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Hydrogenolysis of *n*-Hexane on Al_2O_3-Supported Ir Catalysts of Various Treatments

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A high-dispersion 1 wt% Ir/Al_2O_3 with 1 wt% Cl as well as its counterparts with $<$0.2% Cl with or without sintering were tested in *n*-hexane reactions between 453 and 603 K. The Cl-containing catalyst was considerably less active in this temperature range, unfavorable for bifunctional reactions. Hydrogenolysis was the main reaction with selectivities up to 90%, along with minor amounts of nondegradative products. Single hydrogenolysis with some preference for splitting the molecule in the middle occurred at low temperatures. That was replaced gradually by multiple rupture at higher temperatures. Increasing the hydrogen pressure at 513 K led to higher hydrogenolysis selectivities up to 98%; at the same time, it suppressed somewhat multiple fragmentation. With less hydrogen present (at lower H_2 pressure or higher temperature), a "soft" transition from single to multiple rupture occurred. The multiplicity of rupture was most pronounced on the larger crystallites of the sintered sample, whereas a terminal rupture seemed to appear on the Cl-free high-dispersion sample. Whenever single hydrogenolysis prevailed, the fragment distribution showed a slight preference to propane formation. © 1999 Academic Press

Key Words: **Ir/Al_2O_3; hydrogenolysis; *n*-hexane; Cl in alumina.**

INTRODUCTION

Iridium is a rather active catalyst of alkane reactions (1, 2). Pt–Ir catalysts have also gained an importance in naphtha reforming (2). To understand the action of such catalysts, it is essential to study the catalytic properties of Ir alone or in comparison with those of Pt (1, 3–7). The hydrogenolysis activity of iridium is much higher than that of platinum (1, 4), although recent experiments (7, 8) have not confirmed the large rate differences reported to be several orders of magnitude (1, 4). Correspondingly, the isomerization activity of Ir was, in turn, much lower than that of Pt (3). In spite of the pronounced hydrogenolysis on Ir, the complete rupture of the alkane molecules to methane was not observed: the fragmentation could result in two or just above two fragments per molecule split-up (9, 10). The main direction of splitting occurred in the middle position, to give $2C_3$ on Ir black (11) (at 453 K), whereas an almost random rupture with some preference for terminal splitting was reported at 400 K on Ir black prepared from IrO_2 (4). The ability of Ir to produce skeletal isomers and C_5 cyclics from alkane feed has been reported several times (1, 2, 6–8, 10–13).

Calcination of supported Ir catalysts seems to be a crucial step in determining its further dispersion and morphology (4, 14, 15). Heating in air facilitated the formation of large IrO_2 crystallites, the reduction of which could result in Ir metal of low dispersion (4). In the presence of Pt, highly dispersed Pt–Ir clusters also appeared. The Cl content of the support may have been critical for sintering: Huang *et al.* reported that IrO_2 agglomeration did not occur above a critical Cl content (15). The formation of large iridium oxide crystallites as a precursor of the reduced metal was regarded to be important to bring about "Ir-like" behavior (8).

Several studies have been published using appropriate model reactions, such as skeletal reactions of *n*-hexane (*n*H) for the characterization of the activity and selectivity pattern of various catalysts. These studies included Pt (16–18), Pt–Sn (18, 19), and Pt–Ir (20) catalysts. Whereas a "skeletal" reaction, such as hydrogenolytic opening of the cyclopentane ring, showed a marked structure sensitivity on Pt, it was found to be structure-insensitive on Ir (7). With respect to the possible importance of high-temperature calcination and the role of Cl in determining the final dispersion, it seemed worth investigating the catalytic propensity of Ir/Al_2O_3 catalysts of various Cl contents and dispersions. These results are to be reported here. We found (20) that Ir could catalyze the isomerization of *n*-hexane, varied from an earlier report (21) where isomerization was found with methylpentane reactants only.

METHODS

Catalyst **BS100** was prepared by wet impregnation of a Degussa Al_2O_3 (aluminium oxide C, δ-alumina, BET surface area, 95 m^2/g, pore volume, 0.7 cm^3/g, no micropores)

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by $H_2IrCl_6 \cdot nH_2O$ (Johnson Matthey) to give an Ir content of 1.0%. After drying at 393 K for 12 h, it was reduced in H_2 flow for 2 h at 473 K and subsequently for 2 h at 673 K (Dispersion: 48%, Ir, 1 wt%, Cl, 1.1 wt%, atomic ratio Cl/Ir ~ 6).

