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High-throughput spatial resolved tests over planar model catalyst libraries: A novel reactor approach

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ABSTRACT

The development of two different in-flow scanning reactors that could be successfully used for testing the activity of planar catalysts are presented. The first one, which allows stepwise scans, is composed by a reactor probe which is sealed over the planar system using a Teflon or Viton mask that also defines the reaction chamber volume. The presence of the sealing mask causes various problems that are solved with the second prototype. In this reactor a controlled leakage system is used instead of the Viton seal, which allows continuous scanning test on a reduced circular area (12.5 mm^2). In this paper the results of preliminary tests over palladium based catalysts are presented in order to discuss the applicability of both reactors.

1. Introduction

The design of a new material for heterogeneous catalysis is often a long, impervious and complex path. What variable weight more on the activity of a metal based catalyst? Metal/substrate ratio? Morphology? Metal properties? Whatever? Which catalyst is reasonable to spend money, time, work for? In material science, as for drugs design, a classical trial-and-error approach is a big "*monkey business*". Several different parameters could influence the final resulting properties and often the effects are not singled cause-and-effect but are the result of complex and misunderstood synergy. A classical approach, studying One Variable At a Time (OVAT) implies several hundred of singled manufactured catalyst tested separately and a large database of results. Huge time is probably required and the result does not care about interaction. As an alternative, a smart approach is offered coupling combinatorial chemistry and high-throughput screening (HTS) methodologies [1–2]. This strategy consists of a carefully design of catalyst samples that are characterize by a systematically well-know variation of one or more properties on the surface. The catalytic tests are then performed under spatial resolved condition to link the observed activity with the designed catalyst structure in that limited area. The experimental data are processed to identify the best structure relate to the reaction test. The best catalyst in this first screening is now ready to the next step to optimize other properties. The process is looped several time until the required activity is reached and the catalyst is fully optimized. This approach saves a lot of time with respect to a traditional way, it is more accurate but too much time/money consuming. A further smarter approach is offered by experimental design. The combinatorial chemistry, used in a primitive and intuitive approach, allows a step-by-step optimization that discriminates the best sample among a family defined by a single varied property (i.e. among different thickness or different dimension). In a Design of Experiment (DoE) [3] a set of limited experiments is designed varying all the relevant parameters systematically at the same time. Data are treated all together in a multivariate model to find the best solution, if it exists. Otherwise DoE tells you that there is not a solution for the problem in that imposed terms. This approach represents probably the most elegant and fulfill strategy in combinatorial science. The catalysts used in combinatorial chemistry are named "*catalytic libraries*" because they lock up different catalytic activity spatial located on the surface: the total activity is a sum of the single catalyst activity, the local activity is structure sensitive as well. The combinatorial approach could save time and work but requires a fine plan of every step: the design of the catalyst, the design of a suitable analysis system and the definition of a fast and accurate data handle statistic. Each of these steps claims an extended investigation that has to be linked with the catalyst properties. Reactor's design is the core of this screening and testing approach because through it data are produced and all the analytical works could be carried out. In a classical heterogeneous catalytic test on powder, the gas reactants pass through the catalyst and the contact time/surface is quite high. On a planar

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system, the gas–metal interaction takes place on a limited surface and the relative contact times are very short. The available manufacture methodologies, especially for physical deposition methods (as Physical Vapor Deposition PVD, cluster deposition or Electron Beam Lithography EBL methodologies) [4–6], couple a very good quality with a slow and tricky production rate. The "*value*" of each sample requires robust and well built test reactors. This platform reactor demand had been the topic of this work. The basic reactor design developed in this work follows the scanning probe approach. As the SPM systems (scanning probe microscopy) scan the surface touching it in order to describe the morphology or roughness, as in our reactors a reactive gas mixture (the gas probe) caress the surface well in order to characterize locally the catalytic activity of the surface itself. This kind of approach needs an appropriate micro-reactor system, which should be able to handle small surface areas, small active surfaces, small gas flows and high detection sensitivity [7]. Moreover the catalyst has to be heated in a large range of temperature to allow the test reaction and in-situ pre-treatment and/or cleaning. The dimension, the shape and the reactor geometry controls also the gas-surface contact times, the relative experiment time and could suppress the indiffusion regime. In this type of small volume reactor the gas flow regime has to be free by indiffusion to ensure that the gas inlet concentration is stable along the reactor length.

