The Promotion of Raney Nickel Catalysts.

By Robert B. Blance and David T. Gibson.

[Reprint Order No. 5206.]

Delépine has shown that, in the hydrogenation of ketones, Raney nickel is promoted by treatment with chloroplatinic acid followed by sodium hydroxide. Lieber has shown that treatment with triethylamine and chloroplatinic acid is also effective. We find that a combination of the two techniques is better than either, and that lithium hydroxide can, with advantage, replace sodium hydroxide.

In addition to successive improvements (Adkins, *J. Amer. Chem. Soc.*, 1948, **70**, 695) in the preparation of Raney nickel catalysts it has been shown that for many reductions the catalyst is promoted by treatment with sodium hydroxide, chloroplatinic acid, triethylamine, etc. Delépine and Horeau (*Bull. Soc. chim.*, 1937, **4**, 31) found that Raney nickel platinised with chloroplatinic acid solution was substantially promoted for reduction of the carbonyl group, but not of double bonds, by treatment with a little aqueous sodium hydroxide. Lieber and Smith (*J. Amer. Chem. Soc.*, 1936, **58**, 1417) added to Raney nickel triethylamine followed by chloroplatinic acid solution. The sparingly soluble triethylamine chloroplatinate deposited platinum on the catalyst, so that the platinising is probably more uniform than by direct addition of chloroplatinic acid to the nickel suspension, for then the first particles to encounter the solution would be overplatinised and the remainder unplatinised. The possibility of uneven platinising is confirmed by Delépine and Horeau's observation (*loc. cit.*) that whereas Raney nickel dissolves completely in dilute acid, platinised Raney nickel always leaves a small nickel-containing residue. Heilman, Dubois, and Beregi (*Compt. rend.*, 1946, **223**, 737), using Raney nickel W1, reported the superiority of Delépine's method "sur un grand nombre d'autres composées à fonction carbonyle." We compared the two methods for the reduction of ketones by using Raney nickel W4, and we found that for aliphatic and alicyclic ketones Delépine's method was superior, but that with some aromatic ketones, Lieber's method was slightly better. Further, we found that in all

Table 1. *Time (minutes) for hydrogenation of ketones*

		Promotor for the Raney nickel catalyst.				
Ketone	None	NaOH	Et_3N	Pt + NaOH	Et_3N + Pt	Et_3N + Pt + NaOH
			Reaction at 1 atm.			
Dimethyl	39	24	31	21	25	16
Ethyl methyl	52	38	47	27	47	19
Methyl *n*-propyl	76	36	64	30	83	21
Methyl *n*-pentyl	77	57	83	33	93	25
*iso*Butyl methyl	78	53	—	35	126	27
Diethyl	80	—	—	37	221	27
n-Butyl ethyl	82	—	—	38	265	34
Di*iso*propyl	*i*	—	—	253	*x*	*i*
*cyclo*Hexanone	40	40	—	21	37	17
4-Methyl*cyclo*hexanone	60	45	—	23	36	20
2-Methyl*cyclo*hexanone	88	65	—	45	161	32
2 : 2-Dimethyl*cyclo*hexanone	93	70	—	49	167	32
2 : 2 : 6-Trimethyl*cyclo*hexanone	472	—	—	264	*i*	200
2 : 2 : 6 : 6-Tetramethyl*cyclo*hexanone	*i*	—	—	1600	—	1600
Camphor	580	—	—	329	—	153
Acetophenone	57	30	38	19	15	14
Propiophenone	90	55	65	34	24	24
Benzophenone	70	40	39	38	34	16
			Reaction at 3 atm.			
3-Methyl*cyclo*hexanone	24	—	—	11·5	15	9
4-Methyl*cyclo*hexanone	24	—	—	11	15	9
Fenchone	—	—	—	*i*	—	720

i = incomplete reaction; *x* = no absorption of hydrogen.

cases a combination of the two techniques, *i.e.*, platinising the catalyst by using triethylamine (Lieber), followed by addition of sodium hydroxide (Delepine), was superior to either. The rates of hydrogenation at 1 and at 3 atmospheres pressure were invariably increased, usually by as much as 20%. Table 1 shows that while Lieber's catalyst is fairly efficient for acetone and *cyclo*hexanone, its performance is considerably poorer for higher ketones. Sodium hydroxide, however, extends the range of efficiency and also retards the ageing of the catalyst.

The promoted catalyst (0·5 g.), ethanol (20 ml.), the ketone (10 mmoles), and 10N-sodium hydroxide (1—2 mmoles) were shaken with hydrogen at 200 double strokes per minute. The best results were obtained with a catalyst promoted by adding triethylamine (3·3 mmoles), chloroplatinic acid (0·04 mmoles) and finally 10N-sodium hydroxide (1·2 mmoles) to a rapidly stirred suspension of Raney nickel catalyst (0·5 g.). The catalyst was then washed three times with distilled water and three times with alcohol. Ketones and solvent were left overnight in contact with Raney nickel to remove poisons and were filtered and redistilled. The Raney nickel catalyst was prepared from Murex 50% nickel–aluminium Alloy (80 to dust) by Adkin's and Pavlic's method (*J. Amer. Chem. Soc.*, 1946, **68**, 1471) for Raney nickel catalyst W4.

