

CHEMISTRY

Escaping undesired gas-phase chemistry: Microwave-driven selectivity enhancement in heterogeneous catalytic reactors

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Research in solid-gas heterogeneous catalytic processes is typically aimed toward optimization of catalyst composition to achieve a higher conversion and, especially, a higher selectivity. However, even with the most selective catalysts, an upper limit is found: Above a certain temperature, gas-phase reactions become important and their effects cannot be neglected. Here, we apply a microwave field to a catalyst-support ensemble capable of direct microwave heating (MWH). We have taken extra precautions to ensure that (i) the solid phase is free from significant hot spots and (ii) an accurate estimation of both solid and gas temperatures is obtained. MWH allows operating with a catalyst that is significantly hotter than the surrounding gas, achieving a high conversion on the catalyst while reducing undesired homogeneous reactions. We demonstrate the concept with the CO₂-mediated oxidative dehydrogenation of isobutane, but it can be applied to any system with significant undesired homogeneous contributions.

INTRODUCTION

Nonselective gas-phase homogeneous contributions act as an insurmountable upper temperature barrier in many heterogeneous catalytic processes (1), limiting the operating temperature and selectivity through processes such as thermal cracking (2), regardless of the catalyst used. Oxidative dehydrogenation (ODH) of alkanes to alkenes is a perfect illustration of this challenge: Considered as an interesting alternative to the conventional synthesis of alkenes, the ODH route has not yet been implemented because of insufficient selectivity arising from the formation of (i) deep oxidation products (CO_x) and (ii) undesired products formed homogeneously (3). The first issue can be overcome with a smart design of the catalyst (4, 5) or by replacing oxygen with CO₂ as an oxidant (6), which eliminates the possibility of deep oxidation. However, the second issue is inherent to the chemistry of the system and remains a formidable challenge for industrial application. For instance, consider the ODH of isobutane over a CeP₂O₇ catalyst to produce isobutylene (7), a highly demanded chemical (8) used in the production of methyl and ethyl tert-butyl ether, as well as isooctane and methacrolein. Here, an increase of only 50°C translates into a selectivity decrease of 20 points because of the generation of methane, ethylene, and propylene via homogeneous processes. To offset these undesired gas-phase contributions, especially for isobutane ODH, efforts have been made to develop catalysts able to operate at lower temperatures (9, 10), although this may sacrifice conversion and therefore performance. Other alternative procedures include filling the reactor voids with quartz chips to minimize the volume available for homogeneous reactions (11). However, this increases the pressure drop across the bed, and while it may be suitable for laboratory tests, it would not be a viable solution for a process at industrial scale.

As is well known, the possibility of operating with a substantial solid-gas temperature gap using microwave heating (MWH) has been investigated for more than two decades (12) with the objective of either (i) saving energy by keeping a lower-phase temperature or (ii) achieving a higher reaction selectivity by suppressing further reaction of the desired products. A classical example of the first approach is the work by Zhang and co-workers (13), who reported significantly lower temperatures for a given conversion and apparent equilibrium shifts in the H₂S decomposition reaction under MWH as a result of the formation of hot spots on the catalyst. The second approach is also well represented, especially by works on selective oxidations using microwaves (MWs). A decade ago, Will and co-workers (14) reviewed the pioneering publications of MW-assisted gas-phase catalytic systems and noted that, in selective oxidations, different product distributions were often observed under conventional heating (CH) and MWH, but in general, these differences could be explained assuming the formation of hot spots on the catalyst as a consequence of MWH.

Efforts addressed at comparing reaction performances under CH and MWH have been hampered by the extreme difficulty in obtaining a reliable estimation of gas and solid temperatures under an MW field. Thus, conventional (thermal) thermocouples cannot be used under MWH, while optical fibers are limited in temperature and, in any case, they only provide single-point measurements, which makes unlikely the detection of local hot spots. This has been extensively studied, among others by Stankiewicz and co-workers (15, 16), who pointed out the limitations of conventional measurement techniques. In particular, the external infrared (IR) probes, often used in conjunction with MW units, only measured the temperature of the outside wall of the reactor, leading to gross underestimations of catalyst temperature.

