Chemical Engineering Journal 145 (2008) 135–141

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Supported Nafion catalyst for 1-pentanol dehydration reaction in liquid phase

R. Bringué, J. Tejero, M. Iborra, J.F. Izquierdo, C. Fité, F. Cunill*

Chemical Engineering Department, Faculty of Chemistry, University of Barcelona, Spain.C/Martí i Franquès 1-11, 08028 Barcelona, Spain

ARTICLE INFO

Article history:
Received 29 April 2008
Received in revised form 24 July 2008
Accepted 25 July 2008

Keywords:
Nafion
1-Pentanol dehydration
Di-*n*-pentyl ether

ABSTRACT

Silica-supported and alumina-supported Nafion catalysts that differ in surface area and Nafion contents were prepared using an impregnation technique. Liquid-phase dehydration of 1-pentanol to produce di-*n*-pentyl ether was used to measure their catalytic activity. A reproducible impregnation method was found, which considers a controlled evaporation of water and alcohols and a further washing with methanol before final drying. Only silica-supported catalysts were active for the alcohol dehydration reaction. Acid capacity and 1-pentanol conversion, increased on increasing the initial amount of Nafion. Despite 1-pentanol conversion obtained for all silica-supported catalysts were lower than that obtained for commercial Nafion NR50, turnover numbers were always better for impregnated catalyst. A maximum turnover number was found for 26 wt% loading of Nafion on silica. A kinetic model in terms of compounds activities describes satisfactorily the experimental kinetic data. It is based on a mechanism in which the rate-determining step is the surface reaction between two adjacent adsorbed 1-pentanol molecules. The apparent activation energy was found to be in the range 106–128 kJ mol^{-1}.

1. Introduction

To overcome both economic and environmental drawbacks of many industrial processes catalyzed by mineral acid catalysts, a lot of work during last decades has been devoted to the development of solid acids that could replace the catalytic action of homogeneous systems. Among the acid solids, perfluorinated polymers with sulfonic groups (Nafion) have received considerable attention because of its acidic strength and physicochemical properties. Values of Hammet acidity for Nafion and others acid solid catalysts are compared elsewhere [1]. Nafion acid strength is comparable, or even superior, to that of 100% sulphuric acid, and can be considered as a superacidic catalyst with a terminal –$CF_2CF_2SO_3H$ group in the acid form. The high acid strength and chemical inertness of the fluorocarbon backbone make Nafion resin an attractive replacement for strong homogeneous acid catalysts. Olah et al. [2] have described in detail the use of commercial Nafion beads in many organic reactions such as alkylations, acylations, isomerizations, esterifications, hydrations and dehydrations, nitrations, and etherifications. Unfortunately, the very small surface area of Nafion (typically, 0.02 m^2 g^{-1}) strongly limits the number of available acidic sites, especially in gas phase and non-polar media, and most of active sites are buried within the polymer beads. On the other hand, Nafion is very expensive. Thus, commercially available Nafion in the form of millimeters sized beads, known as Nafion NR50, does not seem to be potentially suited for use as an industrial catalyst.

To surpass the trouble associated to accessibility of acidic sites of Nafion resin-based catalysts, two new classes of solid acid catalysts based on Nafion resin have been developed. The first one is based on the formation of a nanocomposite of nanometer sized Nafion resin particles entrapped within a highly porous silica network using a sol–gel technique [3], wherein solutions of partial depolymerized Nafion are mixed with soluble silicon sources to form a gel, which is dried to a clear hard glass-like material. These composite catalysts yield much higher reaction rates than those observed on the original Nafion resin-based catalyst and were applied to various acid-catalyzed reactions such as isobutene/2-butene alkylation [4], dimerization of α-methylstyrene [5] showing significant activity enhancements [6]. The second procedure consists in dispersing Nafion resin on higher surface area supports such as standard silicas [4] and mesoporous silicas (MCM-41, SBA-15) [7–9]. These last silica-supported catalysts exhibit a much better catalytic activity than Nafion resin-based catalysts since surface area of around 1000 m^2 g^{-1} can be easily reached.

Many works have been performed using the aforementioned catalysts in non-swelling media [3–6,10–12], but only a few ones were done in polar and swelling media. For the latter cases, it is supposed that all acid centers of pure Nafion are accessible because of the resin swelling. A typical system of such characteristics can be found in dehydration of alcohols. To test the support effect of

---

Abbreviations: DNPE, di-*n*-pentyl ether.

