Palladium-Catalyzed Hydrogenation of Soybean Oil

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ABSTRACT

The hydrogenation of soybean oil has been studied using charcoal-supported palladium catalysts at hydrogen pressures between ambient and 70 psig and at temperatures between 80 C and 160 C in three types of stirred reactor. The catalysts employed were 1-10% w/w Pd supported on charcoal and represented differing metal placement on the support. The structure of the catalysts was confirmed by metal surface area measurements, transmission electron microscopy (TEM) and electron spectroscopy for chemical analysis (ESCA). Comparative studies also were carried out under similar conditions using samples of commercial nickel catalysts. Palladium catalysts with the metal placed on the exterior of the charcoal support were the most active and selective at ambient pressure, and although palladium catalysts with metal placed within the charcoal pore system became the most active at higher hydrogen pressures, only the former type of catalyst retained high selectivity over the whole temperature and pressure range. Palladium catalysts gave rise to more trans-acids than nickel, particularly under conditions normally employed with the latter, but if diffusion limitation was avoided, especially at lower temperatures, palladium gave lower quantities of trans-acid than nickel. In addition, the selectivity of a well designed palladium catalyst was superior to that of nickel and its activity was 15-20 times greater. It is concluded that if palladium is deposited on the exterior of the charcoal so that it is accessible to the triglyceride molecules, then its selectivity and activity is superior to that of nickel, even at low temperatures, at which nickel is inactive. This underlines the importance of choosing the correct preparative route to give optimum metal placement, and it is suggested that when previous studies have indicated that palladium is unselective for fat hardening, it is likely that the metal was not dispersed on the exterior surface of the support. Furthermore, whereas nickel is best used under diffusion-controlled conditions because its selectivity is better in the latter situation palladium should be used under diffusion-free conditions, which implies that very careful attention should be paid to the reactor design.

TABLE I

Some Properties of the Charcoal^a-Supported Palladium Catalysts

Catalyst Pd/C-	Metal loading (% w/w)	Metal area m ² (g catalyst) ⁻¹			
1	1.12	3.3			
	3.31	9.6			
	5.10	19.3			
	10.65	35.9			
2	4.91	24.8			
3	4.97	25.4			
4	5.10	21.9			

^aCharcoal support: (i) Area = $871 \text{ m}^2\text{g}^{-1}$; (ii) N₂ pore = 0.75 cm³g⁻¹ volume; (iii) Mean pore = 1.7 mm diameter.

INTRODUCTION

As the demand for more sophisticated frying oils and margarines increases, so the demands on a catalyst in respect of selectivity become greater. An earlier review (1) reported that palladium catalysts were, on the whole, unsuitable for the hydrogenation of triglycerides because (a) they were unselective and (b) gave rise to large quantities of trans-acids in the product. Palladium is well known to be one of the most selective hydrogenation catalysts when multiple olefinic bonds are concerned, although its ability to catalyze cis-trans isomerization and double-bond migration is also superior to other Group VIII metals (2). Even so, the conditions under which it has been compared with nickel were most unfavorable, and only more recently have other workers investigated palladium catalysts more carefully and observed that they may possess some potential in the selective hydrogenation of triglycerides (3,4).

The behavior of a catalyst is a function of its preparation method, its subsequent chemical composition and structure, and the effect of these factors has been reported for nickel catalysts (5-8). It was thought, therefore, that one of the problems with previous studies using palladium has been lack of consideration of the method of preparation



FIG. 1. Rate vs. catalyst weight plots for 5% Pd/C catalysts. Stiπing speed = 1000 rpm; soybean oil = 100 g; ● Pd/C-1; ◦ Pd/C-2; X—X Pd/C-3; ■ Pd/C-4.



(b)



FIG. 2. Electron micrographs of 5% Pd/C catalysts: (a) = Type 1; (b) = Type 2; (c) = Type 3; (d) = Type 4 (x 150,000) (x 135,000) (x 200,000) (x 250,000).

and its subsequent effect upon activity and selectivity.

Four types of charcoal-supported palladium catalysts were selected representing different distributions of metal on the support, since it was felt that this would be a most important factor in the hydrogenation of a molecule as bulky as a triglyceride.