Today, state-of-the-art temperature measurements in MW-heated reactors involve the use of IR cameras coupled to IR-transparent windows that allow direct observation of the catalyst surface (15, 17–19). With the appropriate corrections, this enables an accurate determination of surface temperatures with submillimeter spatial resolution, minimizing the possibility of undetected hot spots. However, measuring simultaneously the gas temperature remains a challenge because of the weak IR response of most gases compared to solids. Recently, we reported for the first time a real-time simultaneous multipoint measurement

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of gas and solid temperatures in a catalyst-coated monolith reactor (17). Our experiments proved that the preferential MWH of suitable solids could lead to a stable solid-gas temperature gap of up to 70° to 80°C under the conditions used. Here, we leverage the selective MWH of the solid phase to operate with a stable solid-gas temperature difference around 50°C. The lower gas-phase temperature allows us to minimize undesired homogeneous reactions during the CO₂-driven isobutane dehydrogenation. Accurate temperature monitoring allowed us to discard the possibility of undetected hot spots as a possible cause of the observed improvement. Operating under MWH led to high yields of isobutylene, approaching those required for commercial implementation.

RESULTS

Preparation of supported catalysts on MW-susceptible silicon carbide monoliths

As already explained, the process of ODH of isobutane with CO₂ as oxidant (CODH) has the advantage of avoiding deep oxidation

products (20, 21). CODH of isobutane is attractive not only because of the importance of isobutylene in the chemical industry but also because the process opens up an alternative way to use CO₂ as a reactant (22, 23). In this work, rather than attempting to develop a more efficient catalyst, we have chosen to prove the concept using a standard catalyst, V/Al₂O₃. In addition, instead of using specific MW-sensitive catalysts, we have used commercial silicon carbide (SiC) monoliths as a common support. This is a strong MW absorber material (24, 25) onto which any catalytic coating can be deployed. In this way, we attempt to demonstrate that the MWH-driven increase of selectivity can be extended to all systems facing the common problem of the emergence of undesired gas-phase contributions at high temperatures.

Gas-phase contributions in isobutane CODH

The rationale for our approach can be ascertained from Fig. 1. The rich chemistry of gas-phase reactions at high temperatures for isobutane CODH is presented in this figure from detailed theoretical calculations using gas-phase kinetics (see Fig. 1A and the Supplementary Materials

