4H_{10} + 3H_2 = 4CH_4$; and (iii) isomerization to isobutane. Hence metal catalysts

can be characterized not only by their global activity, but also by their selectivities in the above reactions. This reaction has been studied on various single metal catalysts (*7, 8, 12, 13*) and on bimetallic catalysts (*14–21*) by many groups.

Concerning bimetallic catalysts, in a previous study (*17, 18*) we have provided evidence for some analogies between Pt–Mo, Pt–Re, and Pt–Ir in catalytic reactions such as the hydrogenation of benzene, dehydrogenation of cyclohexane, hydrogenolysis of butane (*18*), and reactions between hydrogen and hexane or 3-methylpentane (*17*). Particularly in the hydrogenolysis of butane, despite the fact that the hydrogen chemisorption at room temperature decreases as the ratio Mo/Mo + Pt increases, a synergy effect occurred which had been observed for Pt–Re (*15*) and for Pt–Ir (*16*).

[1] To whom correspondence should be addressed.

118

Such a synergy effect for various Pt–Mo systems has also been reported by Yermakov et al. (20) for the hydrogenolysis of ethane on Pt–Mo supported on silica by exchange, and by Tri et al. (21) for the hydrogenolysis of butane on Pt–Mo on zeolite. On the other hand, it has been also shown in Ref. (17) that Pt–Mo on silica exhibits some sulfur resistance since the "efficiency" of thiophene (or the number of active sites poisoned by one thiophene molecule) (22, 23) decreases with the relative atomic percentage of molybdenum in Pt–Mo from 3.8 for Pt to 1.7 when the ratio Mo/(Mo + Pt) was 76.6%, in the reactions between hydrogen and 3-methylpentane (with 61 ppm (mol) of thiophene). Hence, we think that this bimetallic system is of potential industrial interest and that it would be interesting to have more information on the way it acts in hydrocarbon transformations.

Among other hypotheses that have been discarded, two different explanations have been proposed for the occurrence of the synergy effect mentioned above for the hydrogenolysis of butane. The first was given by Tri et al. (21), who assumed that one step of the reaction sequence occurs on platinum (hydrogen adsorption, for example) and that another is faster on Mo than on Pt (hydrocarbon adsorption). In the second explanation (18), we proposed that a mixed site composed of both Pt and Mo atoms could be more active than a site made up of atoms of only one metal.

Now, two important previous results (18) have to be recalled here. First (18, 21) the selectivity of the reaction between hydrogen and butane was very different for Pt and for bimetallic Pt–Mo catalysts, but was the same for all the bimetallic catalysts whatever their composition. Hence for all the Pt–Mo catalysts butane gives the same adsorbed species which are different from those adsorbed on platinum alone. Tri et al. (21) explain this fact easily by their hypothesis of a better adsorption of butane on molybdenum than on platinum. In the frame of

our hypothesis of the intervention of a mixed site, one has to assume in addition that butane is adsorbed on the same mixed site with the same composition on all Pt–Mo solids studied in Ref. (18). On the other hand, when the activity in butane hydrogenolysis is expressed as the reaction rate per H atom adsorbed on the catalyst, it increases with the Mo/(Mo + Pt) ratio up a value of 25–30% which corresponds to the maximum rate (in moles transformed per gram of catalyst and per time unit), then it remains constant at a value of about 600 molecules of butane transformed per hydrogen adsorption site and per hour at 300°C with $P_{C_4} = 0.1$ atm and $P_{H_2} = 0.9$ atm within the margin of error.

Such a behavior can easily be accounted for if butane adsorbs on the same mixed site composed of Pt and of Mo and with a fixed composition whatever the bimetallic catalyst composition. In such a case only the number of these mixed sites will change with the catalyst composition. Before the maximum of activity, Pt is in excess and all the surface Pt atoms which adsorb hydrogen are not included in mixed active sites; hence, the number of mixed sites per H atom adsorbed increases with the relative atomic Mo percentage. Then, after the maximum of activity, Mo is in excess and all surface Pt atoms are in mixed sites; hence, the number of mixed sites per H atom adsorbed and the activity per H adsorption site are constant.

The hypothesis of Tri et al. (21) could also account for these results since, if butane is mainly adsorbed on Mo before reaction, another step of the reaction sequence takes place on Pt. In that case when the Mo content is low (before the maximum of activity) the rate-determining step (rds) is a step occurring on Mo, but after the maximum of activity, with Mo-rich catalysts, the rds takes place on Pt.

To sum up the position, if Tri et al. are right (21), the maximum of activity would correspond to a change in the rds, and hence in the kinetics of the reaction. On the

contrary, in the second hypothesis, the kinetics would change from Pt to Pt–Mo but would obey the same law for all the bimetallic catalysts. Consequently a kinetic study could help us to decide between the two hypotheses which, up to now, can explain all the catalytic results.

For this reason we have studied the kinetics of the hydrogenolysis of butane on a series of Pt–Mo catalysts of various compositions with different Mo/(Mo + Pt) ratios between 0 and 87%.

Since the single hydrogenolysis of butane can occur in two ways,

$$C_4H_{10} + H_2 = CH_4 + C_3H_8 \qquad (1)$$

$$C_4H_{10} + H_2 = 2C_2H_6, \qquad (2)$$

we have studied these two reactions separately.

EXPERIMENTAL

Catalysts

The silica (Aerosil 200 Degussa, surface area = 200 m²/g, average particle size 120 Å) was impregnated by aqueous solutions of chloroplatinic acid (Johnson Matthey) and of ammonium heptamolybdate (Fluka). Water was evaporated with continuous stirring on a sand bath, then the solids were dried overnight in an oven at 110°C and reduced in situ in flowing hydrogen at 500°C (3.6 liter/h for 7 h).

A series of Pt–Mo catalysts were prepared with a constant metal atom content (Pt + Mo) of about $9(\pm 0.5) \times 10^{19}$ atoms per gram of catalyst with various proportions of platinum and molybdenum. These catalysts are designated PMD_x, where P and M signify Pt and Mo, D is for Degussa, and $x = [\text{Mo}/(\text{Mo} + \text{Pt})] \times 100$.