* Corresponding author. Tel.: +34 934021304; fax: +34 934021291.
E-mail address: fcunill@ub.edu (F. Cunill).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.07.045

Nomenclature

%Nafion$_{ac}$	amount of Nafion-supported on the carrier with respect to acidity (%)
%Nafion$_{r_0}$	amount of Nafion-supported on the carrier with respect to initial reaction rate (%)
%Nafion$_{tn}$	amount of Nafion-supported on the carrier with respect to initial turnover number (%)
a_j	activity of compound *j*
d_p	particle diameter (μm)
d_{pore}	pore diameter (nm)
E_a	apparent activation energy (kJ mol^{-1})
Efficiency	relation among the obtained amount of Nafion-supported with respect to acidity and the theoretical one
$\hat{k}$	intrinsic rate constant (mol/(h kg))
K_j	adsorption equilibrium constant of compound *j*
n	number of active sites
n_j	number of moles of compound *j*
r	reaction rate (mol DNPE/(kg h))
r^0	initial reaction rate (mol DNPE/(kg h))
r^0_{eq}	initial turnover number (mol DNPE/(h equiv. H$^+$))
S_{DNPE}	selectivity to DNPE
S_g	surface area (m^2 g^{-1})
t	time (h)
T	temperature (°C)
V_g	pore volume (cm^3 g^{-1})
X_P	conversion of 1-pentanol
W_{cat}	weight of catalyst (g)

Greek letters

θ	porosity
ρ_s	skeletal density (g cm^{-3})

Subscripts

ac	acid capacity
D	di-*n*-pentyl ether
j	catalyst
P	1-pentanol
r^0	initial reaction rate
tn	turnover number
W	water

supported Nafion resin for these media, the dehydration of 1-pentanol to di-*n*-pentyl ether (DNPE) is chosen in this work as the target reaction. On the other hand, DNPE formation is a promising reaction for the production of high-cetane component to diesel fuel. When DNPE is added to diesel, most of the properties, such as high-cetane number and lower cold properties, are sensibly improved [13]. Furthermore, due to the presence of oxygen in DNPE molecule, DNPE was shown to be very effective in reducing diesel exhaust emissions, namely CO, NO$_x$, unburned hydrocarbons, particulates and smokes. In a previous work [14], pure perfluoroalkanesulfonic resin NR50 has shown to be very active and selective catalyst for this reaction.

In the present work, Nafion resin was supported on six different carriers by impregnation, and the resulting catalysts were characterized and tested on 1-pentanol dehydration. Obtained results are compared with commercial NR50 (grain), N-117 (Nafion membrane) and SAC-13 (Nafion/silica composite with 13 wt% of Nafion resin). On the other hand, since to the best of our knowledge there are no references of kinetic studies for this kind of supported catalyst, some experimental runs will be done to propose a kinetic model.

2. Experimental

2.1. Materials

1-Pentanol (99% pure; <1% 2-methyl-1-butanol) was supplied by Fluka (Buchs, Switzerland), and used without further purification. DNPE (≈99% pure, GC) was prepared in our laboratory. 2-Pentanol (98%), 2-methyl-1-butanol (≈98%), 1-pentene (≈97%), *cis*-2-pentene (≈98%), *trans*-2-pentene (≈99%), and 2-methyl-1-butene (>97%), supplied by Fluka, and water were used for analysis. Nafion in its different forms, (NR50, a solid perfluorosulfonic acid resin, Nafion perfluorinated resin solution with 5 wt% in mixture of lower aliphatic alcohols and water, Nafion silica nanocomposite SAC-13 with 13 wt% of Nafion, and pure Nafion 117 (N-117) membrane) were supplied by Aldrich.

2.2. Carriers

Three silicas (nominal surface areas of 200 (abbreviated Si-A), 300 (Si-B) and 500 m^2 g^{-1} (Si-C)), three aluminas, (weakly acidic, pH ≈6 in water, Type 506-C-I Brockman I 155 m^2 g^{-1} nominal area, Al-1; acidic, pH ≈4.5 in water Type 504-C Brockman I 155 m^2 g^{-1} nominal area, Al-2; and α-aluminum oxide 10 m^2 g^{-1} nominal area, Al-3) and a silica–alumina of 600 m^2 g^{-1} nominal area (Si–Al) were used as carriers. In Table 1 relevant physical and structural properties of the carriers are shown.

BET surface area (S_g), pore volume (V_g) and surface (S_{pore}) were measured using a Micromeritics ASAP 2000. Some discrepancies appeared between nominal and measured BET surfaces. Al-3 and Si–Al presented the highest deviations, Al-3 being practically non-porous. Mean particle diameter was determined with a Beckman Coulter LS Particle size Analyzer. Al-3 was rejected as a carrier due to its small size that plugged the reactor outlet filter, and to its non-porous character. Acidic capacity of carriers was measured by direct exchange titration. A known amount of dried catalyst was added to a NaCl solution and stirred overnight. Then, a part of the solution was titrated with standardized NaOH using phenolphthalein as indicator. The last step was repeated at least twice. This method was validated with Nafion NR50 and other ion-exchange resins, comparing obtained values with those of manufacturers. Only the Si–Al carrier presented some acidity by itself. Carriers were used without previous calcination, since the weight loss after drying in a vacuum oven and in a muffle at 600 °C for 2 h was less than 5%.

None of the carriers was active at work conditions, except for the silica–alumina carrier, which gave some 1-pentanol conversion, according to its low acidic capacity.