Catalyst **BS131** was also prepared from sample **BS100** in an Ar flow containing 2% water and 1% H_2 at 773 K for 20 h (Dispersion: 40% (no sintering) but loss of Cl (less than 0.2 wt%, atomic ratio Cl/Ir ~ 1.))

Catalyst **BS105** was obtained by treating sample **BS100** in an Ar flow containing 2% water at 773 K for 20 h (Dispersion: 10% (sintering) and loss of Cl (less than 0.2 wt%, atomic ratio Cl/Ir ~ 1)).

Catalytic measurements were carried out in a closed-loop reactor setup described earlier (16, 18, 19). n-Hexane (nH, Merck, GC grade) was used as model substance at a pressure of 1.33 kPa with mixtures with hydrogen (8–64 kPa). The temperature varied between 453 and 603 K. More detailed investigations were carried out at 513 and 603 K. The amount of catalyst was selected in a way that they should contain approximately the same number of exposed metal atoms, namely, $3.2\text{–}3.4 \times 10^{17}$ $Ir_{surf.}$. This way, 23 mg of **BS100**, 27 mg of **BS105**, and 102 mg of **BS131** were used. Samples were taken after 5 min of reaction time and analyzed by gas chromatography (16, 18). The catalysts were regenerated by an oxygen–hydrogen treatment at reaction temperature (16, 18). Conversions and selectivities were calculated on the basis of moles of nH reacted rather than considering the product moles formed. The hydrogenolysis reaction was characterized by (a) the ζ "fragmentation factor," meaning the average number of fragments per molecules fragmented (9, 13), and (b) the M_f "fission parameter," relating the amount of larger fragments to that of methane (22). The parameter ζ permits us to differentiate between "single" ($\zeta \approx 2$) and "multiple" ($\zeta > 2$) fragmentation, whereas M_f distinguishes "terminal" ($M_f = 1$), "random or internal" ($M_f > 1$), and "multiple" ($M_f < 1$) hydrogenolysis. Whenever hydrogenolysis was close to single rupture, the ω "reactivity factor" (23) could also be used with some caution: it was calculated from the abundance of C_3–C_5 fragments, disregarding multiple rupture.

RESULTS

Temperature Dependence

The conversion values were ca. 1% at 453 K, increasing to above 5% at 603 K (Table 1). These corresponded to turnover frequency (TOF) values of 10–190. The lowest TOF values were obtained on the sample **BS100**. The other two samples, **BS105** and **BS131**, showed higher values, by about 30–40%, being rather close to each other.

Table 1 also shows selectivity values. Hydrogenolysis always predominated, its selectivity being close to 90% in most cases. Of nondegradative products, the selectivity of

TABLE 1

Selectivities of n-Hexane Reactions on Various Ir Catalysts as a Function of Temperature

T (K)	Conv. (%)	Selectivity (%)					TOF (h^{-1})
		$<C_6$	Isomers	MCP	Benzene	Hexenes	
				(A) Catalyst **BS100**			
453	0.40	~70		Sum C_6: ~30[a]			11
483	1.06	81.8	6.7	9.4	2.1	0	29
513	1.80	84.1	5.5	6.2	4.2	0	49
543	2.35	86.1	3.1	4.8	5.7	0.3	64
573	3.90	87.0	1.8	3.0	7.7	0.5	106
603	4.87	89.3	1.0	1.7	6.7	1.3	133
				(B) Catalyst **BS131**			
453	1.17	88.1	4.6	7.3	0	0	34
483	1.85	87.8	5.8	5.1	1.3	0	54
513	2.10	86.9	4.7	5.1	3.3	0	62
543	3.45	87.8	3.3	3.3	5.5	0.1	102
573	4.70	88.2	1.8	2.4	7.3	0.3	139
				(C) Catalyst **BS105**			
453	1.10	87.5	4.3	8.2	0	0	31
483	1.90	90.1	4.1	5.0	0.8	0	53
513	2.80	90.0	3.6	3.9	2.4	0	78
543	3.70	90.0	2.8	3.2	3.9	0.1	106
573	4.75	89.6	1.7	2.7	5.7	0.3	126
603	6.85	89.2	1.4	1.8	6.7	0.9	191

Note. $p(nC_6) = 1.33$ kPa, $p(H_2) = 16$ kPa; sampling time, 5 min.

