Pt/γ-Al_2O_3 catalytic membranes vs. Pt on γ-Al_2O_3 powders in the selective hydrogenation of *p*-chloronitrobenzene

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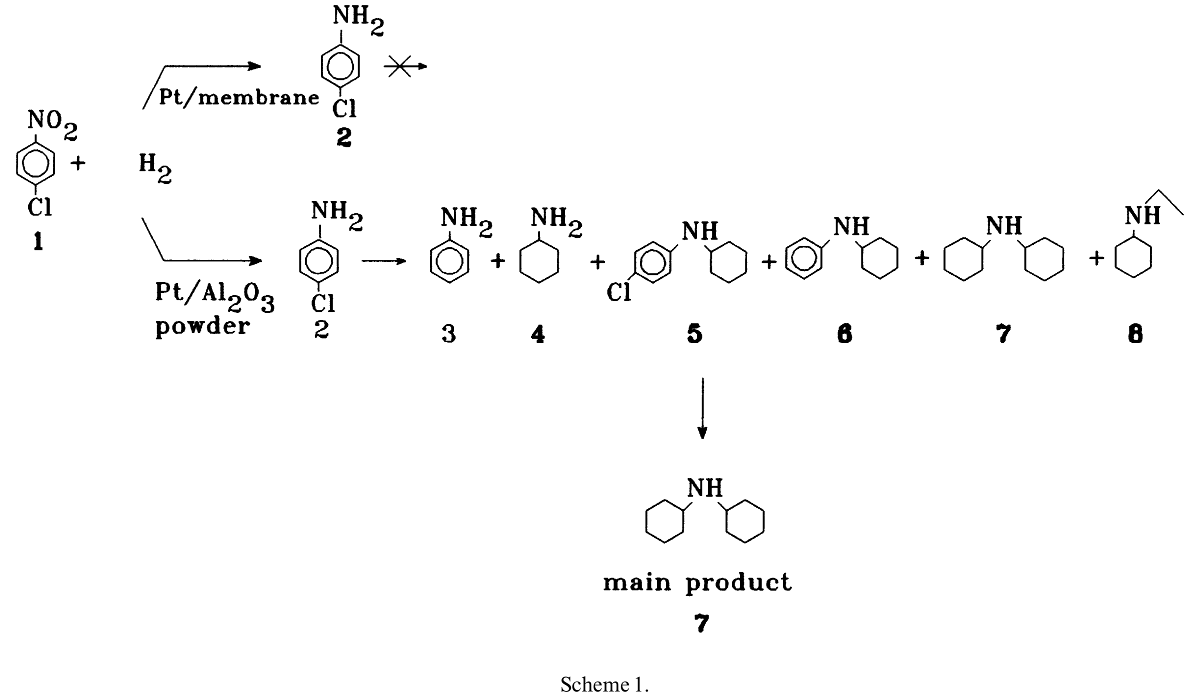
The catalytic activity of Pt/γ-Al_2O_3 membrane reactors, prepared using mesitylene solvated platinum atoms as source of active Pt particles, has been compared with that of analogously obtained Pt/γ-Al_2O_3 powders in the liquid phase hydrogenation of *p*-chloronitrobenzene. A largely different behaviour has been observed, the membrane reactor acting as a H_2 richer system.

Keywords: platinum atoms, catalytic membrane reactors, *p*-chloronitrobenzene hydrogenation

1. Introduction

In recent years, much interest has been given to catalytic membrane reactors: examples have been provided as useful applications in a wide range of gas-phase processes, such as hydrocarbon and methanol dehydrogenation, methane steam reforming, and the Claus reaction [1].

Studies on liquid phase reactions, however, are restricted to very few cases [2]. We report here that the hydrogenation of *p*-chloronitrobenzene in ethanol, using Pt/γ-Al_2O_3 catalytic membranes, yields *p*-chloroaniline as the only reaction product, while using Pt/γ-Al_2O_3 powder systems, under the same reaction conditions, a complex mixture of products is obtained (scheme 1).



Scheme 1.