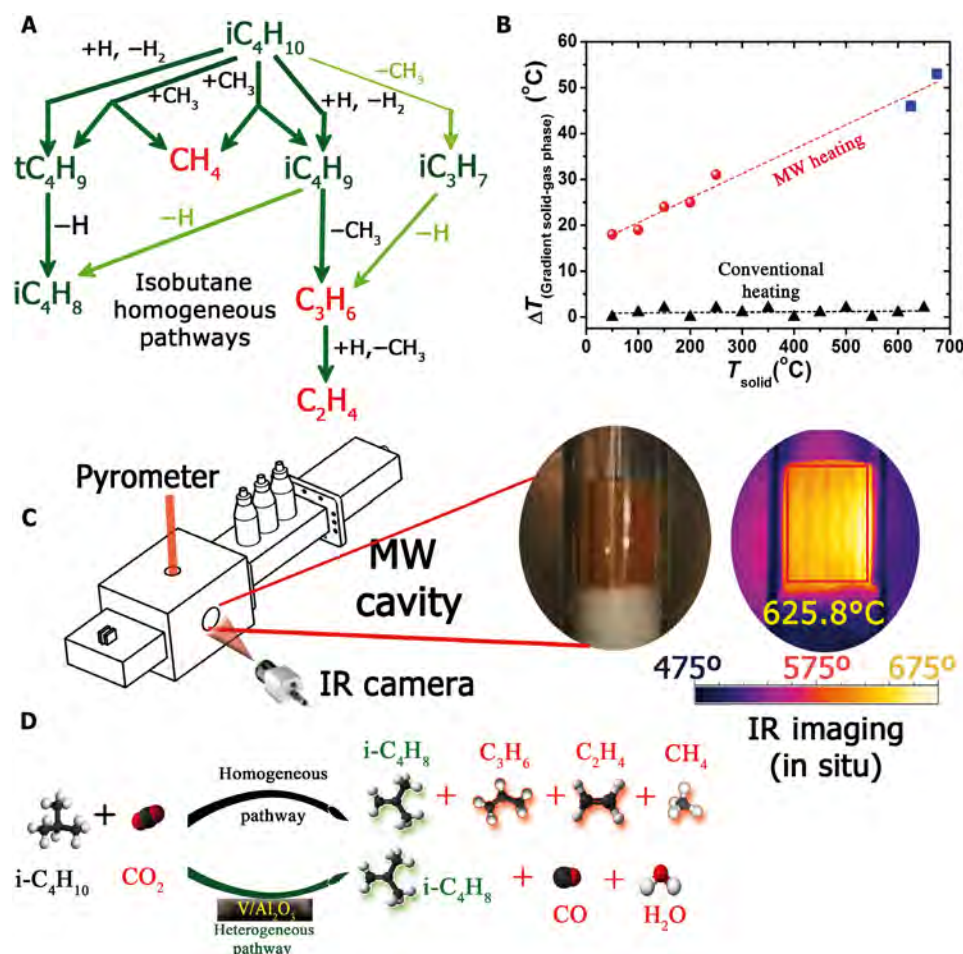


Fig. 1. CO₂-assisted isobutane ODH. (A) Overview of main homogeneous reaction pathways for the CO₂-assisted isobutane ODH, calculated for isobutane-CO₂ mixtures at 600°C. Thick lines denote major pathways, while thin lines correspond to minor pathways. (B) Gas-solid temperature gap for different solid-phase temperatures under CH and MWH [isobutane CODH 50 ml/min⁻¹ (20% isobutane, 10% CO₂, and 70% helium) and MW power = 50 to 80 W]. (C) Three-dimensional sketch of the MW setup and temperature measurement arrangements, with enlarged detail on the nodal position where the monolith is placed (corresponding to the location where the electric field reaches a maximum) and the corresponding lateral (i.e., through the quartz wall) real-time temperature mapping of the monolith surface. The top surface temperature (exit gas side) is provided by a pyrometer that gives the average temperature of the solid monolith top surface during an isobutane CODH experiment. The IR picture is compared with a regular image acquired with a digital camera and shows the homogeneity of temperatures achieved during the MWH (average of 625.8°C within the red square with maximum deviations under 14°C). (D) Schematic overview of the catalytic and homogeneous reaction pathways for isobutane CODH.

for additional details). It can be seen that multiple homogeneous reaction pathways strongly contribute to the formation of undesired products such as ethylene, methane, and propylene. Unlike propane ODH, where gas-phase reactions can have a positive effect on selectivity (26), in isobutane CODH, they can be regarded as strongly undesired. The rates of formation of these products become significant only at high gas-phase temperatures, as will be shown below. However, MWH can increase the catalytic contribution by directly heating the catalyst to a temperature higher than the gas phase. The solid-gas temperature difference (which can be substantial under MWH even at moderate temperatures; see Fig. 1B) can be exploited to favor the catalytic pathway against the homogeneous reactions (Fig. 1D). In contrast, under CH, the temperature difference was negligible, i.e., gas and solid phases were essentially at the same temperature.

Before carrying out CH and MWH experiments, gas-phase kinetics simulations were carried out to ascertain the influence of gas-phase contributions. These indicated that, while under 600°C the production of undesired homogeneous products was negligible, it was substantial above 650°C. The theoretical predictions of the model were validated in blank experiments using the empty (without catalyst load) SiC monolith (fig. S1A), and the results were in good agreement with the theoretical predictions (fig. S2). The results observed depended on the heating method: When MWH was used, the SiC monolith was selectively heated, and for the same solid temperature and gas flow rate, the homogeneous gas-phase reactions were strongly reduced (fig. S1B). Specifically, at 675°C, the yield to the cracking products decreased more than 70% for isobutane CODH. This is due to the response of the monolith under MW field: The chemical activity of SiC is negligible under the conditions used, but it behaves as an excellent MW target, providing a selective and homogeneous heating. Figure 1C shows a representative thermal image of the monolith surface under MWH, displaying a homogeneous temperature (a temperature mapping of the whole lateral surface of the monolith gives an SD of only $\pm 13.2^\circ\text{C}$ at an average temperature of 625.8°C).

Isobutane CODH on V/Al₂O₃ catalyst

For the isobutane CODH catalytic experiments, a standard V/Al₂O₃ catalyst was homogeneously deposited on the surface of the structured SiC monolithic support (see characterization in Fig. 2 and figs. S3 and S4). To explain the reaction results, it was necessary to estimate the temperature difference between solid and gas under MWH at the reaction conditions explored. While our setup allows continuous measurement of the solid temperature using both an IR camera (lateral monolith temperature) and a pyrometer (temperatures at the top monolith surface corresponding to the exit gases) (Fig. 1C and fig. S5), the gas-phase temperature could not be measured directly, because of the temperatures involved, which were too high for optical fiber readings (upper limit 250°C). Up to this limiting temperature, the gas temperature under MWH could be measured using a conventional optical fiber; however, above 250°C, the gas temperature had to be obtained from gas-phase kinetics. This was possible owing to the accurate gas-phase kinetic model predictions. In particular, for CH₄, a species that is only formed homogeneously, the model provided a robust correlation between gas temperature and methane production rates (Fig. 1 and the Supplementary Materials). Thus, from the experimentally observed production rate, we were able to back-calculate the corresponding gas temperature. From the combination of optical fiber readings and gas-phase kinetics data, the temperature curve in Fig. 1B was obtained,