Soybean oil was chosen as the reactant because: (a) its importance relative to other vegetable and marine oils is growing; (b) its composition is relatively constant and well defined, and it is available relatively free from severe contamination; and (c) it represents a challenging problem in selective hydrogenation.

MATERIALS AND METHODS

Bleached and deodorized soybean oil was kindly supplied by Procter and Gamble Limited, and it was stored in a cold room (≤ 10 C) and purged from time to time with nitrogen.

The charcoal-supported palladium catalysts were kindly supplied by Johnson, Matthey and Co., and some of their physical properties are given in Table I. The nomenclature employed for these catalysts is identical to that used by Acres et al. (9). Three commercial nickel catalysts were provided by Procter and Gamble for comparison and were respectively Ni/PG (20% w/w Ni), Ni/Harshaw (25% w/w Ni) and Ni/Harshaw DM3 (25% w/w Ni).

Hydrogen and nitrogen gases were of high purity grade (>99.99% v/v), supplied by BOC Limited or Air Products Limited.

Product analyses were carried out by converting the triglycerides to their fatty acids for trans-acid determination by infrared spectrophotometry (Perkin-Elmer Model 157), and to their methyl esters for gas liquid chromatography. The latter was effected using a Pye Series 104 dual f.i.d. model, fitted with 6 ft. x ¼ in. o.d. columns packed with 20% w/w diethyleneglycol succinate supported on 80/100 mesh Universal E packing; the columns were operated at 180 C, with an injection port temperature of about 300 C, using a carrier gas flow rate of 60 ml min⁻¹. The eluted peaks were recorded by means of a potentiometric recorder connected in parallel with a Spectra-Physics 6300 Autolab Digital Integrator, which provided direct readings of peak areas.

The methods of converting the triglycerides to their fatty acids and methyl esters were kindly provided by Procter and Gamble, along with the infrared technique for trans-acid determination, and were examples of well established methods reported in the literature.

Reactions were carried out in three types of reactor. Studies at ambient pressures were performed in a glass reactor made from a standard 250 ml conical flask, modified by the addition of (a) inlaid baffles; (b) a side-arm for gas inlet; and (c) a B50 ground glass male joint at the neck.

The latter received a mercury-sealed stirrer unit based upon a B50 female joint, fitted with a side arm for gas purging; the stirrer was driven by means of a variable speed (0-2000 rpm) electric motor.

Reactions at pressures greater than ambient were performed either in a 21. mild steel vessel constructed in this Department, fitted with a variable speed-sealed stirring unit or in a Baskerville 500 ml magnetically stirred autoclave. All the reactors were connected to an Engelhard Hydrogenation Control Unit, which was capable of feeding hydrogen at predetermined pressures between 0 and 100 psig to the reactor. Hydrogen consumption was recorded as a function of time on a potentiometric recorder. The large reactors were heated externally by electrical windings, but the smaller glass reactors were heated by partial immersion in an oil thermostat bath capable of giving temperatures up to 200 C. The oil charges to the three reactors were respectively 100 g (small glass), 300 g (Baskerville) and 200 g (large mild steel). To avoid oxidation the soybean oil was purged with nitrogen prior to filling the system with hydrogen and applying heat.

Reactions were carried out, where possible, under conditions where reaction rate was independent of stirring speed and directly proportional to catalyst weight. Under these conditions it is expected that diffusion limitation due to mass transfer of hydrogen from the gas phase to the bulk liquid will be eliminated. However, the Baskerville Autoclave provided most difficulty in this respect as it contained no baffling and was fitted with a simple paddle stirrer only. If a catalyst is sufficiently active, diffusion limitation can occur due to hydrogen mass transfer resistance from the bulk liquid to the catalyst surface, and in this case reaction rate is still directly proportional to catalyst weight. Absence or otherwise of this form of diffusion limitation can be verified by calculation (10), and this is commented upon later.

Solids' content index (SCI) and iodine value (IV) measurements were carried out on our samples by Procter and Gamble, and ESCA and TEM Studies were carried out on the palladium catalysts by Johnson, Matthey and Co.

All plots involving catalyst weight in this paper are based upon catalyst weighed into the reactor. The amount of metal involved can be determined from the information given earlier in this section and in Table I.