2. Experimental

A multi-layered ceramic membrane (SCT-50) of inner diameter 6.7 mm, outer diameter 10.2 mm, has been used. The membrane was 150 mm long, sealed by a vetrification process for an extent of 25 mm to both the ends. As elsewhere reported [3b], the membrane is made by three α-Al_2O_3 layers of decreasing porosity and an inner fourth layer of γ-Al_2O_3 having a thickness of about 4 μm and a nominal average pore diameter of 5 nm.

SCT γ-Al_2O_3, the same kind of the γ-Al_2O_3 membrane layer, and commercial AKZO 000-3P (average pore diameter 12.2 nm) γ-Al_2O_3 have been used as powders.

As already reported [3], mesitylene solvated Pt atoms have been used for the deposition of active Pt particles on the permeable part of the γ-Al_2O_3 layer of the membrane [3a] and on the γ-Al_2O_3 powders [3b]: the amount of Pt in the starting solution was determined by X-ray fluorescence and the Pt coating confirmed via a colorimetric technique after chemical attack with a mixture of hydrofluoric acid and aqua regia [3a,3b].

The size distribution of the Pt particles deposited on the γ-Al_2O_3 layer of the membrane and on the γ-Al_2O_3 powder was evaluated by transmission electron microscopy (HRTEM, Jeol 2000EX).

Hydrogenations with Pt/γ-Al_2O_3 powders have been performed in a 50 ml two-necked flask fitted to a gas-volumetric apparatus containing hydrogen mantained at pressure of ca. 10^5 Pa, under magnetic stirring, following a typical lab-scale catalytic hydrogenation procedure [4]. The reaction runs with membranes were similarly performed, filling the membrane, provided with rubber stoppers at both ends, with the substrate solution and closing it in a glass container (figure 1). The system was connected to a gas volumetric apparatus containing H_2, mantained at ca. 10^5 Pa, and mechanically gently shaken, using a platform lab-line shaker.

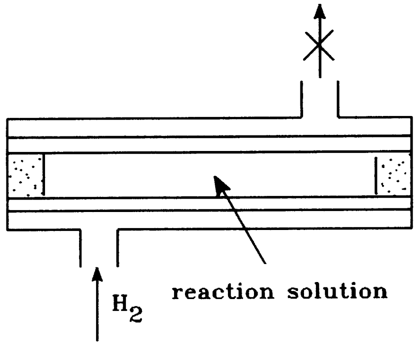


Figure 1. Schematic of membrane reactor.

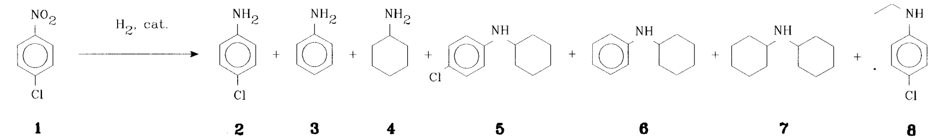
The hydrogenation products were characterized by GC-MS and by ^{1}H-NMR analysis.

3. Results and discussion

In order to test the selectivity of the so prepared catalysts, the polyfunctionalized *p*-chloronitrobenzene has been chosen as a substrate for the hydrogenation.

The results obtained in the *p*-chloronitrobenzene hydrogenation are reported in table 1. It can be seen that

Table 1
Hydrogenation of *p*-chloronitrobenzene on Pt/γ-Al_2O_3 membrane and powder [a]



Catalyst	Time (h)	Conv. (%)	Product yields (%)						
			2	3	4	5	6	7	8
Pt/γ-Al_2O_3	1	85	100						
SCT membrane T1-70 [b]	24	100	100						
	48	100	97						3
	72	100	95						5
Pt/γ-Al_2O_3 1%	1	87	96	4					
SCT powder	24	100	62	12	12	4	t	10	
	48	100	30	14	24	t	t	32	
	72	100	20	4	16	t	t	52	
Pt/γ-Al_2O_3 1%	1	100	72	28					
AKZO powder	24	100	14	35	12	2	6	31	
000-3P	48	100	t	12	32	t	t	56	
	72	100	t	2	12	t	t	86	

[a] Solvent: EtOH; $T = 25°C$; $P_{H_2} = 10^5$ Pa; substrate: 200 mg; catalyst: 100 mg.
[b] 1 mg of Pt deposited.