Operational and analysis conditions have to be reproducible and, last but not least, the sample mounting should be easy and friendly as much as possible. Taking well-fixed these points, two small volume reactor prototypes different from each other in construction and final use were designed and manufactured. The work was arranged with a problem-solving approach: the custom reactors were built around the real sample requirements. Another important parameter was offered by reaction requirements. The hydrogenation of 1,3-butadiene over palladium was chosen as test reaction as it offers high size selectivity at low reaction temperatures (100 °C ca.) [8]. Anyway, the final result was a platform-system, quite flexible and adjustable to different samples and, of course, to other test reactions. Both reactors were fitted on-line to a quadrupole mass analyzer and the gas handling system permits to handle different gas mixtures controlling the temperature, the flow rate and the pressure. With respect to other available HTS reactors [9–10] the application field and the system flexibility are expanded. The scan capability is expanded on continuous catalytic libraries [11] besides a concrete steps surface scan. Catalytic tests under pressure could be performed controlling the pressure of the chamber box enclosure in which the entire reactor is placed. The reactor prototype.01 allows both inflow- and batch-mode tests in order to characterize also a low catalytic activity that requires high contact time and very small flow rates. The reactor probe of prototype.02, heated as the sample, allows an exclusive local reaction and the gas product mix is diluted in situ and sampled by a capillary directly connected with the downstream MS analyzing system. The diluted gas mixture is directly injected into the MS analyzer that also provides the outlet pumping stage.

2. Experimental

2.1. Planar samples synthesis

Tested planar catalysts had different synthesis pathways but all of them are palladium thin films deposited on smooth planar silicon wafers. The 5 nm and the 20 nm thick palladium films, tested respectively with prototype.01 and prototype.02, were produced by Supersonic Cluster Beam Deposition (SCBD) methodology [12] at LGM Laboratory [13] (*Laboratorio Getti Molecolari*), at the Physics Department of the University of Milan. The 20 nm thick palladium film tested on prototype.01 was produced via direct metal sputtering. The AFM (atomic force microscopy) characterization of Pd film specimens highlighted the different roughness of the surfaces (Fig. 1). As expected, the roughness of the 5 nm thick film is higher than the 20 nm thick one. In order to deposit a thicker film, cluster deposition is simply reiterate in time, smoothing continuously the surface of each layer. The 5 nm thick film shows a mean roughness (Ra) of 0.787 nm and the 20 nm thick film shows a mean roughness of 0.601 nm. The "DI Dimension 3000 SPM" instrument driven by NanoScope software were used to AFM data collection (Fig. 1.).

2.2. Catalytic tests

The model reaction used was the hydrogenation of 1,3-butadiene. Small palladium particles promote the mono-hydrogenation process to butene as the main product, while relatively big particles promote the complete hydrogenation to *n*-butane. [14] The reaction was followed monitoring 1,3-butadiene and hydrogen as reagents (on mass channel 53 and 2 amu, respectively), while butene and butane as products (on mass channel 56 and 58 amu, respectively). The mass signals of argon and helium (on mass channel 20 and 4 amu, respectively) were monitored as carrier gas. All the planar samples were pre-treated in-situ in order to fully reduce the metal particles and to clean-up the surface. The reducing step takes place at 100 °C under H_2 (0.5% in He–10 mL/min) in flow condition for 90 min. The sample is then cooled in flowing He down to 50 °C. Sample is now ready to catalytic test. All the gases used to feed both the reactors inlet were manipulated with the same gas handling [15] system. Prototype.01 operational parameters are: inlet gas flow = 1.0 mL/min; outlet gas flow = 0.8 mL/min; testing temperature values = 50–100–150–200 °C. Prototype.02 operational parameters are: inlet gas flow = 1.5 mL/min; outlet gas flow = 1.5 mL/min; testing temperature values = 50–80–100–110 °C.

In both prototypes the reactor probe and the planar catalyst holder are heated separately: in both cases the two different heating elements and their housing were designed to guarantee a uniform temperature of the catalyst surface and of the probe. Temperature gradients of less than 2 °C were recorded at 200 °C on the entire catalyst surface. Quadrupole operational parameters were optimized to obtain high sensitivities on butadiene signals. The QMS analyzer is an HIDEN-HPR20.