RESULTS AND DISCUSSION

Catalyst Activity

The activity of four 5% w/w Pd/C catalysts was measured as a function of catalyst weight at two temperatures (Fig. 1). The most active catalyst was Pd/C-1, which has the lowest surface area, and this will be commented upon further in connection with the TEM and ESCA results. The limiting rates, ca. 950 cm³H₃ (STP) min⁻¹ at 160 C and 650 cm³H₂ (STP) min⁻¹ at 120 C, are due to the onset of hydrogen mass transfer limitation through the gas liquid interface. The same limiting rate is expected for each catalyst at a given temperature and will be lower at 120 C first because the soybean oil will possess a greater viscosity and surface tension at the lower temperature. Second, hydrogen solubility measurements on a number of oils (11-13) have shown that solubility increases with increasing temperature.

At 160 C, two catalysts, namely Pd/C-3 and Pd/C-4 gave an intermediate region in the rate vs. catalyst weight plot and at 120 C Pd/C-2, -3 and -4 gave the intermediate region (Fig. 1). Calculations based on methods reported by Satterfield (13), using hydrogen solubilities and diffusivities determined by Andersson et al. (11) for cottonseed oil and



FIG. 3. (a) Rate vs. Pd_{3d} electron count for Type 1 Pd/C catalysts; (b) metal surface area vs. Pd_{3d} electron count for Type 1 Pd/C catalysts.

assuming first order kinetics, indicated that the reaction rate could well be limited by hydrogen diffusion from bulk liquid to the catalyst surface; it is unlikely that hydrogen solubilities and diffusivities will differ particularly for cottonseed and soybean oil. Catalyst Pd/C-1 did not exhibit the above intermediate behavior even at 80 C, and this can be readily understood by reference to the electron micrographs (Fig. 2(a), (b) (c) and (d)), which show very clearly that the metal is placed increasingly inside the catalyst particles in the order Pd/C-1 \leq Pd/C-2 \leq Pd/C-3 \cong Pd/C-4. In fact for Pd/C-1, the metal is clearly placed on the exterior surface of the support. For the other catalysts, the hydrogen will face longer diffusion paths to gan access to the metal sites, and the effect will be more obvious at the lower reaction temperatures. Hence, Pd/C-1 is predictably the best catalyst for this reaction on grounds of activity, and this superiority is not only confined to triglyceride hydrogenation.

ESCA studies further confirm these ideas, and Fig. 3(a) shows the rate of reaction for the hydrogenation of (a) soybean oil; (b) nitrobenzene in methanol (6% v/v) at 30 C; and (c) oleic acid in methanol (6% v/v) at 30 C as a function of the electron count for the Pd_{3d} peak for Pd/C-1 catalysts containing 1,3,5 and 10% w/w Pd. This technique allows surface composition and chemical state to be determined and analyzes 10-12 atomic layers. For soybean oil, the activity is a linear function of electron count, and an extrapolated rate value of ca. 50 cm³ H₂ (STP) min⁻¹ at



(a)

(b)



FIG. 4. Electron micrographs for Type 1 Pd/C catalysts (magnification = x 200,000): (a) = 1% w/w Pd; (b) = 3% w/w Pd; (c) = 5% w/w Pd; (d) = 10% w/w Pd.

zero count is possible, since metal just inside a pore mouth might be undetectable, yet available to the triglycerides. The observation that the other two reactions gave zero or relatively low rates at significant electron counts is probably due to the low temperatues at which these reactions were studied (30 C). Poisoning effects will be much more marked at such a temperature because the difference in free energy of adsorption between poisons and reactants will be greater. The decrease in activity of 10% w/w Pd/C-1 for nitrobenzene hydrogenation is undoubtedly due to overloading of the support with metal, causing agglomeration of metal particles and blocking of active sites inside pore mouths. This will not be apparent with the larger triglycerides as they cannot pack as easily on the metal surface and cannot, therefore, adsorb on as many sites around and just inside pore mouths as nitrobenzene. Figure 3(b) lends support to these ideas, as although 10% w/w Pd/C-1 has a surface area 1.9 times larger than 5% w/w Pd/C-1, its

electron count is only 1.2 times larger. The strongest evidence is provided by the electron micrographs of the four Pd/C-1 catalysts (Fig. 4(a), (b), (c) and (d)). The 1,3 and 5% catalysts have metal dispersed around the exterior of the particles and around pore mouths with little agglomeration. In the case of the 10% w/w catalyst, there are very evident signs of metal agglomeration and pore mouth blocking.