2.3. Catalysts preparation

As aforementioned, the Nafion-supported catalysts are widely quoted in the literature and they were often prepared following an impregnation technique, but the procedure usually is not explained in detail. The methods of impregnation presented here are based on the previous ones and aim to improve them. Three different methods were tested. The best one was chosen on the criteria of the catalytic activity and reproducibility. It consisted of the following steps: (1) washing and drying of carrier; (2) carrier mixing with a solution of 2-propanol:water (33:67 wt%); (3) addition of the appropriate amount of the commercial solution of Nafion resin (5 wt%) to place Nafion on the carriers and agitation for 6 h; (4) evaporation of the solvents using a rotavapor for 2 h at 60 °C; 5) drying of the impregnated catalyst and then washing with methanol;

Table 1
Physical and structural properties of carriers

Carrier	Short name	ρ_s (g cm^{-3})	S_g [a] (m^2 g^{-1})	V_g [b] (cm^3 g^{-1})	S_{pore} [b] (m^2 g^{-1})	d_{pore} [c] (nm)	d_p (μm)	Acidity (equiv. H$^+$/kg)
Weakly acidic alumina	Al-1	3.19	177	0.2110	188.6	4.5	116	–
Acidic alumina	Al-2	3.22	157	0.233	182.7	5.1	105	–
α-Alumina	Al-3	3.98	0.665	0.002	0.586	14.0	7.7	–
Silica A	Si-A	2.19	221	1.43	233.6	24.4	39.7	0.01
Silica B	Si-B	2.15	306	1.73	314.1	22.0	79.1	0.01
Silica C	Si-C	2.10	487	1.76	514.8	13.7	67.1	0.01
Silica–alumina	Si–Al	2.05	471	0.645	532.4	4.8	63.6	2.7

[a] BET surface.
[b] Determined from adsorption isotherm of N_2 at 77K.
[c] Assuming pore cylindrical model.

and (6) drying in the oven under vacuum. Washing the carrier before and after the impregnation is the main contribution to this process: it allows extracting non-bonded Nafion out of the catalyst. If not, it could act as a homogeneous catalyst and could mask the activity of the supported catalyst.

2.4. Reaction system and experimental procedure

Experiments were performed in a stainless steel (316 SS) reactor operated in batch mode with a nominal volume of 100 mL. The pressure was set at 1.6 MPa by means of N_2 in order to maintain the reacting system in liquid phase. One of the outlets of the reactor was connected directly to a liquid sampling valve, which injected 0.2 μL of pressurized liquid to GLC during the experiments. More detailed information can be found elsewhere [14].

2.5. Analysis

The composition of the reacting mixture was analyzed by a HP6890A GLC apparatus equipped with a TCD detector, which allowed to measure water content, and commanded by the ChemStation HP system controlled, in his turn, by a LabVIEW software. A 50 m × 0.2 mm × 0.5 μm methyl silicone capillary column was used to separate and quantify 1-pentanol, DNPE, water, and byproducts: C_5 olefins (1-pentene, 2-pentene and methyl butenes), branched ethers (di-2-pentyl ether, 1-(1-methylbutoxy)-pentane, 1-(2-methylbutoxy)-pentane and 2-(2-methylbutoxy)-pentane), 2-methyl-1-butanol, and 2-pentanol. The column was temperature programmed with a 6-min initial hold at 318 K, followed by a 30 K min^{-1} ramp up to 453 K, and held for 5 min. Helium was used as the carrier gas at a total flow rate of 30 mL min^{-1}.

2.6. Evaluation of the catalytic activity

The activity of the carriers and synthesized catalysts was evaluated using the dehydration of 1-pentanol to DNPE at 180 °C, with 1 g of carrier or catalyst and 500 rpm. Details on the reaction and byproducts formation can be found elsewhere [14]. In each experiment, 1-pentanol conversion, X_P (%), selectivity to DNPE, S_{DNPE} (%), initial reaction rate, r^0 (mol DNPE/(kg h)) and initial turnover number, r^0_{eq} (mol DNPE/(h equiv. H$^+$)), were determined.

2.7. Reproducibility and reusability

To check the reproducibility of the impregnation method, two different samples of catalyst based on Si-C with 26% of Nafion (Nafion/Si-C_26%) were prepared, and the respective reaction rates were measured. Table 2 shows some properties and the results obtained with both preparations. As the results suggest, the reproducibility of the impregnation method was reasonably good, since structural parameters, acid capacity, reaction rates and turnover number can be practically considered the same within the limits of the experimental error. Besides, this result allows estimating the experimental error. A value less than 5% can be easily calculated from reaction rate data.

Reusability was checked by comparison of the reaction rate for fresh catalyst (1 g of Si-C with 39% Nafion) with that of the same reused catalyst (0.65 g) after filtration and drying. An approximately 23–33% decrease in activity was observed between the first and the second use. Similar initial activity decreases were encountered for Nafion@MCM-41 in the esterifications of octanoic acid with ethanol [8]. Because of the catalyst mass loss, it was impossible to see if further uses would produce additional decreases or a stationary activity would be reached [8]. More work has to be done in this matter.