[a] Uncertain results due to product separation problems in the C_6 range.

skeletal isomers and methylcyclopentane (MCP) decreased and that of benzene increased at higher temperature. The three samples showed no conspicuous differences. Benzene appeared at lower temperatures than that reported for an Ir film (24) (<500 vs 600 K); this film, in turn, showed no isomerization activity.

Figure 1 illustrates that although the hydrogenolysis selectivity was almost constant, the fragment distribution showed conspicuous changes as a function of the reaction temperature. Hydrogenolysis was almost random at 453 K. Higher temperatures increased gradually the amount of methane until it reached about 90% of all fragments. This reaction showed somewhat more marked differences on various samples: catalyst **BS131** produced the lowest amount of methane and the abundance of ethane was not too low, even at 603 K.

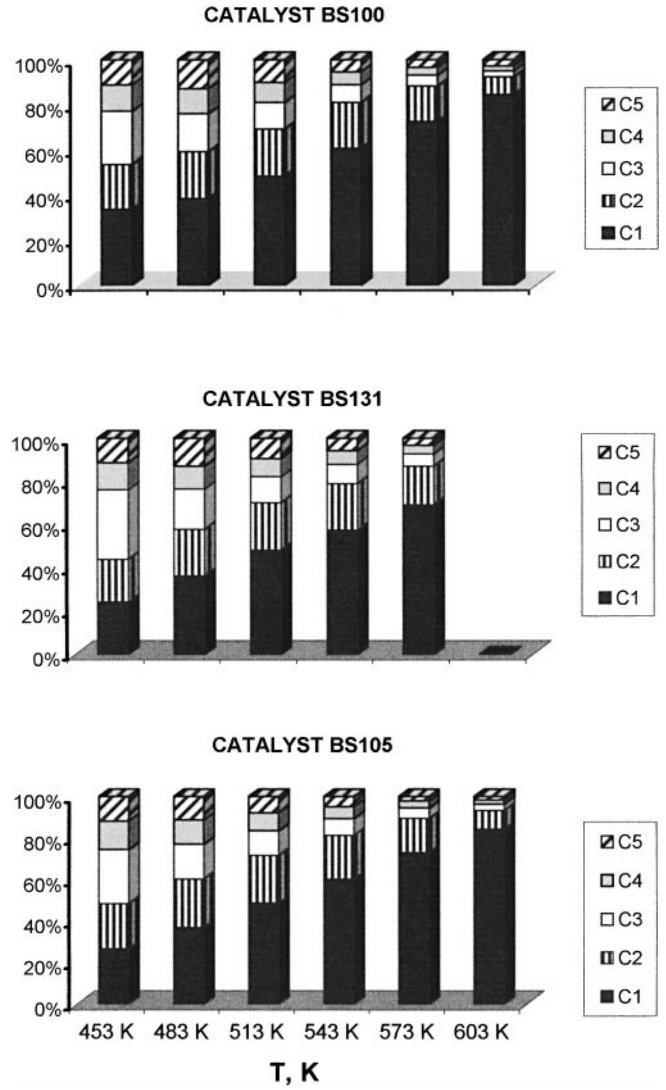

FIG. 1. Fragment distribution as a function of temperature, normalized to Σ (fragments) = 100%; $p(nC_6) = 1.33$ kPa, $p(H_2) = 16$ kPa; sampling time, 5 min.

TABLE 2

Characteristics of *n*-Hexane Hydrogenolysis on Ir Catalysts as a Function of Temperature

	Characteristic value				
T (K)	ζ	M_f	ω_1	ω_2	ω_3
		(A) Catalyst **BS100**			
453	2.43	6.22	0.72	0.75	1.53
483	2.52	4.40	0.94	0.82	1.24
513	2.85	3.02	0.98	0.86	1.16[a]
543	3.44	2.00			
573	4.02	1.21			
603	5.96	0.55			
		(B) Catalyst **BS131**			
453	2.25	8.80	0.69	0.80	1.52
483	2.48	4.88	0.84	0.89	1.27
513	2.88	3.14	0.83	0.93	1.24[a]
543	3.31	2.30			
573	3.90	1.45			
		(C) Catalyst **BS105**			
453	2.29	7.73	0.62	0.68	1.72
483	2.53	4.83	0.92	0.75	1.33
513	2.94	3.14	0.94	0.85	1.22[a]
543	3.46	2.07			
573	4.08	1.23			
603	4.70	0.60			

Note. Reaction conditions: $p(nC_6) = 1.33$ kPa, $p(H_2) = 16$ kPa; sampling time, 5 min. The values of ω were calculated from the corresponding larger fragments, ω_1 from pentane, ω_2 from butane, and ω_3 from propane.

