

Optimization of Decalin/Catalyst Ratio in the Dehydrogenation of Decalin over Pt/C Catalysts via Experiment Design

D. SEBASTIÁN, E. GARCÍA-BORDEJÉ, L. CALVILLO, M. J. LÁZARO and R. MOLINER

*Instituto de Carboquímica (C.S.I.C.),
Miguel de Luesma Castán 4, 50018 Zaragoza (Spain)*

E-mail: mlazaro@icb.csic.es

Abstract

We have supported platinum on a commercial activated carbon with different loadings. The as-prepared catalyst has been used for the dehydrogenation of decalin in a batch-type reactor under boiling and refluxing conditions. The impact of some variables such as temperature, % Pt loading and decalin/catalyst ratio was studied using experimental design tools. The experiments carried out enable us to find the decalin to catalyst ratio which led to the best catalytic performance in our system.

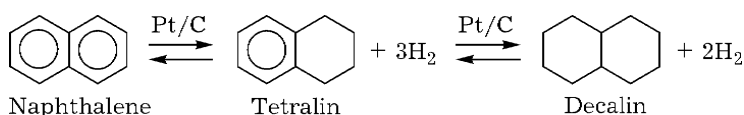
INTRODUCTION

The reversible dehydrogenation-hydrogenation of the so-called liquid “organic hydrides” is one potential system to store and transport hydrogen. Among these liquids decalin is receiving great attention during the last years due to the high hydrogen contents (7.3 mass %, 64.8 kg H₂/m³) satisfying the DOE target values on storage density (6.5 mass %, 62.0 kg H₂/m³). Furthermore, evaporation loss during storage is negligible because of the high boiling points, °C: 187 (*trans*-decalin), 196 (*cis*-decalin) and 218 (naphthalene).

Scheme 1 shows the reversible dehydrogenation of decalin. Because the dehydrogenation of cycloalkane is endothermic, the reactions are usually performed in gas phase at temperatures higher than 400 °C [1, 2]. This might result in the formation of carbonaceous deposits over the catalyst in addition to thermal energy loss. Therefore, these hydrocarbons will

be useful as media for long-term storage and long-distance transportation of hydrogen only if the process of the dehydrogenation of cyclic hydrocarbons is achieved under mild conditions. To this end, efficient hydrogen evolution from cycloalkane dehydrogenation has been met under reactive distillation conditions in batchwise operation [2–7]. In these conditions, an un-steady state takes place due to boiling and refluxing of reactants. This special contact between reactant and catalyst has been called either “liquid-film state” [2–5] or “wet-dry multiphase conditions” [6, 7].

Hodoshima and co-workers found that the reaction rate of decalin conversion to H₂ and naphthalene is very sensitive to the initial decalin to catalyst ratio [3–5]. The maximum reaction rate was met with a value of 3.3 ml/g decalin to catalyst ratio. This optimum occurred when the liquid-film state was reached. Unlikely, Kariya and co-workers only found a slight dependence of the reaction rate on the



Scheme 1.

initial feeding amount of decalin [6]. From these controversial results, it is apparent that every particular catalyst/reactor systems behave differently with regard to the decalin/catalyst ratio. It was found that the optimum initial decalin/catalyst ratio and the resulting reaction rate are influenced not only by the reaction conditions (reaction temperature, nature of the reactant, type and porosity of support, *etc.*) but also by the size and shape of the reaction tube [6]. Therefore, one of the aims of this work is determining the impact of the decalin/catalyst ratio on different parameters such as conversion and selectivity in the case of our catalytic system. Another objective is to develop a catalyst active and stable which are conditions necessary for the catalyst to be implemented in a continuous spray-pulsed reactor [7–10] aimed to supply a continuous H₂ flow to a fuel cell. To this end, we have prepared Pt on carbon catalyst with different Pt loadings using H₂PtCl₆ and a commercial activated carbon. We have tested the catalysts in the dehydrogenation of decalin in a batch-type set-up under boiling and refluxing conditions. The conversion curves have been fitted to a Langmuir-type equation and the parameters of the equation have been studied as a function of reaction temperature and decalin to catalyst ratio. On the basis of these results, we determined the best Pt catalyst loading and optimum decalin/catalyst ratio for our system.

