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Pure hydrogen production from methylcyclohexane using a new high performance membrane reactor

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A high efficiency membrane reactor (Pd based) has been developed for hydrogen generation from methylcyclohexane, which is able to produce a pure hydrogen stream with a reaction yield close to 100%.

The concept of a multifunctional catalytic reactor integrating both a reactor and a separator in the same unit is attracting more and more interest due to the enormous advantages that such a method could provide: *i.e.* attainment of high conversion and product yield, simplified separation of products and cost reduction for plant equipment and maintenance. In particular, its application to hydrogen production reactions is one of the major challenges in catalysis.[1]

The reversible dehydrogenation reaction of methylcyclohexane (MCH) to produce toluene (TOL) and hydrogen (the so-called MTH cycle) was proposed several years ago as a solution for the storage, transport and distribution of hydrogen produced from renewable energy sources.[2] Hydrogen from solar and wind power could meet projected global energy demand in the future, though by now production from natural gas is the most economically favourable option. The recently renewed interest in alternative energy sources and energy carriers opens new prospects for this process to be applied as a feed system for fuel cells.[3] Here we describe the operation of a new highly H_2-selective Pd composite membrane reactor applied to the MCH dehydrogenation reaction using a Pt/Al_2O_3 catalyst. Up to now, membrane research has been strongly focused on the membrane material and much less on the membrane permeation process and its applications. The combined use of a catalytic reactor and a membrane for selective permeation of one of the products requires a multidisciplinary approach that has been studied from three different standpoints: the catalytic performance and stability of the catalyst for the studied reaction, the preparation of a H_2-selective Pd membrane with high permeance suitable to be applied to the reaction, and finally, the analysis of the optimum conditions to obtain a high performance system for H_2 production from MCH.

Regarding the heterogeneous catalysts, those based on platinum as the active phase have been extensively studied for the hydrogenation of aromatic compounds and its reverse process of dehydrogenation of cyclic paraffins due to their superior performance as compared to catalysts containing other transition metals. Furthermore, the combination of the metal with a high surface area acidic support has been shown to result in a highly active bifunctional catalyst over which a spillover reaction mechanism seems to greatly enhance the catalytic activity.[4] Thus, a Pt (0.83 wt%)/Al_2O_3 sample was prepared for the reaction by incipient wetness impregnation of a γ-Al_2O_3 support (S_{BET} = 180 $m^2\ g^{-1}$) with an aqueous solution of H_2PtCl_6. Then, it was dried overnight at room temperature and calcined in air at 773 K for 3 h. Before its use, the catalyst was reduced *in situ* at 673 K for 2 h under an H_2 stream, flushed with He and cooled to the required temperature. The metallic dispersion of the freshly reduced catalyst as determined from the H_2 uptake at room temperature was 78%. For catalytic tests, a gas regulation system, equipped with mass flow controllers and an evaporator-saturator maintained at constant temperature to feed MCH, was used. Usually, a gaseous mixture containing 4.7 vol% MCH in He was the reactant. A gas chromatograph with TCD and FID detectors allowed analysis of the gas phase composition coming from the reactor outlet (retentate side, permeate side or both together) or bypassing the reactor. The temperature in the catalytic bed was determined by a K-type thermocouple located inside the reactor whereas the temperature in the furnace was controlled by a second thermocouple placed close to its inner wall.

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Preliminary catalytic tests were carried out under differential conditions in the temperature range between 453 and 673 K. At temperatures below 623 K, TOL and H_2 were obtained as reaction products. Only traces of CH_4 and hexane were detected in amounts below 0.1 vol%. The specific activities of the catalyst for this MCH dehydrogenation reaction measured at 473 and 523 K were 1.6 and 6.3 μmol $g^{-1}\ s^{-1}$, respectively. At 648 K the amount of by-products increased up to 2.0 vol% and a slight deactivation process began. The rate of deactivation was observed to increase progressively with temperature along with the proportion of by-products. At 673 K, a freshly reduced sample of catalyst completely lost its activity under the used conditions in less than 1 h.† It must be taken into account that frequently, for paraffin dehydrogenation experiments, H_2 is added in quantities of 10–20 mol% in order to avoid or delay catalyst deactivation. However, when high yields are required, a H_2 partial pressure increase in the reaction medium reduces the equilibrium conversion and higher temperatures are required.