Chemical Analysis

The chemical analyses were performed at the Service Central de Microanalyse of the CNRS. Pt and Mo were analyzed by atomic absorption spectroscopy.

Hydrogen Adsorption

The adsorption apparatus was a conventional glass volumetric system (29, 30), equipped with a Texas Instruments precision pressure gauge. The samples were reduced in situ at 500°C in flowing hydrogen and outgassed at 400°C for about 12 h. Then hydrogen adsorption isotherms were determined in a hydrogen pressure range of 50 to 300 Torr. In that pressure range the isotherms were linear and the hydrogen adsorptions were specified by extrapolating these straight lines to zero pressure.

Apparatus

All experiments were carried out at atmospheric pressure in a plug flow reactor already described (4, 31). The gas flow rates were measured by soap bubble flowmeters. The gases were purified by passing through a Pd catalyst (for hydrogen) then through silica and zeolite (13X for hydrogen and nitrogen and 5A for butane). Butane of 99.95% purity (N35 grade) was supplied by L'Air Liquide.

Products were periodically analyzed by an Intersmat IGC 131 chromatograph with FID detectors, and columns (3 m long, 1/8″ diameter) packed with 10% squalane on spherone.

Procedure

The procedure has been described in Refs. (12, 26, 31). The conversion on the undeactivated catalyst was determined by extrapolating the curve of conversion vs time of reaction.

Rates were calculated from the relation

$$r = (F \cdot \tau)/W,$$

where F is the feed rate of butane in moles per hour, τ is the conversion extrapolated to zero time, and W is the weight of the sample of catalyst. The reaction rate was calculated in moles of butane converted per hour and per gram of catalyst.

We have also calculated (12, 31) the rates r_1 and r_2 of reactions (1) and (2) and of bu-
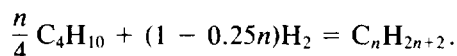
tane isomerization by

$$r_1 = \frac{F(\tau_1 + \tau_3)}{W}, \quad r_2 = \frac{F \cdot \tau_2}{W},$$

and

$$r_i = \frac{F \cdot \tau_i}{W},$$

where τ_1, τ_2, τ_3, and τ_i are respectively the conversions of butane into methane, ethane, propane, and isobutane according to the following formal reactions:

$$\frac{n}{4} C_4H_{10} + (1 - 0.25n)H_2 = C_nH_{2n+2}.$$

The weight of catalyst and the flow rates were adjusted in order to obtain a conversion of less than 10% (except for PMD_{37} and PMD_{50} which were very active catalysts). Under these conditions the secondary reactions due to the conversion of the primary products are negligible.

Experimental conditions are:

—weight catalyst, 0.1 to 1 g.
—temperature, 300°C.
—butane partial pressure, 0.03 to 0.1 atm.
—hydrogen partial pressure, 0.5 to 0.9 atm.
—total flow rate, 4.8 l · h⁻¹ (0.2 mol · h⁻¹).

The activation energies were determined at $P_{C_4} = 0.1$ atm, $P_{H_2} = 0.9$ atm and temperatures between 270 and 320°C.

RESULTS

The orders in hydrogen and in butane have been determined at 300°C by varying respectively the hydrogen partial pressure with the butane partial pressure equal to 0.1 atm, then the butane partial pressure with hydrogen partial pressure equal to 0.9 atm.

The results are presented in Tables 1 and 2 where we have reported the total rate r of butane reaction, together with the rates r_1 and r_2 of the hydrogenolysis of butane into methane and propane (reaction (1)) and in ethane (reaction (2)), respectively, and with the rate r_i of isomerization.

We have also reported in Tables 1 and 2 the ratios C_1/C_3 of the initial mole fractions

of methane and propane in the products, r_1/r_2 and r_i/r. The ratio C_1/C_3 is indicative of the extent of multiple hydrogenolysis of butane according to the reactions

$$C_4H_{10} + 2H_2 = C_2H_6 + 2CH_4 \quad (3)$$

$$C_4H_{10} + 3H_2 = 4CH_4. \quad (4)$$
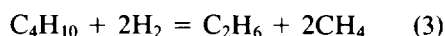
If C_1/C_3 is equal to 1, only single hydrogenolysis occurs (reactions (1) and (2)). If $C_1/C_3 > 1$, then multiple hydrogenolysis occurs. r_1/r_2 is the selectivity of the single hydrogenolysis.

From these values of r, r_1, and r_2 we have plotted $\ln r$ as a function of $\ln P_{H_2}$ (with P_{C_4} constant) or of $\ln P_{C_4}$ (with P_{H_2} constant) in order to determine the orders in hydrogen and in butane when the rates are expressed according to the formal power law

$$r_x = kP_{C_4}^m P_{H_2}^n$$

The results are reported in Table 3, where also given are the values of the activation energies of reactions (1) and (3) determined at $P_{H_2} = 0.9$ atm, $P_C = 0.1$ atm, and at temperatures between 270 and 300°C.

For all the catalysts the various points are reasonably in the vicinity of a straight line taking into account the margin of error, except for the curves $\ln r_x = f(\ln P_{H_2})$ of PMD_{12}, where the rates increase for low hydrogen partial pressures going through a maximum for about $P_{H_2} = 0.67$ atm, after which they decrease for higher hydrogen partial pressures.