2.8. Kinetic experiments

Kinetic runs were performed at temperatures ranging 140–180 °C using Nafion/Si-C_13%), Nafion NR50, Nafion 117 and SAC-13 as catalysts. Reaction rates were calculated from 1-pentanol conversion variation with reaction time according to Eq. (3). Fig. 1 shows experimental 1-pentanol conversion versus reaction time for temperatures abovementioned and Si-C-derived catalyst. Similar pictures were obtained with the rest of catalysts.

3. Results and discussion

3.1. Catalytic activity

Table 3 shows some characteristics of the silica-supported Nafion catalysts (with a nominal content of Nafion 13 wt%), Nafion NR50 and SAC-13, along with 1-pentanol conversion, DNPE selectivity, initial reaction rate, and initial turnover num-

Table 2
Properties and results for replicated catalyst

Catalyst	Acid capacity (mequiv. H$^+$ g^{-1})	Pore volume (cm^3 g^{-1})	d_{pore} (nm)	BET area (m^2 g^{-1})	X_P (%)	r^0 (mol/(kg h))	r^0_{eq} (mol/(equiv. H$^+$ h))
Nafion/Si-C_26%	0.21	0.96	9.7	326	20.0	16.7	79.5
Nafion/Si-C_26% (b)	0.20	0.84	8.7	292	18.3	15.9	79.5

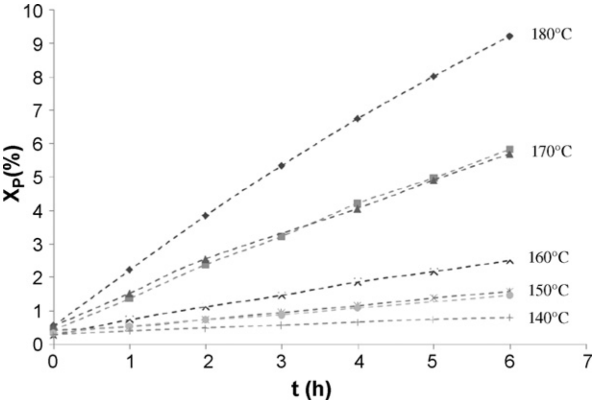

Fig. 1. 1-Pentanol conversion versus time at different temperature for Nafion/Si-C_13% catalyst.

ber, obtained with 1 g of catalyst at 180 °C after 6 h. None of the alumina-supported catalysts are presented, as they gave practically inappreciable (around 1%) 1-pentanol conversion.

It is to be noted that the inactivity of the Nafion-supported alumina catalysts was unexpected. However, similar results were obtained for etherification of C_6 α-olefins with methanol [3]. Probably, the low pore diameters, less than 5 nm, found for Nafion-supported catalyst on alumina and silica–alumina carriers, along with the acidic character of their surfaces, could explain such behavior. In fact, a slightly higher 1-pentanol conversion (1.15%) was achieved with the weakly acidic alumina carrier. As a consequence, the work will be continued only with silica-supported catalysts.

As for previous experiments, 1-pentanol conversion and initial reaction rate increased on increasing the acid capacity [15]. As acid capacity was given by Nafion resin content, the higher the Nafion content, the higher the conversion was. Selectivity to DNPE obtained at 180 °C after 6 h is shown in Table 3 for impregnated catalysts with 13% of Nafion, SAC-13 and Nafion NR50. As similar values were obtained with all of them, and also at higher Nafion amounts, it was concluded that the selectivity to ether was not affected by the carrier and the amount of Nafion impregnated. On the other hand, initial reaction rate per equivalent of H^+, or turnover number, r^0_{eq}, was clearly lower for NR50 than for the other catalysts. This fact could be caused by a better accessibility and distribution of the active centers on the silica. Considering only the three silica-derived catalysts, it seems that there is a relationship between the BET area, acid capacity, and conversion. Since all impregnated catalysts were prepared following the same method, it can be concluded that the amount of Nafion that was supported on the carrier was higher when the BET area of the carrier increased. In order to quantify the amount of supported Nafion on the carrier, the following parameters were defined:

$$\%\text{Nafion}_{\text{ac},j} = \frac{\text{acidity}_j}{\text{acidity}_{\text{NR50}}} \times 100 \qquad (1)$$

Table 4
%Nafion-supported estimated according to acid capacity, initial reaction rate and turnover

Catalyst	%Nafion$_{\text{ac}}$	%Nafion$_{r_0}$	%Nafion$_{\text{tn}}$
Nafion/Si-A_13%	9	11	125
Nafion/Si-B_13%	10	14	142
Nafion/Si-C_13%	10	13	133
Nafion NR50	100	100	100
SAC-13	17	33	197

$$\%\text{Nafion}_{r_j^0} = \frac{r_j^0}{r^0_{\text{NR50}}} \times 100 \qquad (2)$$

+

$$\%\text{Nafion}_{\text{tn},j} = \frac{r^0_{\text{eq},j}}{r^0_{\text{eq,NR50}}} \times 100 \qquad (3)$$

where subindexes ac, r^0, tn and j refer to acid capacity, initial reaction rate, turnover number and the catalyst carrier, respectively. Table 4 shows the values of these parameters.