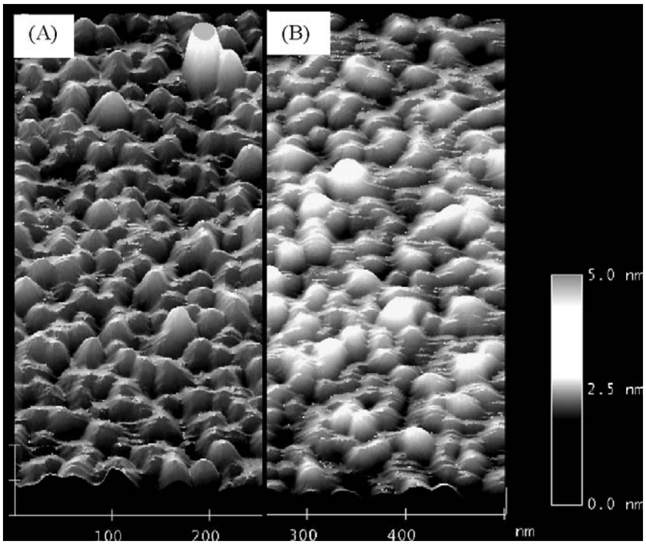

Fig. 1. AFM 3D images of the surfaces of (A) 5 nm thick Pd film; (B) 20 nm thick Pd film.

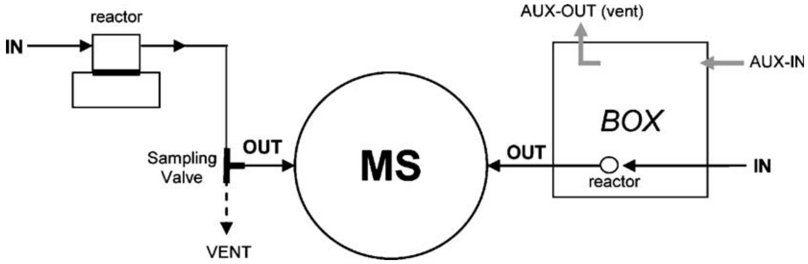

Fig. 2. Reactors/mass analyzer interfaces.

3. Results and discussion

The development of the final "true" scanning reactor prototype that we present here, started with the setting up of a first prototype which is not a truly scanning reactor but rather a step-wise reactor. Anyway even the first prototype will be presented here because it was fundamental to assess the basic working principle of this reactor and also because its applicability is partially complementary to the ones of the second prototype. As we will show later, with the second prototype we tried to overcome the limitations imposed by the first model, designing a completely new system.

3.1. Prototype.01 – overview

The first prototype was used to set the correct dimension of the reaction chamber and to eventually highlight critical points to be carefully evaluated. The overall assembly is mainly composed by three distinct parts: the steel reactor probe (or the reactor head), the seal mask and the aluminum heated sample support (Fig. 3).

Both the reactor probe and the aluminum sample support (upper and lower parts of Fig. 3, respectively) are heated and thermostatted separately, to ensure a homogeneous temperature of the entire assembly. The narrow volume reaction chamber is defined by the confined volume between the catalyst surface and the reactor probe which, in turns, can be tuned through a proper selection of the thickness of the sealing mask that define the perimetrical chamber's wall. PTFE was initially used as building material for the sealing mask, but we experienced some planar samples breaks due to the excessive force that should be applied to the probe to guarantee gas tight conditions. Actually PTFE is not used anymore, as it is substituted by new sealing mask cut out from a Viton foil that coupled a more gentle contact on supported wafer with excellent chemical and thermal propriety, comparable with Teflon. For the data presented in this work we have used a 0.5 mm thick Viton foil which delimits a 2 mm × 20 mm catalytic rectangular surface. Considering a measured 0.2 mm Viton compression, the total reaction chamber volume is thus equal to 12 mm^3: this means that reasonable contact times (0.7 s for a 1 mL/min total feed flow) are expected with this reactor geometry. The equipment parts sketched Fig. 3 are completed by two 1/8" o.d. inlet/outlet welded tubes and by a probe alignment guide (not shown).