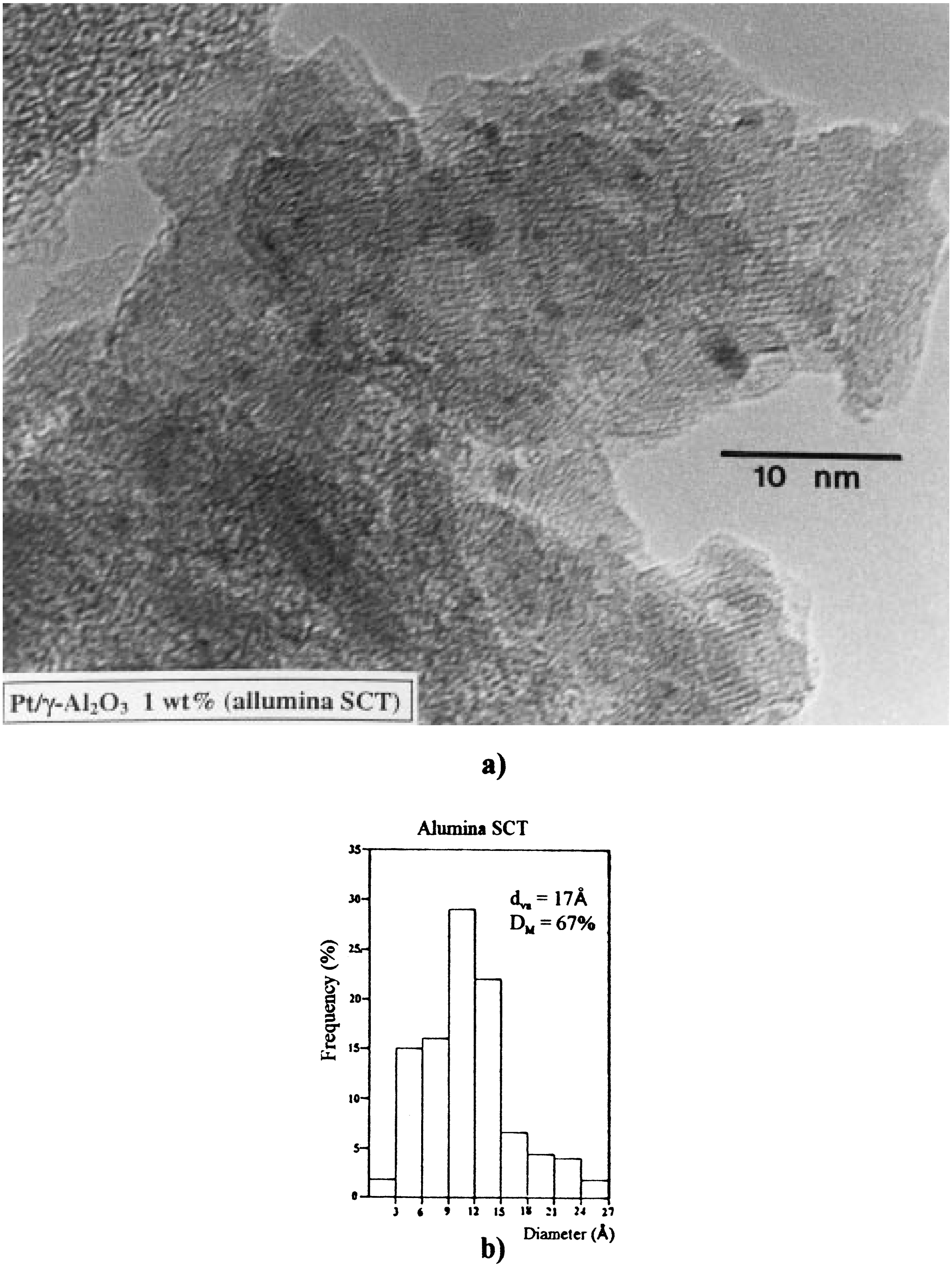


Figure 2. (a) HRTEM micrograph of Pt/γ-Al_2O_3 SCT powder; (b) Pt particle size distribution histograms of Pt/γ-Al_2O_3 SCT powder.