EXPERIMENTAL

Catalyst preparation

An activated carbon supplied by Engelhard italiana S.p.A. was used as catalyst support. Pt was deposited from H₂PtCl₆ · 6H₂O (Alfa Aesar, ACS Premiom). The amount of Pt precursor necessary to get a certain Pt loading was weighted and dissolved in 100 ml of distilled water. 2 g of activated carbon were added to the Pt solution and it was stirred during 18 h. After this time, the solution was filtered and the catalyst was dried first at room temperature overnight and subsequently at 373 K during 1 h. The Pt solutions previously and after Pt adsorption were analysed by ICP-OES to calculate the Pt uptake.

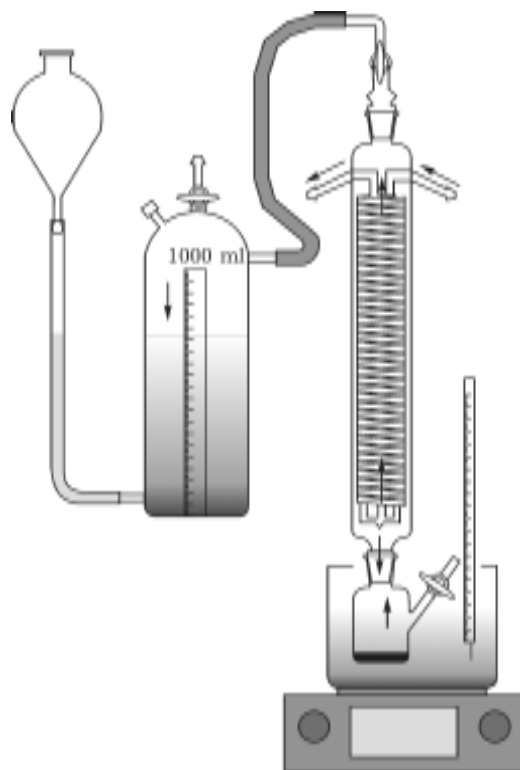


Fig. 1. Experimental set-up scheme.

After drying, the catalyst was reduced with 100 ml/min of 50 % H₂ in Ar while the catalyst was heated at a rate of 3 °C min up to 623 K and a dwell time of 2 h. Finally, the catalyst was passivated with 1 % O₂ in N₂.

Dehydrogenation catalytic tests

Figure 1 shows a scheme of the experimental set-up used for the decalin dehydrogenation catalytic tests. The batch-type operation system described here must be regarded as an experimental rig to test different catalyst formulation in the reaction of decalin dehydrogenation under reactive distillation conditions, *i.e.* under boiling and refluxing conditions.

In a standard experiment, 0.3 g of catalyst is loaded forming a thin layer at the bottom of the reactor vessel. A known amount of decalin (Fluka, reagent grade) is added to the catalyst dropwise to ensure that the whole catalyst is wetted with decalin. Then the experimental set-up is mounted and is swept with N₂ during 15–20 min to remove O₂ completely. In parallel, a silicon bath is heated to the reaction

temperature. When the reaction temperature is reached the reaction is started by introducing the reactor vessel in the bath. The volume of H₂ released during the reaction was monitored by the water volume displaced in a buret. When the reactor is cooled down after reaction, the catalyst and experimental set-up are washed with *n*-hexane. This *n*-hexane is filtered and analysed by gas chromatography (Hewlett-Packard 5890 series II with selective mass detector). Decalin conversions were obtained on the basis of the evolved H₂ after stoichiometric confirmation of naphthalene concentration in the reaction solution from gas chromatographic analysis.

Experiment design

We carried out a factorial experiment design with 3 factors at 2 levels and a central point with three replications, *i.e.* 11 experiments in total. *Via* a suitable design it is possible to maximize the amount of information withdrawn from the minimum number of experiments. Furthermore, it is possible to estimate the effect of the interactions between the factors on the process response. The objective of this study with multiple linear fitting is three-fold: 1) reject variables which have no significance; 2) get estimations of the individual coefficients in a model; 3) arrive to a more effective predictive equation.

The factors chosen for the design were the temperature, the Pt loading and the decalin/catalyst ratio. According to the literature, the decalin conversion and the initial reaction rate depend on the temperature and the decalin/catalyst ratio.