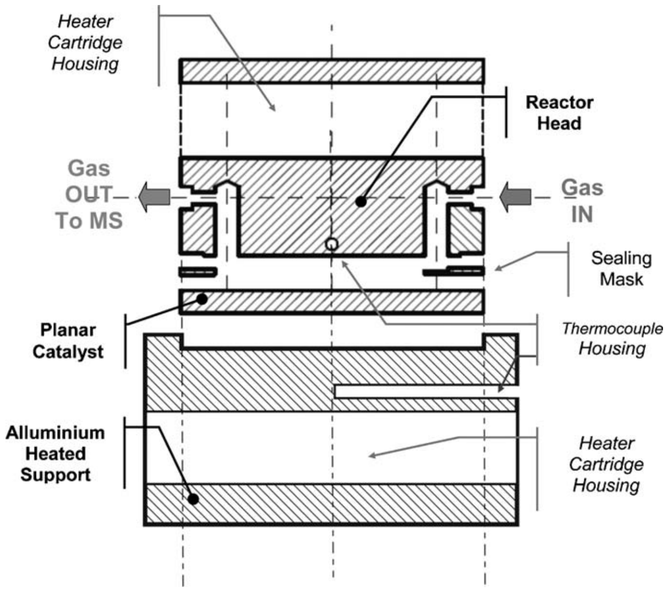

Fig. 3. Prototype.01; overall design.

The utilization of a commonly used jet-separator pumped MS interface is not necessary in this situation as the outlet flows are consistent with the intake MS capability: as the result the original jet separator interface was removed and replaced with a zero dead-volume heated sampling metering valve, which allows a fine control of the MS uptake (Fig. 2).

Although the "sensed" surface is only 2 mm large, the dimensions of the sealing mask equals the dimensions of the reactor probe (10 mm × 26 mm), and represent the lower sample size limit that can be tested with prototype.01. The presence of this sealing mask implies also that this reactor is not able to scan continuously a surface but, rather, it can only perform a limited step-by-step scan.

3.2. Prototype.01 – evaluation of the system performances

Three samples were tested with prototype.01: a clean Si blank reference sample, a 5 nm thick Pd film and a 20 nm thick Pd film. Both Pd films were deposited on planar Si wafer, while two different deposition methodologies were used to produce them (see Section 2). In this way two morphologically different Pd surfaces can be tested to evaluate differences in catalytic performances. Of course a particle size (and shape) dependent reaction, such as butadiene hydrogenation, was chosen for the same purposes.

All planar samples were preliminary activated as described in the experimental section. The test on Si blank reference sample was performed to check the system background activity and reveals that no butadiene conversion is observed up to the maximum temperature value (200 °C). The raw normalized data concerning the catalytic test performed over the 20 nm thick Pd film are reported in Fig. 4(B).

In Fig. 4(A) are reported the overall mean butadiene conversion calculated from the same catalytic test. As it can be seen, butene production is effective even at 50 °C, while a significant butane production can be observed only at 200 °C. Selectivity toward butene is almost 100% up to 150 °C, while it decreases at 200 °C. Starting from 150 °C the system shows a rapid de-activation which is even more marked at 200 °C. Considering that this catalyst does not regain its activity when cooled down to lower temperature, a strong de-activation process is active in these experimental conditions. As a profound structural change in the Pd film

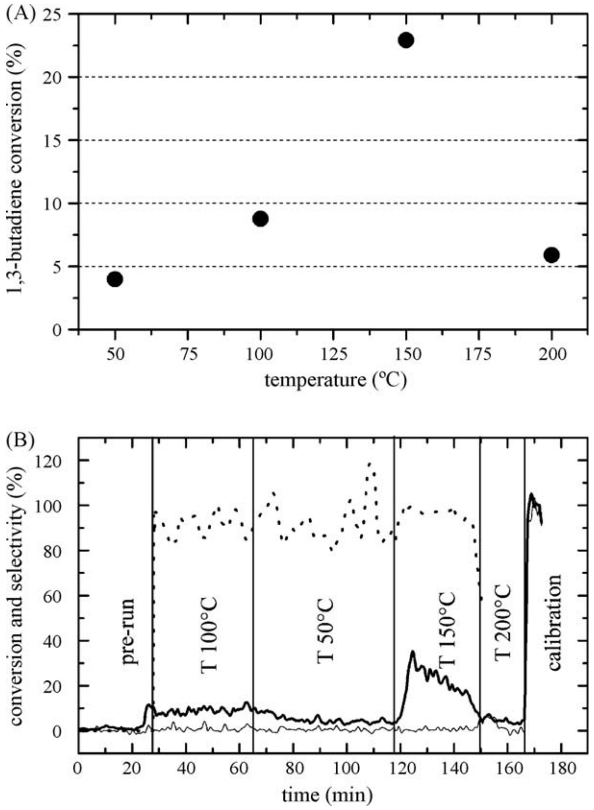

Fig. 4. (A) averaged catalytic butadiene conversions of the 20 nm Pd film at different temperatures – (B) conversions and selectivities of the 20 nm thick Pd film catalyst at different temperatures: thick line = butene conversion; thin line = butane conversion; dashed line = butene selectivity.