[a] Values for ω_1, ω_2, and ω_3 were equal to 0.84, 0.94, and 1.22, respectively, on Ir films at 510 K (24).

The tendency of low temperatures favoring single hydrogenolysis was confirmed by the specific parameters for hydrogenolysis (Table 2). At low temperatures the values of ζ were just slightly above 2, pointing to a prevailing single hydrogenolysis. The actual values of $\zeta > 2$ indicate the superposition of another, multiple hydrogenolysis to single rupture. The continuous increase of ζ (Table 2) shows that this multiple rupture took over at higher temperatures. This agrees well with results reported for an Ir film (24). The decreasing values of M_f below unity indicate the same trend: no terminal hydrogenolysis occurred. Values of the ω reactivity factor are given for the lowest temperatures, where ζ values were below 3; they show an enhanced rupture in the middle of the molecule giving two propane fragments. At 513 K, they are in rather good agreement with the hydrogenolysis pattern reported for an Ir film at 510 K (24). The differences between the reactivities of various C–C bonds decreased as multiple hydrogenolysis became more and more important.

Hydrogen Pressure Effects

Curves with a maximum have been found to be characteristic of yields of various products as a function of hydrogen pressure (16, 17, 25, 26). Earlier studies reporting negative

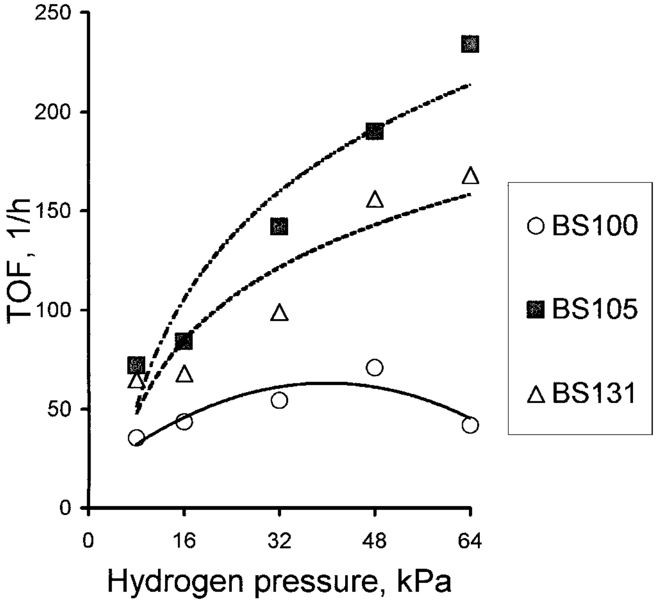

FIG. 2. Overall turnover frequency (TOF) values for three catalysts, as a function of hydrogen pressure, $p(H_2)$, at $T = 513$ K, $p(nC_6) = 1.33$ kPa; sampling time, 5 min.

hydrogen exponents (1, 2) may have been carried out in the hydrogen pressure range higher than that corresponding to the maximum rate. A maximum hydrogenolysis rate has been found on Ir black at around 573 K (10). Higher hydrogen pressures were found recently to promote *n*-hexane transformations with both Ir and Pt–Ir/Al_2O_3 catalysts between 513 and 603 K (20).

Figure 2 depicts TOF values as a function of the hydrogen pressure at 513 K. These were lowest with the "original" sample **BS100**, exhibiting a maximum. Catalyst **BS105** (sintered, less Cl) was, in turn, most active, while the high-dispersion sample **BS131** had an intermediate activity but was closer to **BS105**. The hydrogen pressure monotonically increased the intrinsic activity of these two latter catalysts.