DISCUSSION

As far as the selectivities are concerned, one can see, as already pointed out earlier (18), that the selectivities are very different for PMD_0 and $PMD_{x\neq0}$, since C_1/C_3 is very close to unity at each partial pressure for PMD_0, but it is higher than unity for all $PMD_{x\neq0}$ ($C_1/C_3 = 1.5 \pm 0.1$ for all bimetallic catalysts except for PMD_{12}), indicating that multiple hydrogenolysis occurs (reactions (3) and (4)) but to rather low extent. The ratio r_1/r_2 goes from about 3 for PMD_0 to

TABLE 1

Rates of the Reactions of Butane with Hydrogen at Various Hydrogen Partial Pressures
(P_C = 0.1 atm, T = 300°C)

Catalysts	Mo/(Mo + Pt) (%)	P_{H_2} (atm)	$\tau(\%)$	r	r_1	r_2	r_i	C_1/C_3	r_1/r_2	r_i/r
					(10^{-3} mol · h^{-1} · g^{-1} catalyst)					
PMD$_0$	0	0.9	2.85	0.568	0.368	0.116	0.084	1.01	3.17	0.15
		0.8	2.68	0.534	0.341	0.108	0.085	1.00	3.16	0.16
		0.7	2.62	0.522	0.287	0.110	0.125	1.03	2.6	0.24
		0.6	2.42	0.482	0.286	0.102	0.094	1.02	2.8	0.20
		0.5	2.21	0.441	0.245	0.092	0.098	1.03	2.7	0.22
PMD$_{12}$	13	0.9	5.8	5.77	3.135	2.464	0.168	1.12	1.27	0.03
		0.7	6.54	6.5	3.519	2.785	0.200	1.25	1.26	0.03
		0.6	6.56	6.52	3.529	2.767	0.228	1.2	1.28	0.03
		0.5	6.3	6.27	3.357	2.673	0.236	1.25	1.26	0.04
		0.9	5.7	5.67	3.145	2.350	0.173	1.15	1.34	0.03
PMD$_{25}$	24.5	0.9	9.1	8.86	4.88	3.817	0.163	1.35	1.28	0.02
		0.8	11.0	10.71	6.176	4.359	0.178	1.43	1.42	0.02
		0.7	13.1	12.76	7.276	5.261	0.218	1.5	1.38	0.02
		0.6	14.1	13.73	7.855	5.634	0.240	1.5	1.39	0.02
		0.5	16.9	16.46	9.352	6.767	0.337	1.5	1.38	0.02
		0.9	11.3	11.0	6.245	4.574	0.184	1.33	1.37	0.02
PMD$_{37}$	36.7	0.9	16.8	10.42	6.415	3.818	0.185	1.52	1.68	0.02
		0.8	16.24	10.07	6.071	3.837	0.164	1.52	1.58	0.02
		0.7	20.6	12.78	7.624	4.934	0.217	1.59	1.55	0.02
		0.5	26.1	16.19	9.525	6.369	0.293	1.67	1.5	0.02
		0.9	14.9	9.24	5.62	3.472	0.148	1.46	1.62	0.02
PMD$_{50}$	49.1	0.9	21.	7.59	4.6	2.73	0.203	1.5	1.68	0.03
		0.7	23.2	8.31	5.08	3.01	0.233	1.57	1.69	0.03
		0.5	26.1	9.53	5.66	3.44	0.286	1.64	1.65	0.03
		0.9	21.1	7.56	4.56	2.77	0.234	1.5	1.65	0.03
PMD$_{75}$	72.5	0.9	4.1	0.91	0.506	0.341	0.061	1.38	1.48	0.07
		0.7	4.6	1.02	0.557	0.337	0.083	1.43	1.48	0.08
		0.6	4.63	1.025	0.546	0.362	0.117	1.48	1.51	0.11
		0.5	4.9	1.09	0.572	0.393	0.12	1.55	1.46	0.11
PMD$_{87}$	80.5	0.9	3.3	0.62	0.409	0.2	0.011	1.58	2.05	0.02
		0.8	3.7	0.695	0.454	0.229	0.012	1.58	1.98	0.02
		0.7	4.16	0.78	0.509	0.258	0.014	1.65	1.97	0.02
		0.5	5.00	0.94	0.606	0.317	0.016	1.73	1.91	0.02

much lower values for PMD$_{x\neq0}$ (1.2 to about 2.0). In the same way, the ratio r_i/r decreases by about an order of magnitude when Mo is added to Pt.

Butane partial pressure does not seem to have any noticeable influence on the extent of multiple hydrogenolysis (C_1/C_3 unchanged), nor does it have any influence on the ratios r_1/r_2 or r_i/r for all the bimetallic catalysts. However, it does influence both ratios r_1/r_2 and r_i/r for PMD$_0$, since an increase of butane partial pressure induces slight but meaningful increases of r_1/r_2 and r_i/r.

Now, when considering the influence of hydrogen pressure on the selectivities, one can see that a decrease of P_{H_2} seems to lead to a slight increase of C_1/C_3, but it has no influence on r_1/r_2 and r_i/r ratios for PMD$_{x\neq0}$. On the contrary on PMD$_0$, r_1/r_2 increases and r_i/r decreases when P_{H_2} increases.

Hence the selectivity in the single hydrogenolysis of butane (reactions (1) and (2)) is

TABLE 2

Rates of the Reactions of Butane with Hydrogen at Various Butane Partial Pressures
$(P_{H_2} = 0.9$ atm, $T = 300°C)$