morphology is not expected to be operative at these relatively low temperatures, we may tentatively suggest that the observed deactivation is caused by the release of organic substances from the Viton sealing mask that could dope the catalyst. The 5 nm Pd film sample was instead completely inactive between 50 and 200 °C using exactly the same catalytic conditions: this means that the morphology of the superficial Pd particles of this sample is not adequate for this reaction. From all the above reported preliminary tests we can thus derive some qualitative and quantitative considerations about this prototype: (i) the system is well dimensioned for the chosen model reaction and it seems to be appropriate to evaluate structure/activity correlations of investigated samples; (ii) the presence of a Viton mask does not allow to work for long periods at temperature as high as 150 °C, limiting so thus the reactions that could be studied with this system; (iii) independently from reaction temperature, the portions of catalytic surfaces which are in direct contact with the same mask cannot be tested during a step wise movement, which implies that the step size value cannot be lower than 10 mm even if the sensed surface is only 2 mm large.

All these drawbacks strongly limit the utilization of this system and the second prototype was designed to overcome all these problems. In any case it should be noted that this system (due to the fact that it is gas tight) can work both in flow and in batch mode, which can be very useful to study reactions that require higher contact times.

3.3. Prototype.02 – overview

Most of the problems encountered with the first prototype relates to the utilization of the sealing mask, that therefore should be avoided. As we have cited before, there is only one example of scanning reactor without sealing masks, that is mainly composed by concentric quartz tubes where a vacuum pumping system is used to insulate the small reactor atmosphere from the outer environment [9]. Since the utilization of vacuum is not suitable for our purposes we moved in a different direction which in principle could allow the utilization of the reactor even under pressurized conditions substantially avoiding the presence of relevant pressure gradients between the reaction chamber and the outer environment.

In Prototype.02 this environmental insulation problem was overcame designing the reactor using a sort of "*air cushion*", or better, a controlled gas leakage system. This concept is qualitatively sketched in Fig. 5.

The reactor probe is positioned over the surface to be tested at a sufficiently low distance to reduce the mixing between the inner and the outer atmosphere. Moreover the outer atmosphere could be slightly over pressurized (usually less than 10 mbar) to produce a controlled leakage from the outer to the inner part of the reactor. This strategy could be also reversed to produce a leakage in the opposite direction. To achieve this condition a fine control of the distance between the rector probe and the planar catalysts must be ensured. The new prototype mainly consists of two parts: the sample holder and the reactor probe (Fig. 5). The sample holder is mounted on a tunable *XYZ* stage (opto sigma – straightness of travel <3 μm on each axis) to set the relative 3D position with respect to the reactor probe which is mounted on a fixed position arm. The *XYZ* stage was chosen to gain a fine control of the distance between the two parts and it easily allows the setting up of distances with a precision and accuracy that is lower that 0.01 mm. Basically the sample holder was designed to immobilize the

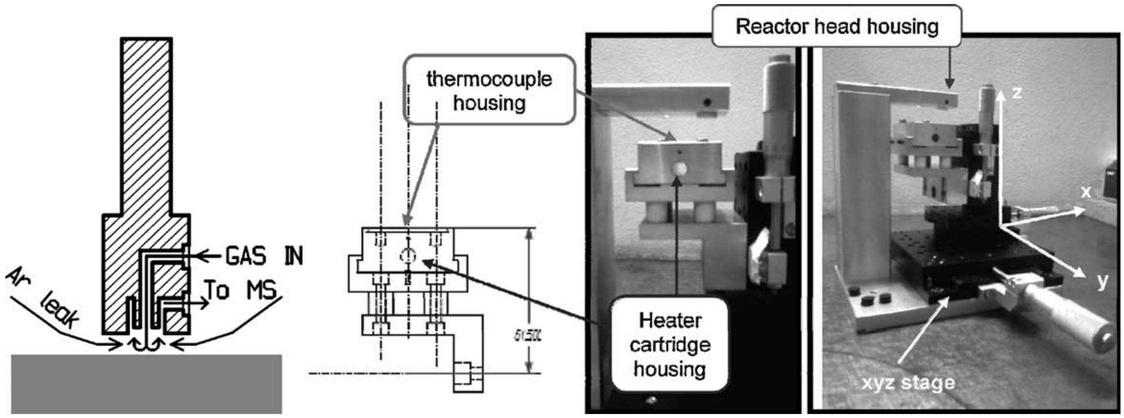

Fig. 5. Prototype.02 – controlled leakage scheme and sample holder overall design.