Selectivity values are shown in Table 3 for all three catalysts at a selected temperature of 513 K where the conversion values were still rather low (2–8%). Even at this not too high temperature, 84–98% of *n*-hexane transformed into fragments. The overall reactions of *n*-hexane were similar for **BS105** and **BS131**, both increasing, as a rule, at higher hydrogen pressures. The maximum appeared also in hydrogenolysis selectivity on **BS100** parallel to the maximum in TOF. The selectivity of nondegradative reactions showed a different $p(H_2)$ response. Their amount was nearly constant on **BS100**—except for unsaturated products diminishing at higher $p(H_2)$—where Cl could, in principle, participate in the reactions. Higher hydrogen pressure suppressed *all* C_6 products in a rather uniform way on **BS105** and **BS131**, possessing only metallic centers.

The hydrogen pressure response of two parameters for hydrogenolysis, ζ and M_f, has been calculated for two reaction temperatures (Table 4). A basically different behavior is seen at these two temperatures.

At 513 K, the average number of fragments hardly exceeded the value of 2 (characteristic of single hydrogenolysis), agreeing well with M_f values much higher than unity, indicating random hydrogenolysis. Increasing the hydrogen pressure shifted the splitting toward single hydrogenolysis over all three samples. The random character of fragmentation (the value of M_f) also increased. It was possible to calculate also the ω reactivity factors for catalysts **BS100**. These values (Fig. 3) indicate a shift of the preferential position of bond rupture toward the middle C–C bond at higher hydrogen pressures. This was analogous to what was reported earlier for Pt black (27).

At 603 K, the ζ fragmentation factor indicated multiple hydrogenolysis. The hydrogen response of the samples was different. Increasing $p(H_2)$ *suppressed* multiple splitting on the sample **BS100** (containing Cl and having the highest dispersion), even at this higher temperature. The values of M_f showed more clearly the transition of multiple to (commencing) single rupture from the lower to the higher hydrogen pressure range. The fragmentation was more pronounced with **BS105** and **BS131** where increasing $p(H_2)$ *increased* its multiplicity. Splitting on **BS105** (large Ir crystallites, no Cl) gave almost entirely methane ($\zeta \approx 6$). The value of M_f being below unity confirmed the true multiple character.

TABLE 3

Selectivities of *n*-Hexane Reactions on Various Ir Catalysts as a Function of Hydrogen Pressure

$p(H_2)$ (kPa)	Conv. (%)	Selectivity (%) $<C_6$	Isomers	Benzene	Unsat. + MCP[a]
		(A) Catalyst **BS100**			
8	1.3	84.1	3.2	8.5	4.2
16	1.6	84.1	4.8	7.9	3.2
32	2.0	87.0	5.1	6.0	1.9
48	2.6	90.8	4.2	4.2	0.8
64	1.5	87.5	4.2	7.4	0.9
		(B) Catalyst **BS131**			
8	2.2	86.7	3.1	5.5	4.7
16	2.3	87.5	4.6	4.9	3.0
32	3.3	92.9	3.0	3.0	1.1
48	5.3	95.3	2.6	1.8	0.3
64	5.7	96.6	1.8	1.6	0
		(C) Catalyst **BS105**			
8	2.6	90.2	2.0	4.6	3.2
16	3.0	91.0	3.0	3.7	2.3
32	5.1	95.6	1.9	1.8	0.7
48	6.8	97.5	1.5	1.3	0.2
64	8.4	98.0	1.1	0.9	0

Note. Reaction conditions: $p(nC_6) = 1.33$ kPa, $T = 513$ K; sampling time, 5 min. No hexenes were observed.

[a] Including hexenes, methylcyclopentane, and methylcyclopentene, observed in some cases.

TABLE 4

Characteristics of *n*-Hexane Hydrogenolysis on Ir Catalysts as a Function of Hydrogen Pressure

	Characteristic value			
$p(H_2)$ (kPa)	ζ (513 K)	M_f (513 K)	ζ (603 K)	M_f (603 K)
		(A) Catalyst **BS100**		
8	3.2	1.8	5.0	0.35
16	2.9	2.5	4.6	0.6
32	2.7	3.5	4.2	0.9
48	2.6	4.0	3.9	1.4
64	2.7	3.6	3.8	1.6
		(B) Catalyst **BS131**		
8	3.2	2.3	4.4	0.8
16	2.9	3.2	4.4	1.0
32	2.8	3.8	4.5	1.1
48	2.7	4.9	4.9	0.85
64	2.7	5.4	5.0	0.8
		(C) Catalyst **BS105**		
8	3.6	2	4.8	0.45
16	3.1	2.9	4.7	0.65
32	3.0	3.6	4.8	0.7
48	2.9	4.2	5.7	0.2
64	2.9	4.4	5.7	0.2

Note. Reaction conditions: $p(nC_6) = 1.33$ kPa, $T = 513$ K; sampling time, 5 min.