Catalysts	Mo/(Mo + Pt) (%)	P_C (atm)	$\tau(\%)$	r	r_1	r_2	r_i	C_1/C_3	r_1/r_2	r_i/r
						$(10^{-3}$ mol $\cdot$ h$^{-1}\cdot$ g^{-1} catalyst)				
PMD$_0$	0	0.1	2.85	0.568	0.368	0.116	0.084	1.00	3.17	0.15
		0.08	3.69	0.588	0.384	0.122	0.082	0.98	3.15	0.14
		0.06	4.49	0.537	0.352	0.113	0.072	0.98	3.12	0.13
		0.05	5.53	0.551	0.359	0.117	0.075	0.99	3.07	0.14
		0.03	7.53	0.450	0.303	0.099	0.048	0.99	3.06	0.11
		0.1	2.85	0.568	0.401	0.126	0.041	1.00	3.18	0.07
PMD$_{12}$	13	0.1	6	5.97	3.15	2.6	0.22	1.16	1.21	0.04
		0.06	7.1	4.24	2.282	1.801	0.154	1.12	1.27	0.04
		0.05	8.4	4.18	2.255	1.769	0.153	1.12	1.27	0.04
		0.03	10.2	3.03	1.696	1.228	0.12	1.07	1.38	0.04
		0.1	5.8	5.77	3.106	2.465	0.198	1.12	1.26	0.03
PMD$_{25}$	24.5	0.1	10.1	9.83	5.629	4.042	0.164	1.33	1.39	0.02
		0.06	10.3	6.02	3.287	2.61	0.12	1.25	1.26	0.02
		0.05	12.1	5.89	3.189	2.58	0.122	1.25	1.24	0.02
		0.03	15.05	4.4	2.373	1.923	0.101	1.25	1.23	0.02
		0.1	8.6	8.37	4.557	3.657	0.161	1.25	1.25	0.02
PMD$_{37}$	36.7	0.1	16.8	10.42	6.433	3.797	0.189	1.52	1.69	0.02
		0.06	19.6	7.29	4.395	2.766	0.133	1.52	1.59	0.02
		0.05	21.6	6.7	4.032	2.542	0.125	1.52	1.59	0.02
		0.03	23.6	4.39	2.642	1.665	0.084	1.52	1.59	0.02
		0.1	17.16	10.64	6.419	4.035	0.188	1.52	1.59	0.02
PMD$_{50}$	49.1	0.1	21.8	7.81	4.66	2.96	0.187	1.64	1.57	0.02
		0.08	25.1	7.2	4.43	2.57	0.202	1.57	1.72	0.03
		0.06	26.2	5.63	3.41	2.07	0.152	1.57	1.72	0.03
		0.05	28.1	5.04	3.09	1.81	0.141	1.57	1.71	0.03
		0.03	34.2	3.68	2.26	1.32	0.103	1.57	1.71	0.03
		0.1	21.8	7.81	4.82	2.78	0.226	1.57	1.73	0.03
PMD$_{75}$	72.5	0.1	4.7	1.04	0.574	0.389	0.077	1.38	1.48	0.07
		0.08	5.5	0.97	0.538	0.365	0.071	1.38	1.47	0.07
		0.06	5.7	0.76	0.416	0.285	0.056	1.28	1.46	0.07
		0.05	6.9	0.763	0.421	0.287	0.06	1.38	1.47	0.07
		0.03	7.8	0.52	0.285	0.192	0.04	1.38	1.48	0.08
		0.1	4.4	0.94	0.529	0.38	0.065	1.33	1.39	0.07
PMD$_{87}$	80.5	0.1	3.3	0.62	0.404	0.208	0.008	1.48	1.94	0.01
		0.06	4.68	0.53	0.347	0.172	0.009	1.58	2.02	0.02
		0.05	5.32	0.5	0.33	0.16	0.006	1.58	2.06	0.02
		0.03	5.74	0.32	0.215	0.103	0.006	1.63	2.09	0.02
		0.1	3.9	0.73	0.483	0.236	0.013	1.58	2.05	0.02

influenced neither by butane nor by hydrogen pressure on bimetallic catalysts (PMD$_{x \neq 0}$). On the contrary this selectivity changes with both pressures on Pt alone (PMD$_0$).

For all the catalysts the partial orders in butane are positive (Table 3), but with respect to bimetallic catalysts PMD$_0$ catalysts exhibit lower orders in butane. All PMD$_{x \neq 0}$ samples have approximately the same orders in butane within the margin of error. It is worth mentioning that orders in butane are always the same for the hydrogenolysis of the two bonds, namely, external (reaction (1)) and internal (reaction (2)).

The influence of hydrogen pressure on

TABLE 3

Orders (at 300°C) and Energies of Activation in the Hydrogenolysis of Butane for the Total Transformation (r) and for the Splitting of the Terminal C–C bonds (1) and of the Middle C–C Bond (2)

Catalysts	Mo/(Mo + Pt) (%)	Order (r)		Order/C_4		Order/H_2		Energies of activation (kJ/mol)		
		/C_4	/H_2	(1)	(2)	(1)	(2)	r	(1)	(2)
PMD$_0$	0	0.16	0.42	0.18	0.19	0.68	0.36	119	112.5	115.5
			Max			Maximum				
PMD$_{12}$	13.0	0.54	at 0.67 atm	0.50	0.59	(0.67 atm)		142	141	141
PMD$_{25}$	24.5	0.57	−0.77	0.55	0.56	−0.77	0.78	130	128.3	129
PMD$_{37}$	36.7	0.63	−0.49	0.64	0.63	−0.52	−0.50	138	129	129
PMD$_{50}$	49.1	0.63	−0.36	0.65	0.65	−0.38	−0.4	142	141.3	141
PMD$_{75}$	72.5	0.54	−0.20	0.57	0.55	−0.20	−0.18	146	145.5	146
PMD$_{87}$	80.5	0.52	−0.68	0.58	0.53	−0.79	−0.72	155	155	156.3

the rates of hydrogenolysis is very interesting (Table 3). If, as has already been observed (21, 26, 27), the orders in hydrogen are positive on Pt, they are negative for all PMD$_{x \neq 0}$, except, as already mentioned above, for PMD$_{12}$ which exhibits maximum rate for $P_{H_2} = 0.67$ atm. PMD$_{12}$ can be considered as an intermediate system between PMD$_0$ and bimetallic Pt–Mo catalysts. At a first glance, it seems that the orders in hydrogen increase with Mo/(Mo + Pt). However, taking into account that these orders decrease for PMD$_{87}$, and considering the rather large experimental error on the determination of orders (low variations of conversion and difficulties in assessing the deactivation curves (26)), it is quite possible that the inhibiting effect of hydrogen on the hydrogenolysis of butane is the same for all Pt–Mo catalysts with orders of about −0.5 ± 0.3.