To achieve a liquid-film state, the temperature has to be higher than the boiling temperature of the reagent but low enough to allow the reflux to the catalytic surface. Thus, the temperature values chosen were 220, 240 and 260 °C. The values of Pt loading chosen were 3, 4 and 5 mass % Pt. From previous results, the decalin/catalyst ratio was chosen on the basis that an optimum value is found in the range 2.0 to 3.3 ml/g catalyst. Since in all the experiments the catalyst amount was 0.3 g, we varied the volume of decalin from 0.6 to 1 ml. Figure 3 shows the experiments carried out.

RESULTS AND DISCUSSION

Experimental design

Table 1 compiles the results of all the experiments carried out according to the experiment design. Figure 3 shows the H₂ production as a function of time-on-stream for selected experiments. All the curves show the same pattern, there is a first step of high H₂ production rate followed by a progressive

TABLE 1

Overview of the experiments carried out and main results

Experiment No.	T, °C	Factor			Variables response		
		Pt, %	V _{decal} , ml	Decalin conversion, %	k, mmol/h	K, ml/mmol	Selectivity to naphthalene, %
1	220	3	0.6	32.02	11.79	8.55	56.32
2	220	3	1.0	33.01	18.28	9.61	16.95
3	220	5	0.6	24.67	8.96	5.49	40.25
4	220	5	1.0	19.07	7.66	12.50	19.08
5	260	3	0.6	56.03	27.02	1.48	73.42
6	260	3	1.0	47.18	21.82	3.97	44.22
7	260	5	0.6	42.73	14.83	1.64	68.42
8	260	5	1.0	28.13	13.40	4.89	62.14
9	240	4	0.8	55.88	31.53	2.55	20.17
10	240	4	0.8	56.20	31.96	0.67	42.85
11	240	4	0.8	58.68	31.51	2.02	53.62

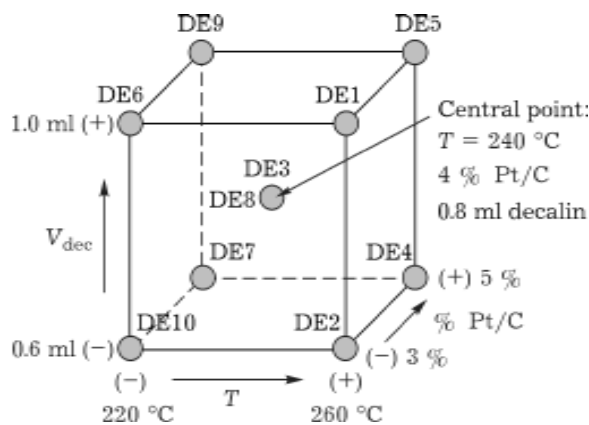


Fig. 2. Design of experiments with points in the vertices and center representing the experiments with different reaction conditions of temperature, % Pt and decalin volume.

decrease of the rate until almost negligible H_2 production. The maximum final conversion obtained is about 60 %.

Table 1 also shows the results of fitting to a Langmuir-type rate equation (eq. 1). This equation has been successfully applied to describe the catalytic dehydrogenation of 2-propanol [2] and decalin [3]:

$$v = \frac{k'[\text{decalin}]}{1 + K[\text{naphtalene}]} \quad (1)$$

The decalin concentration can be considered constant for times shorter than 20 min, *i.e.* conversions <30 %. Thus, eq. (1) can be transformed to (2):

$$v = \frac{k}{1 + K[\text{naphtalene}]} \quad (2)$$

TABLE 2

Results of the experiment design analysis

Decalin conversion					
Variables	Effect	Coefficient	Standard error	p -value	
Constant		b_0	35.355	1.5326	0
T	16.325	b_1	8.162	1.5326	0.004
% Pt	-13.41	b_2	-6.705	1.5326	0.006
V_{dec}	-7.015	b_3	-3.508	1.5326	0.023
$T\%Pt$	2.765	b_{12}	-1.382	1.5326	0.125
TV_{dec}	-4.71	b_{13}	-2.355	1.5326	0.049
$\%PtV_{\text{dec}}$	-3.085	b_{23}	-1.542	1.5326	0.104
$T\%PtV_{\text{dec}}$	0.21	b_{123}	0.105	1.5326	0.864