DISCUSSION

The reactions on alumina-supported Ir catalysts were reported to take place in a bifunctional way (2, 12). The presence of Cl may be important for facilitating the creation of acid sites (5), apart from its reported role in controlling oxidation and sintering of Ir (15). The customary preparation of unsupported (5, 9, 10) and supported Ir catalysts (5–7, 12, 15) used its Cl-containing salt, except for its reduction from IrO_2 (4) or the vacuum-deposited film. Acidification of the alumina support of Ir by HCl enhanced the bifunctional character (5). However, bifunctional reactions would start at higher temperatures than those used here (5, 6) and the oxidative treatment also required higher temperatures to induce sintering (14) than that applied during regeneration. The isomer selectivity in bifunctional isomerization at 650 K could reach values of ∼50% (5) as opposed to the few percent reported here (Tables 1 and 3). So we can assume that the reactions in our case could be attributed mainly to Ir metallic sites, in agreement with the reports of Gault *et al.* (3b, 28). *n*-Hexane contains no tertiary C atom; hence, the "iso-unit" mode of reaction (3a) cannot be valid here. Its ability to isomerize does not exclude the "1,3 bond shift" mechanism reported with methylpentanes (3b, 21) but it is clear now that this is not the only and exclusive method for skeletal alkane isomerization on Ir catalysts.

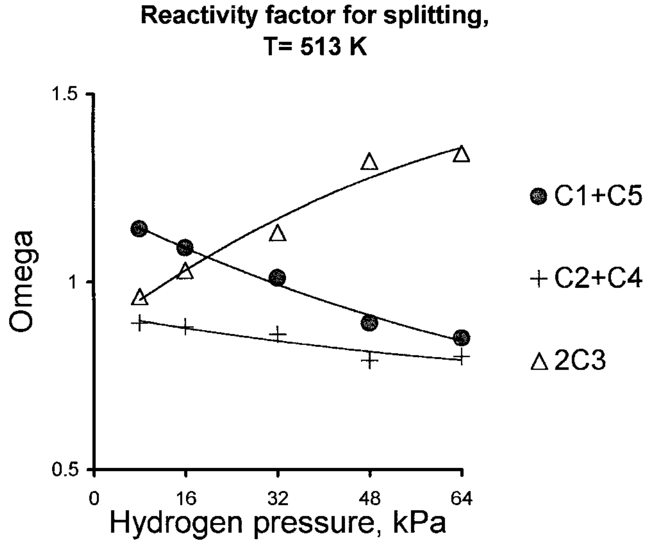

FIG. 3. "Reactivity factors," ω, for splitting *n*-hexane in different directions on catalyst **BS100**, as a function of hydrogen pressure, $p(H_2)$, at $T = 513$ K, $p(nC_6) = 1.33$ kPa; sampling time, 5 minutes.

The intrinsic activity of **BS100** was the lowest at each hydrogen pressure investigated (Fig. 2). The presence of Cl seemed to *hamper* the overall reaction. This effect was not very remarkable at low $p(H_2)$ but rather significant at the highest end of the hydrogen pressure range. The value of $TOF = 29\ h^{-1}$ at 483 K is not far from the $TOF = 6.5\ h^{-1}$ at 478 K reported on Rh/SiO_2 for ethane hydrogenolysis, which should be a more demanding reaction (2). Since hydrogenolysis was the main reaction on all catalysts, this means that more H_2 *accelerated* hydrogenolysis, at least at the selected temperature, 513 K, as opposed to the negative H exponent between 450 and 480 K (1, 2, 4). The differences in hydrogenolysis selectivities of various samples were minor (Table 1). More Cl also reportedly decreased hydrogenolysis selectivity of Pt (30)—an analogous phenomenon may have appeared with the catalyst **BS100**. The accumulation of Cl on the Ir–Al_2O_3 perimeter is not excluded here. Similar experiments with Pt/Al_2O_3 reported Pt–Cl–O entities in the presence of Cl, giving rise to Pt^{n+} ions at these sites and also influencing redispersion (29). The absence of Cl may have been the reason why the two catalysts **BS105** and **BS131** with low Cl content showed closer intrinsic activities and hydrogenolysis selectivities at each temperature and hydrogen pressure. The highest selectivity observed on the most active, sintered sample, **BS105**, is in agreement with the generally accepted mechanism of hydrogenolysis requiring ensembles of several metal atoms (2, 31). Its larger crystallites must have been favorable for multiple hydrogenolysis (highest ζ values, Table 4).