The three types of rate variations with hydrogen pressure are derived from the same curve with a maximum for a given partial pressure; it is simply that the optimum hydrogen pressure is above the investigated hydrogen pressure range for Pt and below it for Pt–Mo with Mo/(Pt + Mo) higher than 12.5%. Such bell-shaped curves have been observed for various hydrocar-
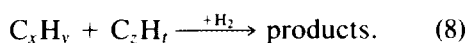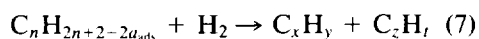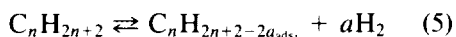
bon reactions with hydrogen (34, 35). Paál and co-workers (34, 35) have explained the occurrence of such an optimum hydrogen partial pressure by assuming that the rate is maximum when the hydrogen concentration on the catalytic active site is optimum, the hydrogen concentration on the catalyst surface being influenced not only by the hydrogen pressure in the gas phase but also by spillover and diffusion of hydrogen into subsurface layers, by the presence of carbon deposits (coke) at the surface of the catalyst or by the presence of strongly adsorbed high-temperature hydrogen, as reported by Menon and Froment (36, 37). Since this "effective surface hydrogen pressure" (34) is likely to be influenced by the adding of Mo to Pt, it could very well explain the shift of the optimal hydrogen pressure towards lower values when Mo is added to Pt.

Now, considering separately the hydrogenolysis of the two types of C–C bonds, one can see that the two reactions have very different orders in hydrogen: 0.68 for reaction (1) and 0.36 for reaction (2) on PMD$_0$. On the contrary, for Pt–Mo both reactions exhibit the same kinetic law. It is then probable that on Pt alone two different adsorbed intermediates are formed which

undergo further C–C bond ruptures with different selectivities, while on Pt–Mo only one intermediate is formed for hydrogenolysis.

All these results indicate that the addition of molybdenum to platinum strongly modifies the kinetics of butane hydrogenolysis. However, for all Pt–Mo catalysts (except PMD_{12} which is a transitional case between PMD_0 and the other bimetallic catalysts), the kinetics of butane hydrogenolysis are approximately the same.

We have attempted to extend this formal analysis of the kinetics and have used a rate expression derived from a kinetic scheme originally proposed by Cimino et al. (24) and then used by Sinfelt (25) for ethane hydrogenolysis:

$$C_nH_{2n+2} \rightleftarrows C_nH_{2n+2-2a_{ads}} + aH_2 \quad (5)$$

$$H_2 \rightleftarrows 2H_{ads} \quad (6)$$

$$C_nH_{2n+2-2a_{ads}} + H_2 \rightarrow C_xH_y + C_zH_t \quad (7)$$

$$C_xH_y + C_zH_t \xrightarrow{+H_2} \text{products.} \quad (8)$$

The rate expression that proved to give the best fit with experimental results of the hydrogenolysis of gaseous alkanes on platinum (26, 27), had the following form:

$$r = \frac{k\lambda P_C P_{H_2}}{P_{H_2}^x + \lambda P_C}. \quad (9)$$

It had been derived from the above kinetic scheme assuming that adsorption–desorption steps (5), (6), (7), and (8) are very fast compared with a step of rupture of a C–C bond. This will be true only if "single hydrogenolysis" takes place (i.e., if only one C–C bond is broken during a single sojourn of a molecule of hydrocarbon on the catalyst) or if "multiple hydrogenolysis" is of not too high extent, as in the case of the catalysts studied here.

k is the rate constant of step (7) of the C–C bond breaking, P_C and P_{H_2} are the partial pressures of hydrocarbon and of hydrogen, respectively. λ and x will have different meanings according to whether hydrogen adsorption is negligible or not compared with that of the hydrocarbon.

If hydrogen adsorption is negligible (26) then:

$\lambda = \lambda_c$: the adsorption equilibrium constant of the hydrocarbon (step (5));

$x = a$: the extent of dehydrogenation of the hydrocarbon adsorbed species (step (5)).

If hydrogen adsorption is not negligible (27) then:

$\lambda = \lambda_C/\lambda_H^{mv}$, where λ_H is the equilibrium constant of adsorption of hydrogen;

the hydrocarbon adsorption site is assumed to be composed of m free neighbour hydrogen adsorption sites and y comes from the approximation of $(1 + \sqrt{\lambda_H P_{H_2}})$ to $(\lambda_H P_{H_2})y$.

$x = a + my$

It has been assumed that the adsorption of hydrocarbon and hydrogen both obey a Langmuir adsorption isotherm which is probably not true over a wide pressure range, especially for hydrogen adsorption, as clearly demonstrated by Frennet et al. (38), but which can be regarded as an acceptable approximation for relatively small pressure ranges such as those used in this study. Consequently the values of λ determined later in this paper are valid for the hydrogen coverages (θ_H) obtained with hydrogen pressures of about 0.5 to 1 atm.

Such a rate expression has been successfully applied to the hydrogenolysis of ethane, propane, butane, and isobutane over nickel (28). We have used it in this study in order to determine the values of k, λ, and x on all the Pt–Mo catalysts for the hydrogenolysis of butane into methane and propane (reaction (1)) on the one hand, and into ethane (reaction (2)) on the other. In these calculations we have assumed that the two reactions take place via the formation of two different adsorbed species and that these species are adsorbed noncompetitively on two different sites of adsorption.