It can be seen that supported %Nafion$_{\text{ac}}$ was always lower than the theoretical one (13%). Taking this value as a reference, an estimation of impregnation efficiency can be defined as follows:

$$\text{efficiency}_j = \frac{\%\text{Nafion}_{\text{ac},j}}{\%\text{Nafion}} \qquad (4)$$

Values of 0.67, 0.74 and 0.76 are obtained for Nafion/Si-A_13%, Nafion/Si-B_13%, Nafion/Si-C_13% catalysts, respectively, which means that part of the Nafion was not bonded to the carrier and/or some was neutralized during the process of anchoring on the surface. As an hypothesis, Nafion could be fixed through a bond formed when silanol groups of silica are neutralized by the sulfonic groups of Nafion. On the other hand, %Nafion$_{r_0,j}$, calculated with respect to initial reaction rate, was higher than %Nafion$_{\text{ac},j}$, which confirms the better behavior of the active centers of supported catalysts than for NR50. SAC-13, which is supposed to have a 13 wt% of Nafion on its silica matrix, showed higher conversions and acidity than expected. Now, the distribution and strength acidity of active centers is still better than in supported catalyst. The same conclusions can be obtained from %Nafion$_{\text{tn}}$ observations.

3.2. *Effect of the initial %Nafion and BET area*

A set of experiments was performed to seek the effect of the initial amount of Nafion on the carrier with the lowest BET area (Si-A) and on the carrier with the highest one (Si-C). The experimental conditions were as mentioned previously. Fig. 2 shows obtained acid capacity for each catalyst. Acid capacity of Nafion NR50 was taken as a reference with a value of 100% by considering it as a carrier with 100% of impregnated Nafion.

It can be seen that acid capacities showed a quasi linear trend with the initial amount of Nafion for both supporters. However, it was slightly higher for Si-C-derived catalysts at Nafion contents below 39%, and from this point the acid capacity was similar

Table 3
Impregnated catalyst (13% Nafion) compared with Nafion NR50 and SAC-13.

Catalyst	BET area ($m^2\,g^{-1}$)	Acid capacity (mequiv. $H^+\,g^{-1}$)	X_P (%)	S_{DNPE} (%)	r^0 (mol/(kg h))	r^0_{eq} (mol/(equiv. H^+ h))
Nafion/Si-A_13%	221.4	0.078	6.3	97.3	4.8	61
Nafion/Si-B_13%	306.4	0.086	8.2	98.0	6.0	70
Nafion/Si-C_13%	486.7	0.088	9.6	98.3	5.7	65
Nafion NR50	0.35	0.89	49.4	97.8	43.6	49.0
SAC-13	176.6	0.15	19.1	97.1	14.5	96.7

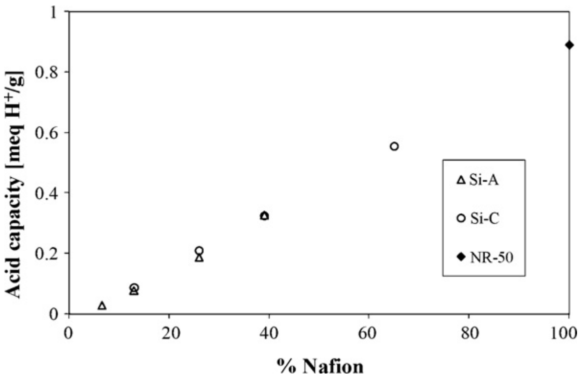

Fig. 2. Effect of initial %Nafion charge on the acid capacity of Si-A and Si–C supported catalysts.

for both carriers. *X*-axis intercepts of the linear relationships are 4.4 and 3.5% of Nafion, which could be considered as minimum threshold values to show acidity for silica-supported Nafion catalyst prepared by impregnation. In other words, such amounts could also be deemed as the ones used to anchor the Nafion on the silica surface.

Fig. 3 depicts 1-pentanol conversion after 6 h of experiment with impregnated catalysts versus the initial amount of Nafion. As data suggest, conversions for catalyst derived from Si-C were slightly higher than those derived of Si-A catalysts up to when acid capacity becomes similar (39% Nafion) for both catalysts. This fact agrees with the acid capacity values showed in Fig. 2. Furthermore, for 13%Nafion, where the three silicas can be compared, the highest conversion was achieved by the Si-C-derived catalyst, followed by Si-B and Si-A. Thus, the higher the BET surface area, the better the impregnation and catalytic activity. Conversion values were always lower than the achieved with NR50.

Fig. 4 shows the efficiency of the impregnation process for Si-A and Si-C derived catalysts obtained using Eqs. (1) and (4). Again, better results were obtained with the silica with larger surface area and, as already pointed above, efficiency values are very close to 1 for both carriers over 39% Nafion content.

In Fig. 5, it can be seen that higher turnover numbers are obtained for the silica with larger BET surface (Si-C), what confirms the conclusions abovementioned. Besides, the presence of a maximum can be noticed for both carriers, after which the turnover decreases on increasing the %Nafion until reaching NR50 level.