If catalyst activities are compared for the 5% Pd/C-1, -2, -3 and -4 catalysts (Fig. 5), the activity is related to the electron count and therefore to the amount of palladium on the exterior surface. However, the results do show that for soybean oil hydrogenation at 160 C, the increased mobility of the molecules has overcome, to some degree, the pore resistance of Pd/C-3.

Finally, the activity at 160 C of the most active nickel catalyst, Ni/Harshaw (DM3), was compared with the activity of Pd/C-1 at various temperatures (Fig. 6) and with



FIG. 5. Rate vs. Pd_{3d} electron count for 5% Pd/C catalysts for three different reactants.

all 5% Pd/C catalysts, in terms of rate per unit weight of metal (Table II). These results show all too clearly that a carefully designed palladium catalyst can be greatly superior to nickel in terms of activity. It is equally evident that the method of catalyst preparation can easily remove a good deal of that activity by placing the metal in inaccessible places on the support.

Catalyst Selectivity

Temperature effects. The selectivity of a catalyst for soybean oil hydrogenation is, unlike simpler reactions, impossible to define quantitatively by means of a single parameter which relates to a single desired product. In the case of soybean oil, an ideal catalyst would promote linolenate removal without catalyzing hydrogenation of linoleate and oleate. Since even the best catalysts are a compromise they should (a) not catalyze the formation of much stearate; (b) be more selective for linolenate removal than linoleate; and (c) not catalyze to any large extent the conversion of the naturally occurring cis-isomers to transisomers.

Table III provides a comparison of the product distributions obtained from four types of palladium catalyst at a number of temperatures. The Type 1 catalyst is by far the most selective, and that selectivity is maintained over a range of 80 C. It is also clear that *cis-trans* isomerization is markedly reduced at the lower temperatures, but this is true for all the catalysts and is probably more a function of the kinetics than of the catalyst structure.

It is expected that the catalyst with metal placed inside the support structure will give rise to more stearate, since a molecule inside a pore will be more likely to undergo multiple hydrogenation before regaining the bulk liquid phase. This is true of Types 2 and 4 but not Type 3, and it is concluded that the preparation chemistry and perhaps the metal dispersion (Type 3 is the most highly dispersed) may well have an influence on selectivity. However, no more detailed comment can be made since the catalysts are in commercial use.

The behavior of the Type 1 catalyst was further explored in a number of small-scale pilot plant trials in the laboratories of Procter and Gamble. These results are



FIG. 6. Rate vs. catalyst weight plot for 5% Pd/C-1 and Ni Harshaw DM3 at various temperatures.

presented in Table IV and confirm those obtained in our own laboratories. The selectivity of a Type 1 catalyst was maintained over the whole temperature range and was compared with Ni/Harshaw DM3 run under typical hardening conditions; unfortunately, information was not obtained regarding *trans*-acid levels, but it is significant that the SCI values are often lower than those for nickel.

The nickel catalysts did not show appreciable activity at temperatures <150 C, but low concentration ($\leq10\%$ w/w) nickel catalysts supported on silica and charcoal have been prepared recently in these laboratories and have displayed good activities at 120 C and 140 C. However, under diffusion-free conditions, the selectivity of the latter catalysts was lower than at 160 C, and this was manifested in greater stearate production (14).

It is concluded, therefore, that a significant factor in respect of the performance of Type 1 catalysts is the accessibility of the palladium on the support.

Effect of hydrogen pressure variation. Our studies with

TABLE II

RETAILIVE ACTIVITIES OF FAHAUTUHE AND INCLED CALARYST		Relative	Activities ^a	of	Palladiumb	and	Nickel	Cataly	/st	s
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	Rate of reaction (cm ³ H ₂ (STP)min ⁻¹ (mg metal) ⁻¹)					
Catalyst	160 C	120 C				
Pd/C-1	132	108				
Pd/C-2	100	50				
Pd/C-3	78	38				
Pd'/C-4	42	20				
Ni(DM3)	6					

^aLinear portion of rate vs. catalyst weight plot employed for comparison.

^b5% w/w Pd/C catalysts.