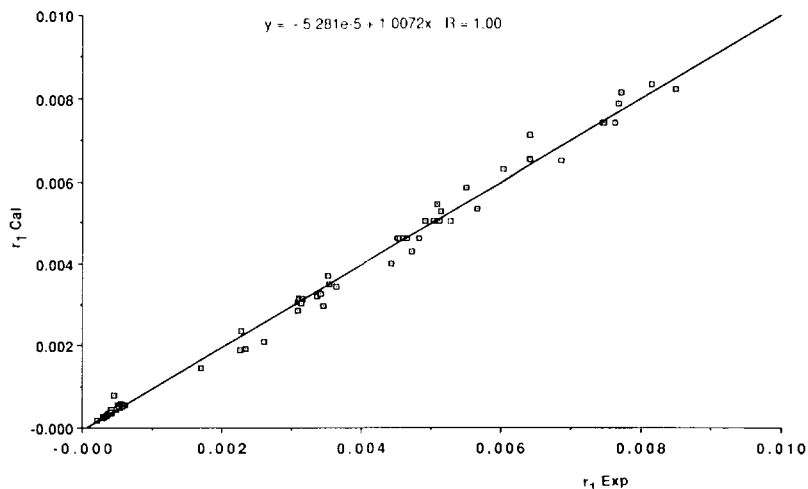In previous studies (26–28) we have de-

FIG. 1. Comparison of the experimental rates of the hydrogenolysis of the terminal C–C bonds in butane to that calculated using kinetic parameters of Table 4 for $P_{C_4} = 0.1$ atm, $P_{H_2} = 0.9$ atm, and $T = 300°C$; r_1 in mol/h · g of catalyst.

termined these parameters by graphic methods. Here, considering that in most cases the points on the straight lines ($1/r$ vs $1/P_C$ and $P_C \cdot (P_{H_2}/r)$ vs $P_{H_2}^a$) are not numerous enough to obtain a good accuracy in the determination of the slopes and intercepts which lead to the kinetic parameters, we have used two different methods of optimization to determine k, λ, and x. These two

methods are those of Hooke and Jeeves (32) and Marquardt (33), both of which give very similar results. The results reported in Table 4 were obtained with Marquardt's method.

In order to have an idea of the validity of the values of the kinetic parameters we have compared in Figs. 1 and 2 the experimental rates r_1 and r_2 with the calculated
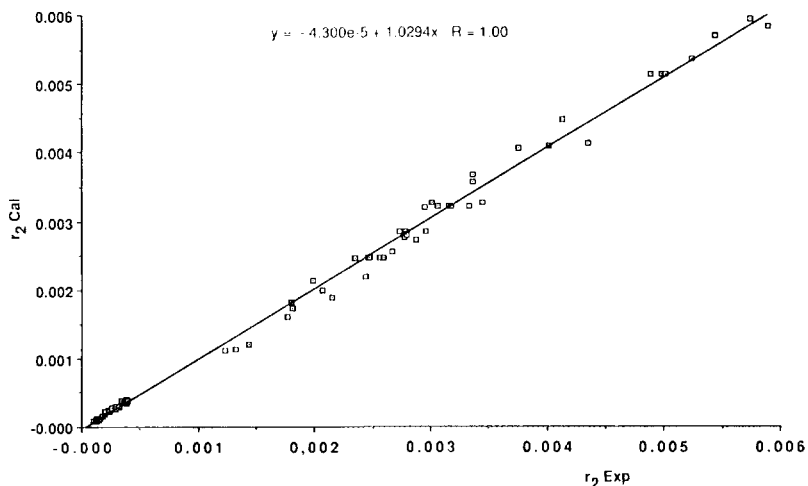

FIG. 2. Comparison of the experimental rates of the hydrogenation of the middle C–C bond in butane to that calculated using kinetic parameters of Table 4 for $P_{C_4} = 0.1$ atm, $P_{H_2} = 0.9$ atm, and $T = 300°C$; r_2 in mol/h · g of catalyst.
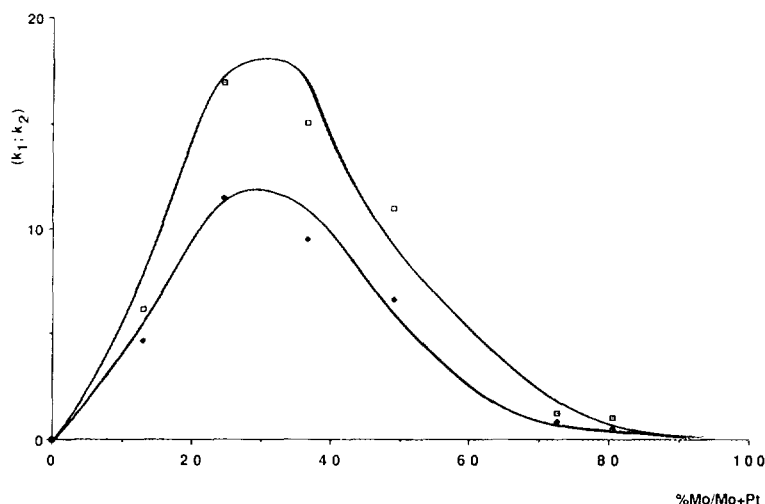
FIG. 3. Changes of the rate constants of the rupture of the terminal C–C bonds (k_1) and of the middle C–C bond (k_2) in butane as a function of the relative Mo atomic percentage in Pt–Mo/SiO$_2$. (□) k_1[10^{-3} mol/(atm · h · g of catalyst)] and (◆) k_2[10^{-3} mol/(atm · h · g of catalyst)].

ones. All the points are in the vicinity of straight lines with a slope very close to 1 and intercepts close to zero ($r_{1calc.}$ = -5.38×10^{-5} + 1.007 $r_{1exp.}$ and $r_{2calc.}$ = -4.3×10^{-5} + 1.03 r_{2exp}).

The variations of k_1 and k_2 vs the ratio Mo/(Mo + Pt) are represented in Fig. 3. One can see that both constants increase with the relative molybdenum percentage, then go through a maximum for a value of Mo/(Mo + Pt) between 25 and 30% and finally decrease. But for all Pt–Mo, the ratio k_1/k_2 is approximately the same (1.5 ± 0.5) taking into account the margin of error, and it is much lower than for Pt alone (k_1/k_2 = 3) (Table 4).