Fig. 6 tries to picture an ideal approximation to all these facts. A description of what occurs in the impregnation process could be explained as follows:

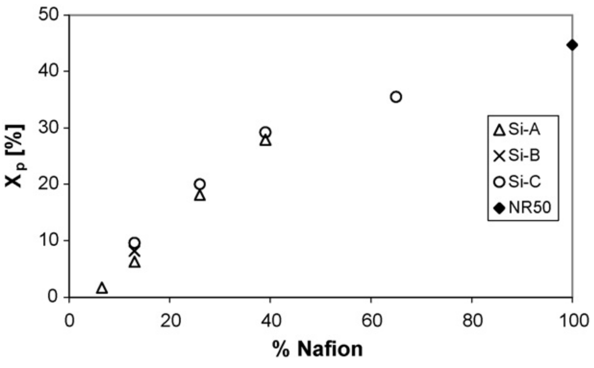

Fig. 3. 1-Pentanol conversion dependence on the initial amount of Nafion, after 6 h of experiment at 180 °C and using 1 g of catalyst.

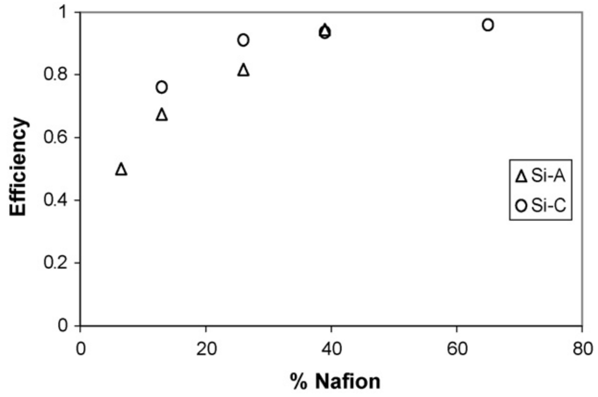

Fig. 4. Efficiency of impregnation process for Si-A and Si-C derived catalysts as a function of the initial %Nafion.

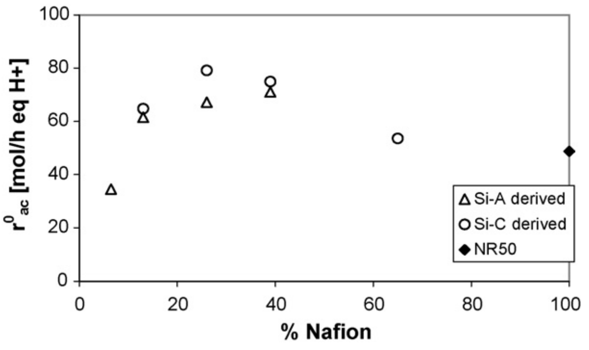

Fig. 5. Comparison of turnover number for Si-A and Si-C derived catalysts.

1. As %Nafion increases, the amount of Nafion-supported on the carrier increases, and so the activity on 1-pentanol dehydration. Firstly, the deposition is mainly bonded to the carrier, with neutralization of some sulfonic groups, and leading to low impregnation efficiencies (as defined in Eq. (4)).
2. When more Nafion is added, it covers all accessible surfaces, reaching an optimum on the turnover number, i.e., the actives sites are perfectly distributed and accessible.

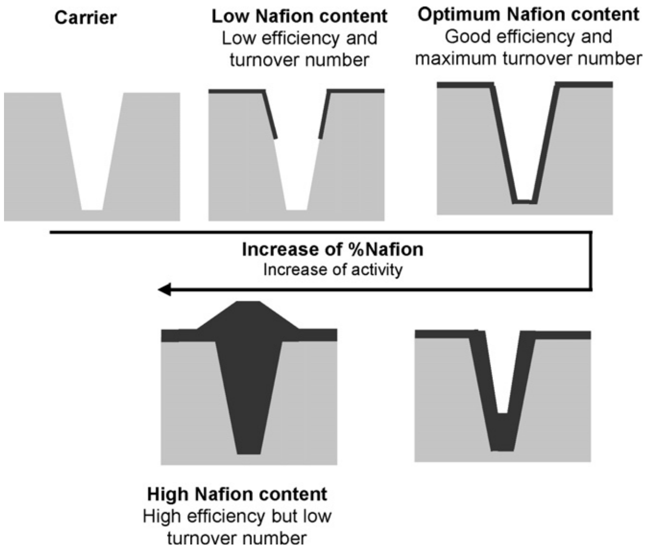

Fig. 6. Proposed scheme for Nafion deposition on carriers.

3. On increasing %Nafion, it would be mainly bonded to other Nafion chains, the efficiency increases, but it could block some pores or make them smaller. So the accessibility to the inner active centers would be more difficult, resulting in a decrease of the turnover number.
4. Finally, at higher %Nafion, impregnated catalysts would behave as NR50, with very high impregnation efficiencies and activities but low accessibility to inner active centers in non-polar medium.

BET analysis of impregnated catalysis backs up the exposed model.

For Si-A derived catalysts, the maximum efficiency is shifted to higher % Nafion because on more Nafion is needed to fill up the pores as the pore diameter is larger.