Aiming to determine the long-term stability of the catalyst under our conditions, a sample was kept in reaction for a period of 48 h at 573 K showing no activity loss. Then, the sample was cooled in He and a temperature programmed hydrogenation was performed. CH_4 was the only hydrogenation product detected and it was formed at temperatures above 573 K. A total amount of 0.34 mmol g^{-1} was obtained by hydrogenation up to 873 K. These carbonaceous deposits hydrogenated at high temperatures are probably located at the support surface, given that no activity loss was observed in the catalyst. Therefore, considering the best conditions for catalyst operation, the reaction temperature should not surpass 623 K.

For the conditions used (atmospheric pressure and MCH partial pressure in feed gas stream of 4.8 kPa) thermodynamics predicts equilibrium conversions over 99% at temperatures above 523 K. Therefore, there is an interval of temperatures between 523 and 623 K that ensures operation at high conversion level without catalyst deactivation.

In order to separate the hydrogen produced from the reaction medium, Pd and Pd alloys based dense membranes are usually the preferred choice because of their high permselectivity. The mechanism of H_2 permeation through this type of membranes takes place *via* a consecutive process of dissociative chemisorption, dissolution, diffusion of atomic hydrogen through the Pd film and finally desorption from the permeated side. Aiming to obtain high permeance values and high mechanical resistance, a thin Pd film was deposited by the electroless plating technique on the surface of a porous 316L stainless-steel support (Mott Corp.). According to the manufacturer's specifications the grade of the PSS was 0.5 μm with an average pore diameter of 3 μm and a porosity of 17%. By considering the specific activity of the catalyst and its specific volume, the permeable zone of the membrane module was designed to have approximately a volume of 2 cm^3 (OD: 9.5 mm, wall thickness: 1.6 mm, length: 60 mm). The porous part was welded at both extremes to two 15 cm long pieces of non-porous 316L stainless-steel.

The membrane synthesis involved a cleaning process of the support followed by successive sensitising, activation and plating cycles according to the procedure described by Mardilovich *et al.*[5] These plating cycles, followed by drying at 393 K, were repeated until no permeation of inert gas was detected through the membrane at room temperature. The Pd layer obtained in this way had a thickness of 11.9 μm as estimated from the weight increase of the module. The tube was fixed to a stainless-steel shell with an inlet and an outlet to feed a sweep gas stream. The use of independent Swagelok fittings with graphite ferrules to integrate the membrane in the reactor and to connect it to the experimental set-up provided a gas-tight sealing of easy handling, which avoided leakage problems between the retentate and the permeate sides.

H_2 permeation experiments were carried out at temperatures above 573 K to avoid H_2 embrittlement. Special care was taken during the heating and cooling processes, which were carried out at low rates (1 K min^{-1}) under inert gas flow. At 573 and 673 K the H_2 permeated flows for a transmembrane pressure of 40 kPa were 8.36×10^{-5} and 9.52×10^{-5} mol s^{-1}, respectively.

For reaction tests, 1 g of catalyst was loaded inside the membrane tube all along the permeation zone and the experimental conditions were changed in order to explore the system performance. Four different parameters were tested to look for optimum operation of the system: *i.e.* the MCH feed flow rate at the reaction side, the sweep gas flow rate at the shell side, the operation temperature and the pressure in the reaction side. As is illustrated in Fig. 1, for a constant sweep gas stream of 3 l h^{-1} and at 573 K, the system shows improved efficiency when using low MCH feeding flow rates. As regard to a conventional reactor, for which the distribution of components at the reaction side would correspond at complete conversion to 25% TOL and 75% H_2, the TOL concentration can be doubled in this membrane reactor by reducing the MCH feeding rate to values below 0.5 μmol s^{-1}. For high MCH feed flow rates, due to the low H_2 separation efficiency, the products distribution in the reaction side tends to resemble the conditions of a conventional reactor. It should be noticed that, even when the catalytic activity data indicates that at 573 K the amount of catalyst should be enough to obtain complete reactant conversion in all the feeding conditions interval explored, the highly endothermic nature of the reaction causes a temperature decrease in the catalytic bed when increasing the reactant amount too much.[6] This effect leads the system to operate under non-isothermal conditions, for which the temperature difference between the catalytic bed and the external reactor wall can reach as much as 50 K at the highest MCH feeding rate. Thus, the MCH feed rate was finally fixed at 1.75 μmol s^{-1}.