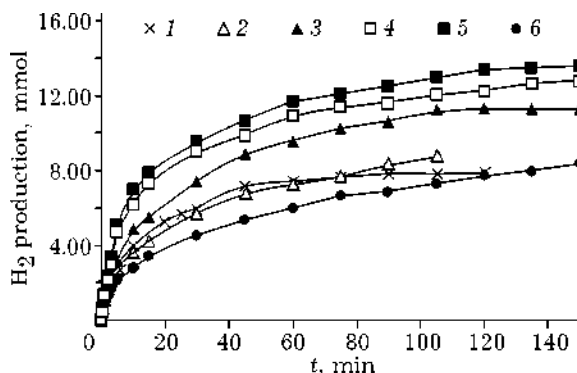


Fig. 3. H_2 productivity for a few selected experiments: 1 - 1 mass % Pt at 533 K, 2 - 3 mass % Pt at 513 K, 3 - 3 mass % Pt at 533 K, 4 - 4 mass % Pt at 513 K, 5 - 4 mass % Pt at 533 K, 6 - 5 mass % Pt at 533 K.

where v is the hydrogen evolution rate (mmol/h), k is the reaction rate constant (mmol/h) and K is the retardation constant (ml/mmol).

The conversion for the first 20 min of reaction was fitted with eq. (2) for the different catalysts tested. In all the fittings the correlation factor was higher than 0.98. The impact of the studied variables on the average decalin conversion, along with the fitting coefficient, were calculated with MINITAB, following the fundamentals of the experimental design analysis, for a significance level of $\alpha = 0.05$. The results of the analysis of the experimental design are compiled in Table 2 and Fig. 3.

The variables which have a significant effect on the response have a p -value lower than the significance level of $\alpha = 0.05$. Thus, the

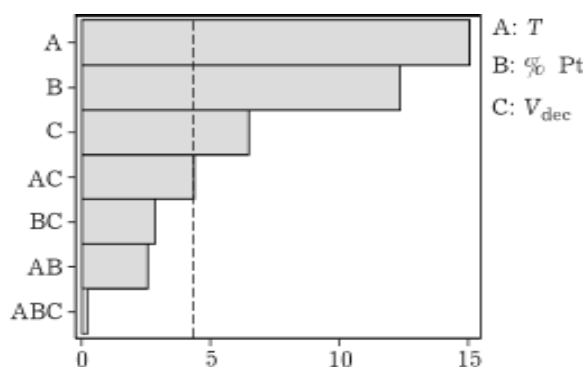


Fig. 4. Pareto chart of the standardized effects: A, temperature; B, Pt loading in %; C, decalin volume. The response is conversion and the vertical line is for a significance level of $\alpha = 0.05$.

temperature, the Pt loading, the decalin volume and the interaction between temperature and decalin volume are significant parameters. The evaluation of the relative effect of the response variables can be estimated from a statistic tool as the Pareto diagram (Fig. 4). The vertical line is the minimum level of significance, *i.e.* those effects that cross this line are significant. We can observe that the effect of higher significance is the temperature, followed by % Pt, decalin volume and the interaction AC corresponding to temperature and decalin volume.

Impact of the decalin/catalyst ratio

We carried out dehydrogenation experiments at 533 K with a 3 mass % Pt catalyst and different decalin/catalyst ratios. Figure 5 shows that the conversion decreases for decalin/catalyst ratio above approx. 2.7 ml/g. Thus, the optimum decalin/catalyst ratio in our system is about 2.7 ml/g. The decrease of conversion when reactant supply increases has been already reported by others [7]. There, it was demonstrated that the temperature of the catalyst surface decreased for reactant supply exceeding a certain value. This occurs because a large amount of liquid reactant covers the catalyst surface and the reaction occurs under conditions equivalent to those in liquid phase.

The selectivity to naphthalene (see Fig. 5, curve 2) is in most cases above 60 %. For decalin/catalyst ratios smaller than 3.5 ml/g, the selectivity decreases when the ratio increases, reaching a minimum selectivity (43 %) at

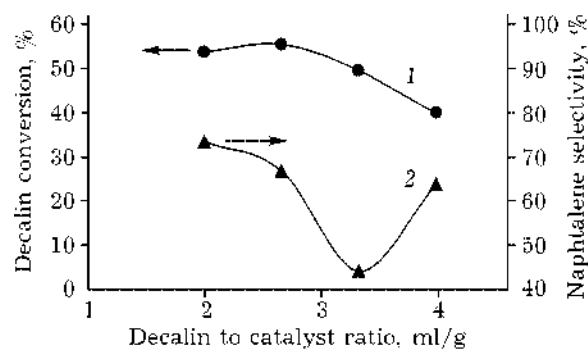


Fig. 5. Decalin conversion (1) and selectivity to naphthalene (2) as a function of the decalin to catalyst ratio. 3 mass % Pt catalyst, 533 K.