sample to the position it plumbs with respect to the reactor probe axis, to heat up the sample and to thermally insulate the heated part from the XYZ stage. The reactor probe is a little steel cylinder (7 mm o.d.) dug to obtain a little open chamber on the bottom which can test a 12.5 mm^2 circular surface. This sensed surface value was chosen considering that the data collected with prototype .01 (that reflects the activity of a 40 mm^2 surface) tell us that a three-fold decreasing of the sensed surface will lead to still acceptable results. In the center of this chamber, a hose keeps the feed gas (reactant gas mix) and on the side another hose takes off the gas mix probe-sample after reaction. As in the previous prototype both the sample holder and the reactor probe are thermostatted separately.

The entire system (reactor probe and sample holder) is located in a sealed PMMA box whose inner atmosphere is continuously purged with an Ar flow from an auxiliary inlet located in the bottom part of the box.

To perform a catalytic test the following sequence is normally adopted: (i) the sample is loaded under air, then the PMMA box is sealed and purged with Ar until a good quality of the box is reached (as monitored by the MS analyzer); (ii) the reactor probe is draw up to the sample surface at a proper distance; (iii) if necessary, the catalyst is activated under proper temperature and gas composition conditions; (iv) the reactant gas mix is routed on the active sample area through the Gas IN port; (v) the gaseous products (eventually diluted by the external Ar atmosphere) which leave the reaction chamber through the Gas OUT port are analyzed by the downstream mass spectrometer (Fig. 2).

3.4. Prototype.02 – behavior of the controlled leakage system

In the controlled leakage design inner vs. outer gas mixings occurs in-situ just above the reactive catalysts surface and is mainly determined by several factors: (i) the utilization of different gas-in, gas-out flows; (ii) the distance between the probe and the surface; (iii) the temperature of the gases; (iv) the presence of concentration and pressure gradients. Most of these parameters can be easily adjusted to tune leakage conditions. As an example the outlet flow rate is generated by the UHV system of the mass spectrometer and can be regulated by the proper metering valve. To preliminary evaluate the behavior of the controlled leakage system, we performed a pressure- and flow-balanced leakage test where only the distance between the probe and the surface is varied in the range 40–100 μm. This test (Fig. 6) was carried out following the 1,3-butadiene signals on channel mass 53 amu, with a fixed IN and OUT gas flow rate of 1.5 mL/min as in the normal operational setting, breaking apart each concrete gap step with an initial 1-min-pulse of the IN gas at 5 mL/min. This gas pulse is clearly observable on graph where a spike signal was produced. The pulse helped the system to fast recover the local equilibrium condition in order to obtain a stable useful signal. Later each reactor re-position signals were accumulated for 20 min c.a. Test were performed at room temperature (25 °C) on a clean and flat silicon surface.

The high flow rate pulse was up to saturate the small volume beneath the reactor probe, to break the local pressure equilibrium and to limit the back stream external gas leakage. At every distant gap in the test range the spike peak at 5 mL/min correspond almost to the undiluted 1,3-butadiene signal (about 416 ppmv). Thus, from the recorded butadiene concentration it is possible to gain a rough estimation of the dilution effect which, as expected, increases with the probe/catalyst gap. Starting from an undiluted concentration of 416 ppmv, the observed concentrations varies from about 290 to 240 ppmv in the distance range 40–100 μm, that correspond to a relative concentration decrease ranging from 30% to 42%, respectively. Of course this dilution can be enhanced or lowered by a proper modification of the other parameters. In any case, for our goals the insulation level reachable with balanced pressures and flows is fully satisfactory.