showing that, for the reaction conditions used, a solid-gas temperature difference around 53°C can be expected for isobutane CODH at a catalyst temperature of 675°C under MWH.

As could be expected from the experimental and theoretical results, the lower temperature in the gas phase under MWH translates into a strong reduction of the production of unwanted cracking products such as propylene, methane, or ethylene in a lesser extent (see Fig. 3, A and B, and table S1). At the same temperature, the conversion is higher under CH because of the gas-phase contributions, but this increase in conversion is largely nonselective. When comparing at different reaction temperatures, it can be seen that the selectivity to isobutylene is higher under MWH (Fig. 3C). At yields around 25%, the selectivity is more than 30 points higher under MWH (28.7% yield to isobutylene with 76.5% selectivity compared to 25.3% yield to isobutylene with 45.8% selectivity under CH at the same catalyst temperature of 675°C). Figure 3D compares the selectivity obtained under CH and MWH for the same reactor at three different conversion levels. These are obtained at three different temperatures by adjusting the space velocity to achieve the same conversion under CH and MWH (see Materials and Methods). It can be seen that the selectivity obtained under MWH is significantly

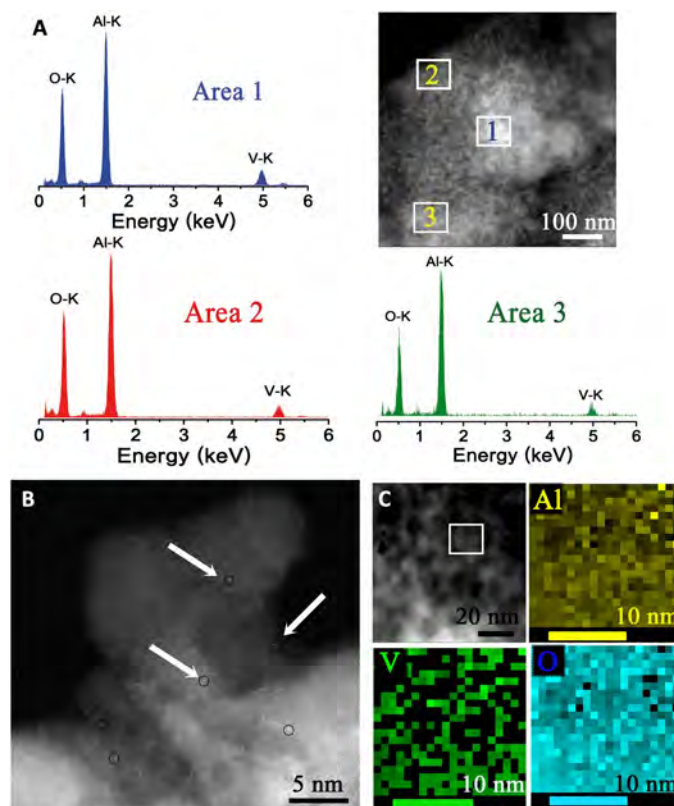


Fig. 2. Catalyst characterization. (A) Combined scanning transmission electron microscopy energy-dispersive x-ray (STEM-EDX) characterization of the V/Al₂O₃ catalyst that was used in the isobutane CODH reaction after deposition on a SiC monolith. The dispersion of vanadium was highly homogeneous, and the multiple EDX analyses throughout different areas of the catalyst rendered a very similar composition. (B) High-resolution STEM identified the presence of well-dispersed vanadium oxide clusters onto the alumina support (for the sake of clarity, some of them have been marked with black circles and/or with arrows). (C) EDX mapping analysis of Al-K, V-K, and O-K edges enabled the identification and distribution of these elements at the nanoscale level.