Activities as well as hydrogenolysis selectivity values increased monotonically at higher temperatures (Table 1). The slight decrease of hydrogenolysis selectivity at higher temperature (12) did not appear here. At the same time, increasing the hydrogen pressure had a similar but not very marked effect (Table 3). Increasing temperatures should have decreased the hydrogen coverage at constant H_2 pressure. The hydrogen coverage should have increased at higher $p(H_2)$ values. However, both increasing temperature and hydrogen pressure increased hydrogenolysis activity. A closer inspection of hydrogenolysis characteristics seems to resolve this apparent disagreement. The results indicate *two* more or less *independent* fragmentation processes superimposed on each other: *single* and *multiple* hydrogenolysis. The former is favored at higher hydrogen coverages: at lower temperatures (Fig. 1, Table 2) and higher hydrogen pressures (Table 4). As the amount of available surface hydrogen decreased, more and more molecules suffered a total disruption in addition to the less and less important single hydrogenolysis (Tables 2 and 4). The competition of the two processes is seen as a function of hydrogen pressure at 513 K, whereas single splitting is no more important at 603 K (Table 4). The continuous decrease of M_f values with the temperature indicates a "real" multiple rupture, i.e., the disruption of the reactant into several fragments during one sojourn on the surface rather than "slicing off" end methyl groups step by step. The value of M_f decreased from 17 to 8 from 450 to 550 K on Ir/Al_2O_3 (32). These values are somewhat higher than those reported here. With the continuous decrease of M_f from $\sim$8 to below 1 (Table 2), its value necessarily will reach and cross unity at a certain temperature. This, however, may be an intermediate stage rather than "true" terminal splitting. One possible interpretation of these results may be the increasing role of carbene-type intermediates of multiple rupture with increasing temperature, the formation of which reportedly has a high probability on Ir (3b, 28). This is in agreement with the decreasing steady-state hydrogen coverage at higher temperatures and also with increasing multiplicity at low $p(H_2)$ values (Tables 2 and 4).

The importance of the two types of hydrogenolysis was different with the three catalysts. The single-rupture character was preserved on **BS131** in the widest temperature range (Fig. 1, Table 2), where the values of ζ were closest to those observed on an Ir film (24). At 603 K, in turn, complete methanation was almost reached on the sintered **BS105**, its larger crystallites being favorable for multiple rupture: ζ approached 6 and the M_f values were lowest at almost each hydrogen pressure (Table 4). The position of single rupture was also different with the three samples. A rather even distribution of fragments was reported with Ir reduced from IrO_2 (4). This was approached at a higher reaction temperature (Table 2). With single rupture becoming more and more important, splitting in the middle of the molecule became favored (Table 2, Fig. 3), in agreement with the results obtained with *n*-hexane on Ir black (9), and Ir/SiO_2 (32). The internal splitting of *n*-pentane was also enhanced at higher H_2 excess (33). Terminal hydrogenolysis was attributed to "Pt–C" ensembles (34). Indeed, hydrogenolysis selectivities at the same conversion level on EUROPT-1 (6% Pt/SiO_2) were higher at 6-fold hydrogen excess, but the M_f values were as low as 2–3 as opposed to $M_f \sim 8$ at a 48-fold hydrogen excess (16). Some authors regarded the formation of "Ir–C" ensembles less likely (5, 6, 12). However, Sárkány attributed the isomerization ability of Ir to some adsorbed hydrocarbons also influencing the method of reactive adsorption of the alkane feed (33). Ponec (2, 12, 34) reported higher hydrogenolysis selectivity at the low- and the high-temperature ends of the temperature range. Such a marked temperature effect was not observed here.

To sum up, dispersion and Cl content strongly influence the activity of Ir/Al_2O_3 catalysts but the selectivity changes are not profound. The overwhelming hydrogenolysis arises by superposition of a "single" and a "multiple" rupture, higher temperatures and lower hydrogen pressures favoring the latter process.

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