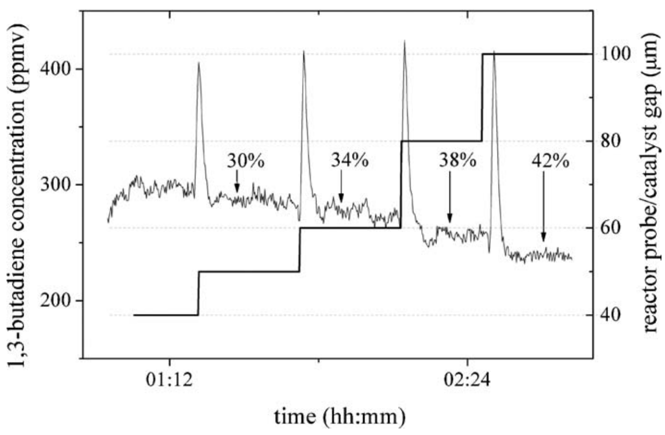

Fig. 6. Butadiene concentrations (thin line) recorded at different. Reactor probe/surface distance gap (thick line). Reported percentages relates to the relative signal decrease with respect to undiluted 1,3-butadiene.

3.5. Prototype.02 – catalytic tests

A Si blank reference sample and a 20 nm thick Pd film deposited on Si wafer were tested using the conditions reported in the experimental section.The blank reference (Si) sample is totally inactive, and signal shows a little increasing due to thermal effects. The Pd based catalyst shows a significant activity starting from about 60 °C as shown in Fig. 7(B), where butene signal increases with respect to the consumed butadiene. At 100 °C the butadiene signals almost decreases to one half its initial magnitude, while the

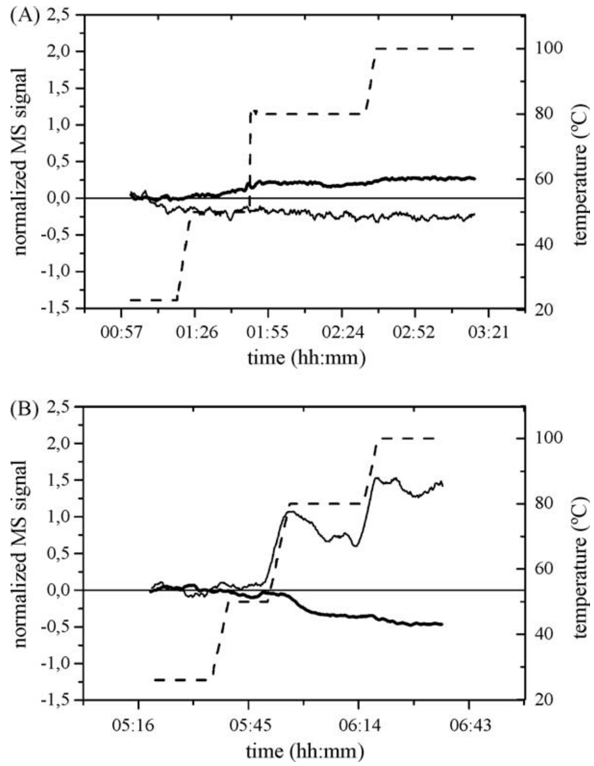

Fig. 7. Normalized butadiene signals (bold line) and normalized butane signal (thin line) trend during conversion – temperature program profile (dashed line) – (A) Si blank reference sample (B) 20 nm thick palladium film deposited on Si by SBCD.

butane mass channel at 58 amu, does not significantly increase with respect to the background noise. This preliminary catalytic test show that the utilized experimental conditions together with the design of the reactor and the well balanced residence time are achieved. It is evident that this system is completely free from the problems encountered with prototype.01: here a step-wise surface scan as well as a true continuous scan could be easily carried out.

Finally, we would like to underline that the utilisation of an high precision *XYZ* stage that can be easily motorized with PC controlled stepping motors, will allow to perform any desired scan pattern of the catalyst surface in a reproducible way. Considering that a fast response time gas analysis system is coupled with the scanning reactor, the overall assembly will be able to perform high throughput catalysts testings.

4. Conclusions

The problem solving approach used in this work led up to the development of the two prototypes and the preliminary data here reported highlights the main systems criticality. Both reactors are well dimensioned and suitable to test the catalytic activity of small planar surfaces. Prototype.01 allows a step-by-step scanning test on a confined surface portion; whereas prototype.02 allows a continuous scanning test along the *XY* plane. The work will continue focusing the attention on the fine tuning of the best working conditions, on the development of an operational analytical protocol and on an improving of the general system performances via reactor design modifications. All these steps coupled with a data handling methodology will standardize the operational procedure to carry out quantitative catalytic tests.

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