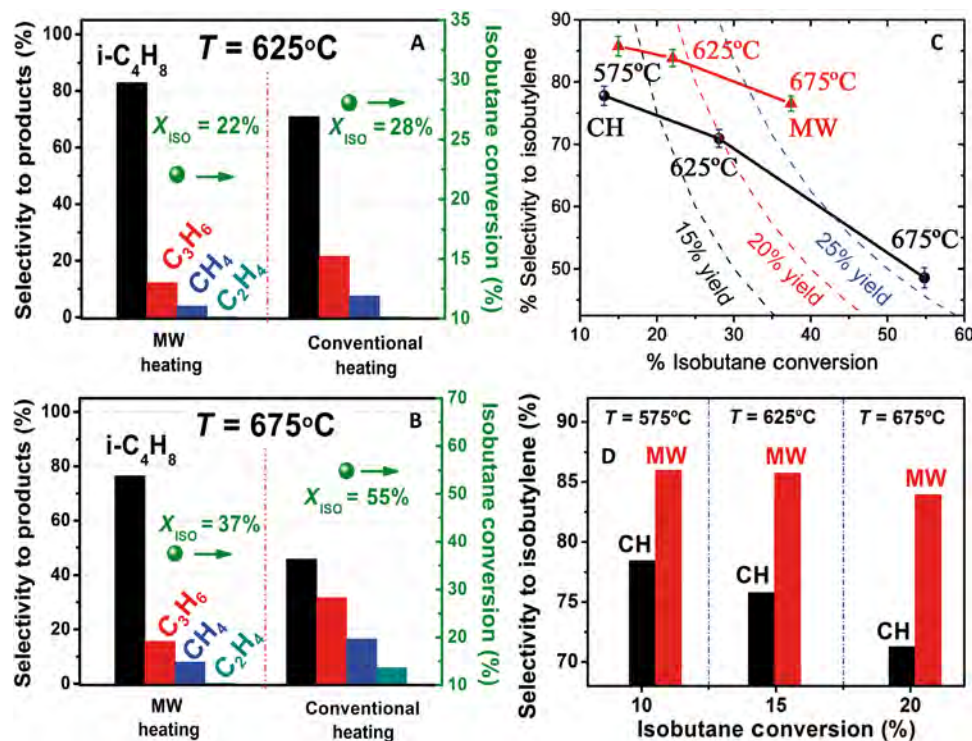


Fig. 3. CH versus MWH. Comparative catalytic performance in isobutane CODH: (A and B) Selectivity to products and isobutane conversion (displayed as solid green circles) at 625° and 675°C, respectively, under both CH and MWH conditions. (C) Selectivity-conversion plots in isobutane CODH reaction under CH or MWH. Dashed lines represent equal yields, and reaction temperatures at each condition are included. (D) Evaluation of the selectivity to isobutylene under CH and MWH at three solid temperatures (575°, 625°, and 675°C) for equivalent isobutane conversion levels. Isoconversion conditions were achieved by varying space velocities from 30,000 to 45,000 ml g⁻¹ hour⁻¹.

higher throughout the interval explored and that the difference increases with conversion. This can also be seen in fig. S6, where data at different space velocities and reaction temperatures are plotted together to give a selectivity-conversion curve over a wide interval. In the overlapping conversion zone, (from 10 to ~38% isobutane conversion) the selectivity values are consistently and significantly higher under MWH. Note that, during isobutane CODH, the absence of O₂ in the gas phase gave rise to coke formation that progressively deactivated the V/Al₂O₃ catalyst (27). This is due to the absence of oxygen and is irrespective of the heating method used. However, the catalytic performance could be easily recovered by combustion in air over a series of cycles (fig. S7), i.e., MWH does not contribute to permanent catalyst deactivation. Last, note that an enhanced formation of CO was detected under MWH (Fig. 1D and table S2). We tentatively attribute the enhancement to the Boudouard reaction (CO₂ + C → 2CO) on the newly formed coke species (28), which seems to be more favorably driven under MW conditions in the presence of the heterogeneous catalyst but is not accounted in the gas phase-only kinetic experiments.

DISCUSSION

The key factor for the selectivity improvement observed in isobutane CODH under MWH is the ability to operate with a significantly lower gas temperature for the same temperature of the catalyst. This strongly diminishes the formation of the radical intermediates that promote the formation of methane, ethylene, and propylene due to the lower gas temperature. Therefore, there is no MW effect, other than the selective heating of the solid phase, but

the results discussed above show that this is a powerful tool to boost the overall selectivity of the process. Our detailed gas-phase kinetic model allowed us to substantiate this claim by providing quantitative estimations of the selectivity gains obtained for different gas-phase temperatures.