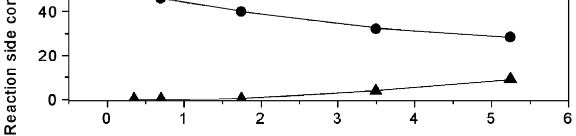

Fig. 1 Products distribution at the reaction side as a function of the MCH feed rate. H_2 (■), TOL (●), MCH (▲). Reaction temperature: 573 K. Sweep gas feed stream: 3 l h^{-1}.

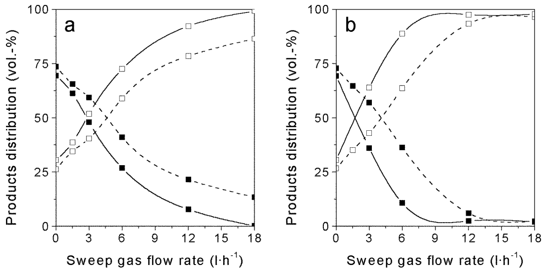

Fig. 2 Products distribution at the reaction side as a function of the sweep gas flow rate. MCH feeding rate: 1.75 μmol s^{-1}. H_2 (□); TOL (■); dotted lines: 101 kPa; solid lines: 142 kPa; (a): 573 K; (b): 623 K.

Both the increase in the sweep stream flow rate and the increment of pressure at the reaction side improve the H_2 removal efficiency by favouring hydrogen diffusion through the Pd film, as shown in Fig. 2. At 623 K and 142 kPa of pressure at the reaction side, *ca.* 99% of the H_2 produced in the reaction could be extracted from the reaction side with a sweep stream of 9 l h^{-1}. Under those conditions, 0.42 l h^{-1} of H_2 are obtained at the shell side at partial pressure of 4.5 kPa whereas TOL remains at the reaction side along with the 1% unpermeated H_2 of the whole amount produced (reaction side composition: 97 vol% TOL, 3 vol% H_2). It must be mentioned that the system showed excellent long-term stability by operating continuously under stationary conditions for more than 96 h. By increasing the temperature up to 648 K a slight decrease in conversion was observed along with the formation of small quantities of by-products. This deactivation became increasingly pronounced as far as the H_2 partial pressure in the reaction side decreased for high sweep gas flow rates. This indicates that the limit of temperature for maintaining a good catalyst stability must be fixed at 623 K.

In conclusion, a high performance membrane reactor for H_2 production from MCH has been developed. Three fundamental points have been considered for the study: the catalyst performance, the membrane synthesis and its permeance, and the working conditions. The designed system showed excellent long-term stability within the temperature range between 573 and 623 K operating at yields close to 100%. The use of a palladium/stainless-steel composite membrane for selective H_2 separation confers good thermal and mechanical resistance to the module and allows an easy handling of the system. High efficiency for H_2 recovery has been obtained by adjusting the sweep gas flow rate. The application of a vacuum pump to remove H_2 from the shell side could even improve the system by producing an undiluted pure H_2 stream.

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Notes and references

† Similar behaviours are reported in the literature for this type of catalysts, where these deactivation processes are attributed to a stronger adsorption of the aromatic compounds at those temperatures, which finally decompose to form coke on the Pt surface.[7]

1 J. N. Armor, *J. Membr. Sci.*, 1998, **147**, 217.
2 N. F. Grünenfelder and Th. H. Schucan, *Int. J. Hydrogen Energy*, 1989, **14**(8), 579; S. Tshudin, T. Shido, R. Prins and A. Wokaun, *J. Catal.*, 1999, **181**, 113.
3 G. W. H. Scherer, E. Newson and A. Wokaun, *Int. J. Hydrogen Energy*, 1999, **24**, 1157.
4 P. Antonucci, N. Van Truong, N. Giordano and R. Maggiore, *J. Catal.*, 1982, **75**, 140; P. Reyes, M. Oportus, G. Pecchi, R. Fréty and B. Moraweck, *Catal. Lett.*, 1996, **37**, 193.
5 P. P. Mardilovich, Y. She, Y. H. Ma and M.-H. Rei, *AIChE J.*, 1998, **44**(2), 310.
6 J. K. Ali and A. Baiker, *Appl. Catal. A: Gen.*, 1997, **155**, 41.
7 L. I. Ali, A-G. A. Ali, S. M. Aboul-Fotouh and A. K. Aboul-Gheit, *Appl. Catal. A: Gen.*, 1999, **177**, 99.