On Pt (PMD$_0$) the values of λ which are related to the equilibrium constant of adsorption of the hydrocarbon are much higher than on Pt–Mo, and the constants (λ$_1$ for reaction (1) and λ$_2$ for reaction (2)) are different for reactions (1) and (2). In the same way the values of x are different (1.7 and 4.7) for this catalyst. These results are in good qualitative agreement with those obtained on Pt/Al$_2$O$_3$ (26, 27) at 313°C. On the contrary, for all Pt–Mo the two values of λ$_1$ and λ$_2$ are almost the same for a given

catalyst, and the two values of x are close to each other. These observations, together with the values of the ratio k_1/k_2 are consistent with the fact that on Pt two different intermediates are formed while, on Pt–Mo, butane adsorbs as only one intermediate species which leads to the splitting either of an external or of an internal C–C bond.

Now one can consider that on the Pt–Mo catalysts the values of λ, on the one hand, and those of x, on the other are about the same (5.6 + 2.7 for λ and 3 ± 1 for x) taking into account that the margin of error is large. Once again PMD$_{12}$ is particular and is intermediate between Pt and Pt–Mo, but it is much closer to the other Pt–Mo than to Pt alone.

All these results confirm that on Pt–Mo catalysts an intermediate adsorbed species is formed which has exactly the same properties for all the bimetallic catalysts (same values for λ, x, and k_1/k_2). This intermediate is probably adsorbed on an active mixed site Pt–Mo which has the same composition for all bimetallic catalysts whatever their composition.

Now, if on Pt–Mo catalysts, butane is adsorbed on the same active site, the values

TABLE 4

Kinetic Parameters According to Eq. (9) in the Hydrogenolysis of Butane
on Pt–Mo Catalysts (T = 300°C)

Catalysts	Mo/(Mo + Pt) (%)	Reaction	k (10^{-3} mol/h · g · atm)	k_1/k_2	λ(atm.$^{x-1}$)	x	X^2
PMD$_0$	0	(1)	0.48		67.5	1.7	5.8
				3			
		(2)	0.16		37.5	4.7	15
PMD$_{12}$	13	(1)	7.0		6.6	4.0	4.2
				1.23			
		(2)	5.7		6.2	3.8	7.7
PMD$_{25}$	24.5	(1)	21.3		4.9	2.5	36
				1.51			
		(2)	14.1		4.7	3.1	39
PMD$_{37}$	36.7	(1)	18.3		3.4	2.85	30
				1.49			
		(2)	12.3		3.1	2.7	24
PMD$_{50}$	49.1	(1)	13.8		4.6	2.9	40
				1.57			
		(2)	8.8		4.2	2.8	18
PMD$_{75}$	72.5	(1)	1.2		8	3.0	10
				1.5			
		(2)	0.8		8.3	3.1	7
PMD$_{87}$	80.5	(1)	1.5		3.5	3.0	12
				1.74			
		(2)	0.86		2.9	3.0	14

of k_1 and k_2 reflect the variations of the number of these active sites per gram of catalyst.

TABLE 5

Hydrogen Chemisorption (HC) and Values of the Rate Constants of the Hydrogenolysis of the Terminal C–C Bonds (k_1) and of the Middle C–C Bond (k_2) of Butane Expressed in Molecules of Butane Transformed per Hydrogen Atom Adsorption Site

Catalyst	HC[a] (10^{-6} mol H$_2$/g cat.)	k_1	k_2
		molec./h · H$_{atom\ adsorbed}$ · atm	
PMD$_0$	44.5	5.4	1.8
PMD$_{12}$	38.7	90.4	73.6
PMD$_{25}$	15.4	691	458
PMD$_{37}$	8.8	1040	699
PMD$_{50}$	6.7	1030	657
PMD$_{75}$	1.0	600	400
PMD$_{87}$	0.8	938	537
PMD$_{100}$	0	—	—

[a] HC = Number of moles of dihydrogen chemisorbed on 1 g of catalyst at room temperature.

In Table 5 we have calculated the values of k_1 and k_2 per hydrogen adsorption site. The changes of k_1 and k_2 are very similar to those of the activity per H atom adsorbed on the catalyst that have been recalled in the Introduction of this paper. k_1 and k_2 increase up to PMD$_{37}$ and then they are approximately constant and equal to about 1000 and 630 h^{-1} · atm^{-1}, respectively. For PMD$_{75}$, k_1 and k_2 are lower than these values, but it has to be noted that these values are associated with higher values of λ_1 and λ_2 than for the other catalysts (Table 4). Probably in that case k_1 and k_2 have been underestimated, while λ_1 and λ_2 have been overestimated.

CONCLUSION

The kinetic study of the hydrogenolysis of butane has shown that the kinetic law is strongly modified when molybdenum is added to platinum, but this law can be considered similar for all Pt–Mo (except for

PMD_{12} which behaves like a mixture of Pt and Pt–Mo); no noticeable change in the kinetics could be observed when going through the maximum of activity.

On Pt alone butane is adsorbed as two different intermediates in which one C–C bond will be broken further with different selectivities. The values of λ_1 and λ_2 which are related to the equilibrium constants of adsorption of the hydrocarbon are high; on the contrary, the rate constants of the steps of C–C bond-breaking are low. The addition of molybdenum to platinum leads to an important decrease of λ_1 and λ_2 and for a bimetallic catalyst of a given composition the intermediate adsorbed species which leads to the splitting of a terminal C–C bond has the same values of λ and x (related to the degree of dehydrogenation of the intermediate species and to the size of the adsorption site) than that which leads to the splitting of the internal C–C bond. Hence probably on Pt–Mo bimetallic catalysts, only one single intermediate species is formed which leads to the hydrogenolysis of butane into methane and propane on the one hand or to ethane on the other hand. This intermediate seems to be less strongly adsorbed on Pt–Mo (lower λ values) than on Pt, but it is much more reactive (higher k values).