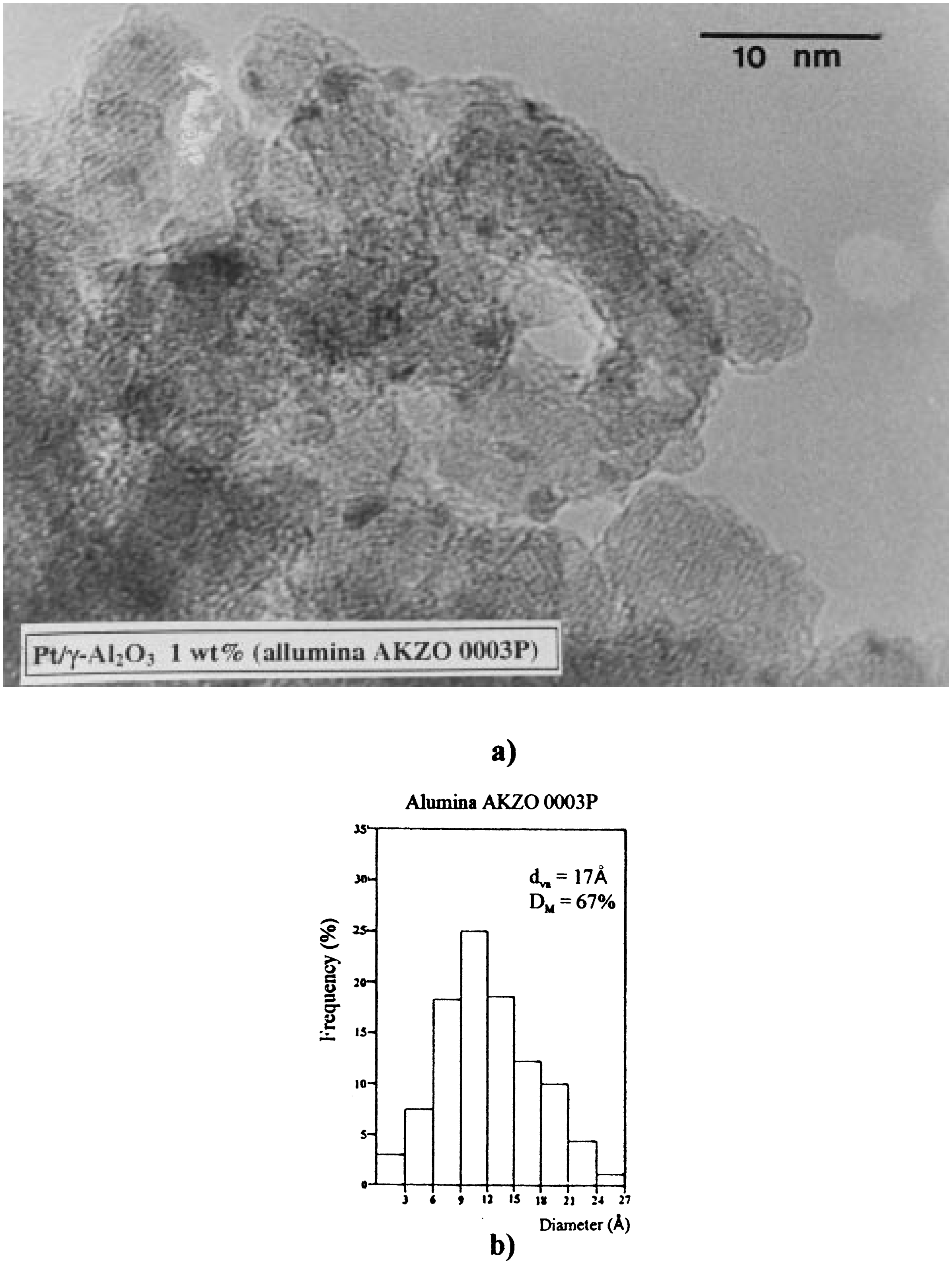
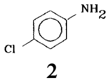
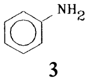
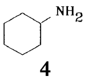
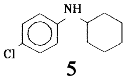
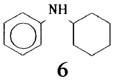
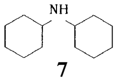
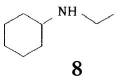


Figure 3. (a) HRTEM micrograph of Pt/γ-Al_2O_3 AKZO 0003P powder; (b) Pt particle size distribution histograms of Pt/γ-Al_2O_3 AKZO 003P powder.