TABLE III

A Comparison of Product Composition for 5% w/w Pd/C Catalysts^a

Catalyst Pd/C-	Temp °C	Tomp Product composition					Solids'	content in	0%		
		P	S	0	L ₂	L ₃	50 F	70 F	92 F	Trans	IV
	160	10.9	4.0	49.3	33.9	1.9	5.8	1.2		30	105.6
1	100	10.6	4.9	47.3	35.2	2.0	2.3	0.25		14	106.5
-	80	10.4	5.2	51.6	30.9	1.9	5.04	1.41		13	102.6
	160	11.0	6.1	45.5	34.4	3.0	11.36	6.08	2.21	22	104.4
2	120	10.6	8.2	42.9	34.9	3.4	8.76	5.72	3.46	14	106.1
	160	10.7	4.4	48.1	33.9	3.0	8.86	3.07	0.67	28	104.7
3	120	10.6	5.2	39.3	41.0	3.9	3.50	1.71	1.14	19	113.7
	160	10.8	6.1	45.3	34.9	2.9	7.87	3.51	1.59	25	105.3
4	120	10.8	6.8	43.1	36.3	3.0	7.30	3.88	2.02	21	106.6
Soybean oil	-	10.5	3.9	23.2	53.4	9.0				4	135.2

aOil charge = 100 g; stirring speed = 1000 rpm; catalyst weight = 100 mg. P = Palmitite; S = Stearate; O = Oleate; L_2 = Linoleate; L_3 = Linolenate.

TABLE IV

Pilot Plant Trials for 5% Pd/C-1

Temp °C	Metal concentration		Product	composit	Solids' o					
	(% w/w)	P	S	0	L ₂	L ₃	50 F	70 F	92 F	IV
80	0.005	10.4	4.6	48.4	36.1	0.5	4.6	1.1		105.5
93	0.005	10.3	4.7	47.4	36.3	0.5	4.2	1.1		105.0
121	0.005	9.9	4.6	45.6	36.6	1.4	5.0	0.8		106.3
132	0.0025	10.6	4.8	46.1	37.2	1.1	6.3	1.5		107.0
132	0.005	10.1	3.8	47.5	35.7	1.8	5.9	1.5		107.3
132	0.01	10.6	3.9	50.2	34.6	0.6	8.0	2.3		104.7
160	0.005	10.5	4.0	45.1	34.8	1.3	8.3	2.2		105.9
160	0.01	10.5	4.0	49.9	34.2	1.3	9.5	2.6		105.2
171 ^a	0.04	10.6	5.3	51.6	30.6	1.7	7.5	2.7		102.9

a= Ni/Harshaw DM3.

some commercial nickel catalysts have indicated that the latter behave less selectively as hydrogen pressure increases (Table V). This was very evident for Ni/PG for which stearate increased and linolenate removal was suppressed; the trends for Ni/Harshaw were less marked for linolenate removal, but stearate production increased with increasing hydrogen pressure. These results appear to be at variance with some published recently for Ni/Harshaw DM3 (15), but it is suspected that the latter was used under diffusioncontrolled conditions, which are inherently more selective. Our own experience with the latter catalyst has indicated somewhat greater stearate levels in the absence of diffusion limitation (14). These ideas are further supported by the effect of increased hydrogen pressure upon trans-acid levels, which decreased with increasing pressure. No such effect was reported (15) in the results for Ni/Harshaw DM3, there being little effect on trans-acids and selectivity from either pressure or temperature changes.

5.3

10.0

106.3

Kinetic measurements in these laboratories have indicated the following relationships for nickel catalysts:

rate of hydrogenation
$$\propto p_{H_2}^1$$
 C_{soy} C¹ catalyst
rate of isomerization $\propto p_{H_2}^{1/2}$

Under surface-controlled conditions, it is expected that increasing the hydrogen pressure will depress *trans*-acid formation.