3.3. *Kinetics aspects*

Obtaining intrinsic reaction rate data involves running experiments free of mass transfer effects. In the present case, external mass transfer effect can be discarded because the small size of the reactor and the rather high agitation rate (500 rpm) [15]. Internal mass transfer can also be discarded for supported catalyst because of very small particle size (Table 1), giving values of Weisz–Prater modulus much lower than unity. The possible effect of internal mass transfer on the reaction rate could be shown for the catalyst with the highest size, namely, Nafion NR50 (2–2.8 mm) and SAC-13 (extrudates with length of 1–4.5 mm). For NR-50 the effect could also be discarded because data obtained in previous experiments showed that its activity was similar to N-117 resin, which is presented in slim membranes (0.17 mm width) for which it is rather difficult to find internal mass transfer effects. Besides, a significant swelling was observed for both two solids. As for SAC-13, no mass transfer effect is expected because of the observed swelling. Besides, its catalytic activity was higher than supposed, showing that, as it will be shown later, all active sites are accessible. All the same, an assessment and discussion of the internal mass transfer will be checked further down when apparent activation energy for each catalyst is estimated. Meanwhile, during the process of deducing and appointing a kinetic model, it will be assumed that there are no mass transfer effects.

The kinetic analysis will be done using activities instead of compounds concentration, because the estimated activities coefficients for DNPE and water are much higher than unity, whereas that of 1-pentanol is close to unity. The kinetic models considered in this work are based on those proposed in a previous work [16] for an ion-exchange resin at similar temperature. They are inferred from mechanisms wherein two 1-pentanol molecules, adsorbed each one on a single acid center, react to give DNPE and water adsorbed on a single center, assuming that the rate-limiting step is surface reaction.

For other temperature range and catalyst, another possibility is the existence of an Eley–Rideal mechanism in which one adsorbed molecule of 1-pentanol reacts with one non-adsorbed 1-pentanol molecule. This mechanism leads to the presence of the unity for the exponent of the denominator and it implies that either the term of ether or water in the denominator of the Langmuir-derived model vanishes [15,17].

As the equilibrium conversions are higher than 90% [18] in the whole working temperature range and X_P exceeded 40% only in a few experiments, it was assumed that the influence of the reverse reaction on the global rate was very reduced. Thus, the kinetic model could be reduced by deleting the contribution of the reverse reaction.

Table 5
Kinetic models considered

Class	Equation type	Kinetic equation
A	1: Water adsorption is not significant	$r = \dfrac{\hat{k}a_P^2}{(a_P + (K_D/K_P)a_D)^2}$
	2: DNPE adsorption is not significant	$r = \dfrac{\hat{k}a_P^2}{(a_P + (K_A/K_P)a_A)^2}$
	3: 1-Pentanol adsorption is not significant	$r = \dfrac{K_P^2\hat{k}a_P^2}{(K_D a_D + K_A a_W)^2}$
	4: Water and 1-pentanol adsorptions are not significant	$r = \dfrac{\hat{k}}{(K_D/K_P)^2}\left(\dfrac{a_P}{a_D}\right)^2$
	5: DNPE and 1-pentanol adsorptions are not significant	$r = \dfrac{\hat{k}}{(K_W/K_P)^2}\left(\dfrac{a_P}{a_W}\right)^2$
	6: Full equation	$r = \dfrac{\hat{k}a_P^2}{(a_P + (K_D/K_P)a_D + (K_A/K_P)a_W)^2}$
B	7: Water and DNPE adsorptions are not significant	$r = \dfrac{\hat{k}K_P^2a_P^2}{(1 + K_P a_P)^2}$
	8: Water and 1-pentanol adsorptions are not significant	$r = \dfrac{\hat{k}K_P^2a_P^2}{(1 + K_D a_D)^2}$
	9: DNPE and 1-pentanol adsorptions are not significant	$r = \dfrac{\hat{k}K_P^2a_P^2}{(1 + K_W a_W)^2}$
	10: Water adsorption is not significant	$r = \dfrac{\hat{k}K_P^2a_P^2}{(1 + K_P a_P + K_D a_D)^2}$
	11: DNPE adsorption is not significant	$r = \dfrac{\hat{k}K_P^2a_P^2}{(1 + K_P a_P + K_W a_W)^2}$
	12: 1-Pentanol adsorption is not significant	$r = \dfrac{\hat{k}K_P^2a_P^2}{(1 + K_D a_D + K_W a_W)^2}$
	13: Full equation	$r = \dfrac{\hat{k}K_P^2a_P^2}{(1 + K_P a_P + K_D a_D + K_W a_W)^2}$

Table 6
Comparison of activation energy with literature data [15]

Resin	E_a (kJ mol^{-1})
NR-50[a]	106 ± 5
N-117[a]	117 ± 7
SAC-13[a]	128 ± 1
Nafion/Si-C_13%[a]	122 ± 4
NR50	109 ± 3
CT224	119–128
Dow50	115 ± 2
A-36	110 ± 2
A-70	115 ± 5

[a] Present work.