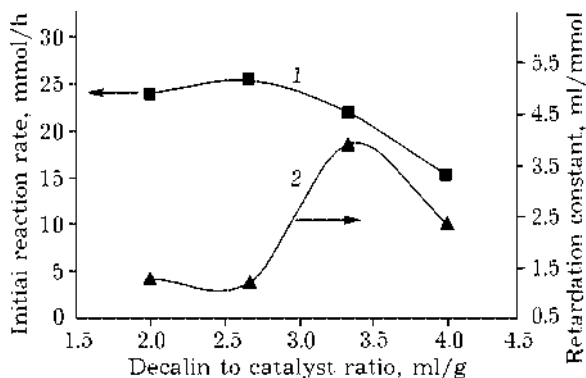


Fig. 6. Initial reaction rate constant (1) and retardation constant (2) as a function of the decalin to catalyst ratio. 3 mass % Pt catalyst, 533 K.

3.3 ml/g. The decrease of selectivity occurs because more partially dehydrogenated product (tetraline) is obtained, leading to less efficient use of decalin.

Figure 6 shows the parameters of fitting to the Langmuir-type rate equation (eq. 2) as a function of the decalin/catalyst ratio. The reaction rate constant (k) follows the same pattern as the final conversion in Fig. 5, and the retardation constant (K) increases significantly for decalin/catalyst ratios above 2.7 ml/g. Thus, the optimum values, *i.e.* a maximum reaction rate constant and a minimum retardation constant, are met with a decalin/catalyst ratio of 2.7 ml/g.

CONCLUSIONS

We have prepared Pt/C catalysts from H_2PtCl_6 and a commercial activated carbon. The catalysts have been used for decalin dehydrogenation to produce H_2 , exhibiting high decalin conversion (up to 60 %) limited mainly by thermodynamic reasons. The statistical analysis showed that temperature, % Pt and decalin/catalyst ratio have a significant impact on conversion. The optimum decalin to catalyst ratio is met with 2.7 ml/g. This ratio maximizes conversion and kinetic rate constant and minimizes retardation constant. Above this ratio, the catalyst is supposed to be flooded by the reactant but not in the liquid-film state. The Pt/C catalyst seems to be a suitable candidate to be used as feed for a PEM fuel cell in a H_2 -driven vehicle.

Acknowledgements

Engelhard is acknowledged for supplying the carbon support. We are also grateful to the Aragon Government for the financial support and to P. Castell for the XRD measurements and fruitful discussion.

REFERENCES

- 1 F. Buonomo, D. Sanfilippo, F. Trifiro, in: Handbook of Heterogeneous Catalysis, in G. Ertl, H. Knözinger and J. Weitkamp (Eds.), VCH, Weinheim, 1997, p. 2140.
- 2 N. Meng, S. Shinoda, Y. Saito, *Int. J. Hydro. Ener.*, 22 (1997) 361.
- 3 S. Hodoshima, H. Arai, S. Takaiwa, Y. Saito, *Ibid.*, 28 (2003) 1255.
- 4 S. Hodoshima, H. Arai, Y. Saito, *Ibid.*, 28 (2003) 197.
- 5 S. Hodoshima, S. Takaiwa, A. Shono *et al.*, *Appl. Catal. A: Gen.*, 283 (2005) 235.
- 6 N. Kariya, A. Fukuoka, M. Ichikawa, *Ibid.*, 233 (2002) 91.
- 7 N. Kariya, A. Fukuoka, T. Utagawa *et al.*, *Ibid.*, 247 (2003) 247.
- 8 R. B. Biniwale, H. Yamashiro, M. Ichikawa, *Catal. Lett.*, (2005) 23.
- 9 R. B. Biniwale, N. Kariya, M. Ichikawa, *Ibid.*, 105 (2005) 83.
- 10 I. Kobayashi, K. Yamamoto, H. Kameyama, *Chem. Eng. Sci.*, 54 (1999) 1319.