Since Patterson and Degering (*J. Amer. Chem. Soc.*, 1951, **73**, 611) have reported poisoning of Raney nickel by chloride ion, we avoided the use of chloroplatinic acid by preparing the catalyst from a specially made aluminium–nickel alloy containing 2% of platinum. Table 2 shows that this catalyst is not only better than the unpromoted catalyst, but is at least as efficient and much easier to use than our promoted catalyst for the more difficult hydrogenations.

TABLE 2. *Times of hydrogenation of ketones with Raney nickel catalysts perpared from* Ni–Al *containing* 2% *of platinum.*

	Unpromoted	Promoted by NaOH		Unpromoted	Promoted by NaOH
Dimethyl ketone	41	23			
*cyclo*Hexanone	40	27	2 : 2′ : 6-Trimethyl*cyclo*hexanone	352	159
2-Methyl*cyclo*hexanone	54	28	(+)-Camphor	273	155

Since the completion of these experiments, Cornubert and Phélisse (*Bull. Soc. chim.*, 1952, **19**, 403) have confirmed that Raney nickel is poisoned by chloride ion, but showed that at a chlorine : catalyst ratio of 1 : 100 the effect is scarcely detectable. As we had used 1 mole of chloroplatinic acid per 500 moles of catalyst, it is evident that even if *none* of the liberated chloride had been removed in the subsequent washing, its effect on the catalyst would have been negligible.

The promoting effect of sodium hydroxide has been ascribed by Dupont and Piganiol (*ibid.*, 1939, **6**, 322) to localised adsorption of ketone on areas containing adsorbed sodium ions. Assuming that the hydrogen is adsorbed on areas free from sodium, they postulated that reaction takes place at the boundaries. While their view may account for the existence of an optimum amount of sodium hydroxide (which we found to be 0·4 mmole per g. of catalyst)(cf. Cornubert and Kaziz, *ibid.*, 1952, **19**, 410) it suggests that sodium hydroxide should, in the absence of an acceptor, diminish the amount of hydrogen taken up by Raney nickel. Actually, we found that addition of sodium hydroxide caused adsorption of an additional 5 ml. of hydrogen per g. of nickel. Our results are more in harmony with Bremner and Keey's views (*J.*, 1947, 1079) that the catalyst may be regarded as an electron donor or acceptor, and that addition of electropositive ions to it will tend to increase its electron-donor characteristics, so that alcohol will tend to be desorbed. The increased rate of hydrogenation of carbonyl compounds following the addition of alkali may therefore be due to an increase in the catalyst area made available by the more rapid desorption of the alcohol resulting from the reduction.

In a study of the catalytic reduction of ethylenes in solution in various alcohols, Schmidt (*Z. physikal. Chem.*, 1936, *A*, **176**, 254) considered that a measure of the relative affinities of the solvent and of the ethylene for the catalyst surface was given by the ratio of their heats of vaporisation. Thus, where the ratio was large, reaction was slow because of a preferential adsorption of solvent molecules on the surface, tending to prevent access of ethylene.

A similar correspondence was noted in the present work; the activity of the catalyst was enhanced by the presence of sodium hydroxide in cases where the heat of vaporisation of the product is substantially greater than that of the original ketone. This is confirmed by the results of Samuelson, Garik, and Smith (*J. Amer Chem. Soc.*, 1950, **72**, 3872) for the majority of simple nitro-compounds examined. On the other hand the ratio of the heats of vaporisation of *cyclo*hexene and *cyclo*hexane is nearly unity and addition of sodium hydroxide slightly retards reaction. Some of these results are collected in Table 3.

TABLE 3.

Substrate	Heat of vaporisation, kcal. mole^{-1}	Reduction product	Heat of vaporisation, kcal. mole^{-1}	Effect of NaOH
Acetone	7·26	2-Propanol	9·56	Promotes
Ethyl methyl ketone	7·59	2-Butanol	9·92	,,
*cyclo*Hexanone	9·50	*cyclo*Hexanol	10·70	,,
Nitrobenzene	7·94	Aniline	9·91	,,
*cyclo*Hexene	7·28	*cyclo*Hexane	7·34	Retards

Cornubert and Phélisse (*loc. cit.*) demonstrated elegantly the selective character of promotion by sodium hydroxide by showing that in its absence unsaturated ketones were rapidly and sharply converted into saturated ketones, and that thereafter the reduction could be continued to give the saturated alcohol by adding sodium hydroxide.

The similarity between the ionic radii of lithium and of nickel suggested that if promotion is due to adsorption of sodium ions lithium hydroxide might function better. The results in Table 4 show that lithium hydroxide is about 20% better than sodium hydroxide. Optimum results are obtained by using 0·6 mmole of lithium hydroxide per g. of Raney nickel.

TABLE 4. *Times for hydrogenation of ketones with Raney nickel and alkali.*

Ketone	Un-promoted	Promoted by NaOH	Promoted by LiOH	Ketone	Un-promoted	Promoted by NaOH	Promoted by LiOH
Dimethyl	39	31	25	Methyl *n*-propyl	70	41	34
Ethyl methyl	54	35	30	*n*-Butyl methyl	81	60	42

Potassium hydroxide was a less efficient promoter than sodium hydroxide for reduction of ethyl methyl ketone (1·17 : 1) and *n*-butyl methyl ketone (1·33 : 1).

The authors thank the Mond Nickel Co. for the loan of diffusion apparatus, Messrs. Murex for making special alloys containing platinum, Messrs. Glaxo for a gift of ketones, and Mr. Steele for assistance with the lithium hydroxide experiments.

UNIVERSITY OF GLASGOW.

[*Received, March* 12*th*, 1954.]