The behavior of Pd/C-1 was not straightforward, as indicated by Table VI. First, the selectivity is not impaired by increased hydrogen partial pressure either in respect of linolenate removal or stearate production. The situation in respect of *trans*-acid formation appears to be inconsistent but arises because of: (a) the very high activity of palla-

	Effect of I Composition	Increased for Soyb	Hydrog ean Oil	en Pressu Hydrogen	re upon l nation ove	Product er Nickel	a	
Catalyst	Hydrogen		Produc		0			
	(psig)	P	S	0	L ₂	L ₃	trans	IV
	10	10.0	4.1	52.7	28.6	4.6	18.5	106.8
	25	10.0	4.7	50.3	30.6	4.4	17.0	108.4
Ni(Harshaw)	40	10.0	5.1	48.7	34.0	2.9	14.0	108.4
,	55	10.0	6.1	51.3	29.6	2.9	13.0	103.0
	70	10.0	5.4	46.0	35.2	3.4	10.5	109.5
	10	10.0	5.5	53.9	26.7	3.9	20.0	102.8
	25	10.0	5.2	50.0	30.7	4.0	16.0	106.7
Ni(PG)	40	10.0	6.3	51.3	28.5	3.9	15.0	103.7
	55	10.0	7 1	54.6	22.6	5.7	13.0	101.0

TABLE V

^aTemp = 160 C; stirring speed = 1500 rpm; oil charge = 2000 g; catalyst charge = 1.5 g (Ni (Harshaw)); 2.25 g (Ni(PG)).

47.6

28.8

7.6

70

10.0

TABLE VI

Catalyst	Pressure	Temp	Product Composition					Solids	Conten	%		
	(psig)	(°C)	Р	S	0	L ₂	L3	50 F	70 F	92 F	Trans	IV
	10**		10.0	4.7	62.1	20.6	2.5				39.0	95.4
5% Pd/C-1	25**		10.0	4.1	53.8	30.7	1.3		NOT	38.0	103.9	
	55**	160	10.0	4.8	50.4	32.2	2.5	MEASURED			32.5	105.6
	70**		10.0	4.5	50.2	32.2	2.7				30.5	106.9
Soybean			10.0	3.5	20.5	59.5	6.5					137.7
5% Pd/C-1	0.1*	160	10.9	4.0	49.3	33.9	1.9	5.80	1.20		30	105.6
	30+	100	10.9	3.9	43.4	38.9	2.9	5.10	1.75		39	108.9
	0.1*		10.6	4.9	47.3	35.2	2.0	2.30	0.25		14	106.5
5% Pd/C-1	30+	100	11.0	4.0	41.6	40.3	3.1	2.15	0.43		31	112.2
	70+		11.1	4.1	42.0	40.2	2.6	1.87	0.49		29	111.4
	0.1*		10.5	4.4	47.7	35.0	2.4	3.26	0.52		17	105.9
10% Pd/C-1	30+	100	11.2	4.0	45.1	37.2	2.5	3.77	0.93		33	105.5
	70+		11.1	4.1	43.9	39.4	1.5	3.99	0.86		30	109.4
Soybean			10.5	3.9	23.2	53.4	9.0				4	135.2

Effect of Hydrogen Pressure upon Product Composition for Pd/C-1 Catalysts^a

a* = Stirred glass reactor; + = Baskerville autoclave; ** = 2 litre reactor.

dium; and (b) the characteristics of the different reactors employed. Thus, the studies carried out in the stirred glass reactor were probably just inside a surface-controlled region, those carried out in the 2 litre stirred vessel may well have been borderline between surface and diffusioncontrol, but those carried out in the Baskerville autoclave were almost certainly diffusion-controlled. The latter reactor was equipped only with a simple paddle stirrer and had no baffling. This would certainly account for: (a) the high trans-acid content at 100 C; and (b) the relatively small effect of increasing hydrogen pressure upon trans-acid levels at 160 C.

It is worth pointing out that the effect of increased pressure resulted in Pd/C-3 becoming more active than Pd/C-1 as would be expected, but the selectivity of the former becomes worse, mainly due to stearate levels being increased to 6-7% at an IV of ca. 105. Again this is hardly surprising if the triglycerides undergo multiple hydrogenations inside the catalyst pore system.

The results obtained clearly indicate the need for careful design of a supported palladium catalyst for the active. selective hydrogenation of soybean oil. The problem is further aggravated by the high activity of palladium, which means that reactor design is of equal importance, if diffusion limitation is to be avoided in the use of palladium. Detailed kinetic studies are required for palladium catalysts over a wide range of temperature, but it is clear that a well designed palladium catalyst is active and selective, and further studies are being carried out in respect of: (a) effect of poisons; (b) rerun capability; (c) improved catalyst design-, and (d) modification of activity and selectivity via alloying with other metals.

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