On the basis of these simplifications, all the possible derived kinetic equations have been considered and grouped in two classes, as shown in Table 5, depending on if the amount of free active sites is negligible or not. For all the assayed catalyst and temperatures, the best model from a statistical standpoint (minimum sum of squares and random residuals) with physicochemical meaning (positive activation energy and negative adsorption enthalpies and entropies) appeared to be:

$$r = \frac{\hat{k} a_P^2}{(a_P + (K_D/K_P) a_D)^2} \tag{5}$$

The activation energy for the four catalysts was obtained from temperature dependence of rate constant, $\hat{k}$ (based on Arrhenius's law).

Table 6 shows that obtained activation energies are between those quoted in the literature for ion-exchange resins, which means, on the one hand, that Nafion dispersion on silica does not alter the dehydration mechanism and, on the other, that internal mass transfer effect is negligible, as abovementioned, for the supported catalyst, N-117 and SAC-13, since the same apparent activation energy is obtained, within the limits of the experimental error. However, this cannot be concluded for Nafion NR50, since lower apparent activation energy is obtained. Values for K_D/K_P ranging from 0.6 to close 3 do not allow reaching definitive conclusions about the adsorption strength of DNPE compared to 1-pentanol.

The absence of water in the adsorption term in Eq. (5) is another point to be commented, because it appeared on previous works [16]. This fact could be explained because water adsorbs preferably on sulfonic groups due to its high polarity, and it is possible that water occupies a large, but almost constant, amount of active sites. As a result, the effect of water cannot be noticed in the range of studied concentrations. However, its presence does affect the intrinsic rate constant because it is well known that water presence decreases the activity of the resins.

4. Conclusions

Silica-supported Nafion catalysts prepared by a reproducible impregnation method were very active and selective for 1-pentanol dehydration. A percentage of about 4% of impregnated Nafion is estimated to be necessary to anchor the polymer on the carrier surface. As for the effect of carrier it can deduced that the higher the BET surface area, the better the impregnation and catalytic activity. Conversion values were always lower than the achieved with NR50, but turnover numbers were always higher for impregnated catalysts. A turnover maximum was obtained for both carriers at about 26 wt% of Nafion content. A kinetic model in terms of compounds activities describes satisfactorily the experimental kinetic data. It is based on a mechanism in which the rate-determining step is the surface reaction between two adjacent adsorbed 1-pentanol molecules. The apparent activation energy was 106–128 kJ mol^{-1}.

References

[1] E.G. Lunsquist, K. Beshah, 213th ACS National Meeting, San Francisco, 1997.
[2] G.A. Olah, S.I. Pradeep, G.K.S. Prakash, Synthesis 7 (1986) 513–531.
[3] M.A. Harmer, W.E. Farneth, Q. Sun, J. Am. Chem. Soc. 118 (1996) 7708–7715.
[4] P. Botella, A. Corma, J.M. López-Nieto, J. Catal. 185 (1999) 371–377.
[5] Q. Sun, W.E. Farneth, M. Harmer, J. Catal. 164 (1996) 62–69.
[6] M.A. Harmer, Q. Sun, Appl. Catal. A: Gen. 221 (2001) 45–62.
[7] S. Wang, J.A. Guin, Energy Fuels 15 (2001) 666–670.
[8] M. Alvaro, A. Corma, D. Das, V. Fornés, H. García, Chem. Commun. 8 (2004) 956–957.
[9] A. Corma, H. García, Adv. Synth. Catal. 348 (2006) 1391–1412.
[10] B. Török, I. Kiricsi, A. Molnár, G.A. Olah, J. Catal. 193 (2000) 132–138.
[11] F. Frusteri, L. Spadaro, C. Espro, A. Parmaliana, F. Arena, J. Nat. Gas Chem. 11 (2002) 180–185.
[12] B. Rác, G. Mulas, A. Csongrádi, K. Lóki, A. Molnár, Appl. Catal. A: Gen. 282 (2005) 255–265.
[13] M. Marchionna, R. Patrini, D. Sanfilippo, A. Paggini, F. Giavazzi, L. Pellegrini, Stud. Surf. Sci. Catal. 136 (2001) 489–494 (Natural Gas Conversion VI).
[14] J. Tejero, F. Cunill, M. Iborra, J.F. Izquierdo, C. Fité, J. Mol. Catal. A: Chem. 182–183 (2002) 541–554.
[15] R. Bringué, M. Iborra, J. Tejero, J.F. Izquierdo, F. Cunill, C. Fité, V.J. Cruz, J. Catal. 244 (2006) 33–42.
[16] J. Tejero, C. Fité, M. Iborra, J.F. Izquierdo, R. Bringué, F. Cunill, Appl. Catal. A: Gen. 308 (2006) 223–230.
[17] F. Cunill, J. Tejero, C. Fité, M. Iborra, J.F. Izquierdo, Ind. Eng. Chem. Res. 44 (2005) 318–324.
[18] R. Bringué, J. Tejero, M. Iborra, J.F. Izquierdo, C. Fité, F. Cunill, Ind. Eng. Chem. Res. 46 (2007) 6865–6872.