Table 2
Hydrogenation of *p*-chloronitrobenzene using 1 wt% Pt/γ-Al_2O_3 (AKZO 000-3P) at different pressures [a]

$p(H_2)$ (10^5 Pa)	Time (h)	Product yields (%)						
		 **2**	 **3**	 **4**	 **5**	 **6**	 **7**	 **8**
1	24	14	35	12	2	6	31	–
20	24	41	9	31	2	–	5	13

[a] Solvent: EtOH (5 ml); $T = 25°C$; substrate: 200 mg; catalyst: 100 mg; conversion: 100%.

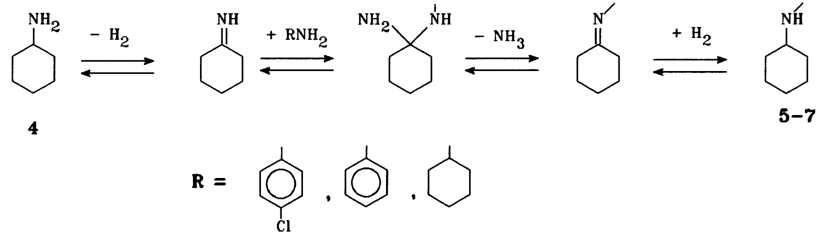
using the catalytic membrane, the *p*-chloronitrobenzene is rapidly reduced to *p*-chloroaniline, which is no further hydrogenated even at long reaction time (72 h). Few amounts of ethyl-*p*-chloroaniline, formally derived from a condensation reaction of **2** with ethanol, are formed.

In runs performed using Pt/γ-Al_2O_3 powders, after the hydrogenation of *p*-chloronitrobenzene to *p*-chloroaniline, the aromatic aloamine **2** undergoes hydrodechlorination to aniline, and further ring hydrogenation to cyclohexylamine; after longer reaction times, dicyclohexylamine is observed as main reaction product. Such behaviour is more evident in samples prepared using AKZO 000-3P as γ-Al_2O_3 powder.

It appears from the reported data that there is a very large difference in product distribution using Pt/γ-Al_2O_3 membrane or powders. The selectivity in the hydrogenation of *p*-chloronitrobenzene has been strongly related to the sizes of the Pt particles [5]. However, HRTEM analysis of the Pt/γ-Al_2O_3 powder samples (figures 2 and 3) and catalytic membrane [3a] indicates a quite comparable Pt particle size distribution, most of the particles having sizes of 1–1.5 nm.

In trying to explain such a different behaviour, some additional experimental data should be considered. If the reactions on Pt/γ-Al_2O_3 powders are performed under higher H_2 pressure, the amount of by-products strongly decreases and *p*-chloroaniline is still present as major hydrogenation product. The results obtained using Pt/γ-Al_2O_3 AKZO 000-3P powder, at 2×10^6 Pa, are reported in table 2 and compared with the data obtained with the same catalyst at atmospheric pressure. The very low amount of products **5**–**7** working at atmospheric pressure of H_2 can be easily understood considering that their formation should involve as key step amine dehydrogenation to imines, which is unlikely to occur under H_2 pressure (scheme 2).

The presence of *p*-chloroaniline as major reaction product in experiments performed at 2×10^6 Pa of H_2 is also of interest. Under H_2 pressure competitive adsorption of *p*-chloroaniline and H_2 on the Pt particles should be considered: it could account of the more difficult dechlorination of **2** to aniline and further hydrogenation to cyclohexylamine, according to the consideration made by Coq et al. [5] in the hydrogenation of *p*-chloronitrobenzene on Pt/γ-Al_2O_3 catalysts. It is well known that the hydrogen availability could strongly affect the selectivity in hydrogenation reactions [6]: the above observation can allow one to consider that a possible role of the catalytic membrane can be to supply more H_2 with respect to powder systems, accounting for the different catalytic behaviour. These results appear to support the idea that a catalytic reactor can efficiently improve the contact between gas, liquid and solid because the volatile reactant does not have to diffuse through a liquid film covering the solid catalysts, as in conventional reactors [7].



Scheme 2.

Acknowledgement

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