For all the bimetallic Pt–Mo catalysts, the similar values of λ_x, x_x, and of the ratios k_1/k_2 of the rate constants of the two different kinds of C–C bond-breakings suggest that the intermediate adsorbed species is the same for all Pt–Mo whatever their composition. This is probably due to the fact that these intermediates are adsorbed on the same active sites with the same composition for all Pt–Mo. The number of these active sites, reflected by the values of the rate constants k_1 and k_2, is maximum for a value of the ratio Mo/(Mo + Pt) between 25 and 30%. These active sites are obviously mixed sites composed of Pt and Mo atoms. At low Mo contents, all surface Pt atoms which are able to adsorb hydrogen cannot be included in such mixed sites and the

number of these sites increases with Mo/Pt ratios (this is shown by the changes of k_1 and k_2 calculated per H adsorbed). Then at higher Mo contents (starting from the maximum of activity), all the surface Pt atoms are in mixed sites (Mo is in excess) which explains why the rate constants per H adsorbed are constant for Mo/(Mo + Pt) higher than 30% and why the activity decreases with Mo content.

REFERENCES

1. Sinfelt, J. H., and Yates, D. J. C., *J. Catal.* **8**, 82 (1967).
2. Maire, G., and Gault, F. G., *Bull. Soc. Chim. Fr.*, 894 (1967).
3. Matsumoto, H., Saito, Y., and Yoneda, Y., *J. Catal.* **22**, 182 (1971).
4. Maurel, R., and Leclercq, G., *Bull. Soc. Chim. Fr.*, 1234 (1971).
5. Guczi, L., Gudkov, B. S., and Tétényi, P., *J. Catal.* **24**, 187 (1972).
6. Boudart, M., and Ptak, L. D., *J. Catal.* **16**, 90 (1970).
7. Kempling, J. C., and Anderson, R. B., *Ind. Eng. Chem. Process Des. Dev.* **11**, 146 (1972).
8. Dowie, R. S., Whan, D. A., and Kemball, C., *J. Chem. Soc. Faraday Trans. 1* **68**, 2150 (1972).
9. Plunkett, T. J., and Clarke, J. K. A., *J. Chem. Soc. Faraday Trans. 1* **68**, 600 (1972).
10. Paál, Z., and Tétényi, P., *Nature (London)* **267**, 234 (1977).
11. Machiels, C. J., and Anderson, R. B., *J. Catal.* **58**, 253, 260, and 268 (1979).
12. Leclercq, G., Leclercq, L., and Maurel, R., *Bull. Soc. Chim. Fr.* **11**, 2329 (1974).
13. Bond, G. C., and Xu, Yide, *J. Chem. Soc. Faraday Trans. 1* **80**, 769 and 3103 (1984).
14. Haining, I. H. B., Kemball, C., and Whan, D. A., *J. Chem. Res. (S)N* **7**, 170 (1977); *J. Chem. Res. (R)* **7**, 2056 (1977).
15. Bétizeau, C., Leclercq, G., Maurel, R., Bolivar, C., Charcosset, H., Frety, R., and Tournayan, L., *J. Catal.* **45**, 179 (1976).
16. Leclercq, G., Charcosset, H., Maurel, R., Bétizeau, C., Bolivar, C., Frety, R., Jaunay, D., Mendez, H., and Tournayan, L., *Bull. Soc. Chim. Belg.* **88**, 577 (1979).
17. Leclercq, G., Romero, T., Pietrzyk, S., and Leclercq, L., in Actas Simposio Iberoamericano de Catalisis, U.L.A. Merida 1986. I.U.T. Merida Region Capital PDVSA. A Montes, Ed., 1986, p. 886.
18. Leclercq, G., Romero, T., Pietrzyk, S., Grimblot, J., and Leclercq, L., *J. Mol. Catal.* **25**, 196 (1988).
19. Bond, G. C., and Gelsthorpe, M. R., *J. Chem. Soc. Faraday Trans. 1* **85**, 3767 (1989).

20. Yermakov, Yu. I., Kuznetsov, B. V., and Ryndin, Yu. A., *J. Catal.* **42,** 73 (1976).

21. Tri, T. M., Candy, J. P., Gallezot, P., Massardier, J., Primet, M., Védrine, J. C., and Imelik, B., *J. Catal.* **79,** 396 (1983).

22. Maurel, R., and Barbier, J., *J. Chim. Phys.* **74,** 995 (1976).

23. Leclercq, G., Pietrzyk, S., Peyrovi, M., and Karroua, M., *Entropie* **113–114,** 88 (1983); *Int. Chem. Eng.* **27,** 218 (1987).

24. Cimino, A., Boudart, M., and Taylor, H. S., *J. Phys. Chem.* **58,** 796 (1954).

25. Sinfelt, J. H., *Catal. Rev.* **3,** 175 (1970).

26. Maurel, R., Leclercq, G., and Leclercq, L., *J. Catal.* **44,** 68 (1976).

27. Leclercq, G., Leclercq, L., and Maurel, R., *Bull. Soc. Chim. Belg.* **88,** 7, 599 (1979).

28. Leclercq, G., Leclercq, L., Bouleau, L. M., Pietrzyk, S., and Maurel, R., *J. Catal.* **88,** 8 (1984).

29. Benson, J. E., and Boudart, M., *J. Catal.* **24,** 482 (1972).

30. Leclercq, G., and Boudart, M., *J. Catal.* **71,** 121 (1981).

31. Leclercq, G., Leclercq, L., and Maurel, R., *J. Catal.* **50,** 87 (1977).

32. Hooke, R., and Jeeves, T. A., *J. Assoc. Comput. Math.* **8,** 212 (1961).

33. Marquardt, D. W., *J. Soc. Ind. Appl. Math.* **11,** 431 (1963).

34. Paál, Z., and Menon, P. G., *Catal. Rev.-Sci. Eng.* **25** (2), 229 (1983).

35. Paál, Z., Zimmer, H., Günter, J. R., Schlögl, R., and Muhler, M., *J. Catal.* **119,** 146 (1989).

36. Menon, P. G., and Froment, G. F., *J. Catal.* **59,** 138 (1979).

37. Menon, P. G., and Froment, G. F., *Appl. Catal.* **1,** 31 (1981).

38. Crucq, A., Degols, L., Lienard, G., and Frennet, A., *Acta chimica Academia Scientiarum Hungaricae* **III(4),** 547 (1982).