Specifically, for a catalyst temperature of 675°C, we have used our kinetic model to estimate a gas-phase temperature of 619°C using the methane formation rate (since methane formation on the catalyst is negligible). Then the homogeneous contributions to the yield of the different products were calculated at this temperature using detailed gas-phase kinetic simulations (29) (see the Supplementary Materials) and subtracted from the experimentally observed overall formation rates to estimate the contribution of the catalytic pathway (table S2). The catalytic contribution in this case is close to 100% selectivity (98.6% selectivity at 19.7% conversion; table S2), and therefore, the lower selectivity observed under CH can be almost exclusively attributed to homogeneous reactions, something that MWH helps to suppress. Note that the beneficial effect of MWH allows operation with a higher temperature even for a monolithic reactor, where the gas-phase volume is high.

Owing to this higher operating temperature, the productivity obtained stands out among those reported in the literature for CODH (Fig. 4): The production rate of isobutylene achieved at 675°C under MWH is about five times higher than that obtained on V/C_{act}, the best catalyst for isobutane CODH (30) among the available literature (7, 10, 27, 31–35). This is due to the fact that the V/C_{act} catalyst was used in a conventionally heated reactor, and therefore, the operating temperature was limited to 600°C to avoid the dominance of homogeneous contributions. Under MWH, the catalyst temperature can be

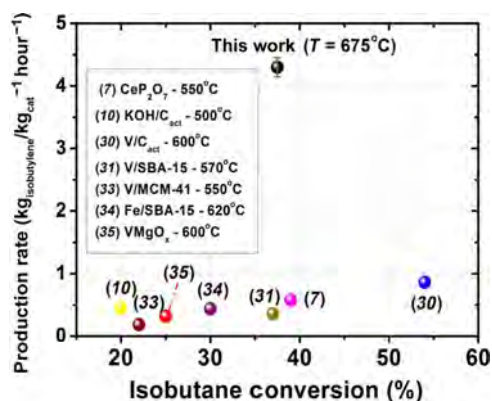


Fig. 4. Catalytic performance in comparison with the best state-of-the-art catalysts reported in the literature. Production rates (in $\text{kg}_{\text{isobutylene}}/\text{kg}_{\text{cat}}^{-1} \text{ hour}^{-1}$) obtained in this work under MWH against the best catalysts reported in the open literature for isobutane CODH. Reaction temperatures are also indicated. The use of MWH allows operating at higher temperatures, thereby increasing productivity.

increased to 675°C, and this (even with a standard $\text{V}/\text{Al}_2\text{O}_3$ catalyst) increased the production rate to $4.3 \text{ kg}_{\text{isobutylene}}/\text{kg}_{\text{cat}}^{-1} \text{ hour}^{-1}$, reaching values that are considered close to the levels required for commercial implementation (3). To our knowledge, this is the first clear evidence of the use of MWH to enhance selectivity in heterogeneous systems by suppressing gas-phase reactions.

In summary, MWH allows increasing catalyst temperature while keeping the gas phase significantly cooler. As such, it is a powerful tool to boost reaction selectivity and the productivity in catalytic systems, where homogeneous contributions become critical at high reaction temperatures. The fact that the catalyst itself does not need to be MW sensitive enables extension of this concept to any system, provided that highly selective catalysts can be deployed on inert, MW-absorbing supports (such as SiC). Potential applications extend to all systems with unfavorable gas-phase chemistry, from reactions with an unwanted homogeneous parallel path to systems where the desired products are not stable in the gas phase at reactor temperatures.

MATERIALS AND METHODS

Catalyst preparation and coating on structured supports

The preparation of the $\text{V}/\text{Al}_2\text{O}_3$ (10 weight %) catalyst was done according to the work of Argyle *et al.* (36). Ammonium metavanadate (227 mg) and oxalic acid (454 mg) were added to deionized water (1.5 ml) and stirred under complete dissolution. Then, alumina (1 g) was impregnated with the solution, dried at 120°C for 10 hours, and calcined at 500°C for 3 hours. The preparation of catalyst-coated reactors was done according to our recent work (17). Briefly, the catalyst deposition was carried out by controlled immersion of the structured supports in ethanolic suspensions (0.5 g of catalyst in 30 ml) inside an ultrasonic bath for 15 min, followed by calcination for 2 hours at 250°C. This process was repeated several times until the desired catalyst loading was achieved (~100 mg of total $\text{V}/\text{Al}_2\text{O}_3$ loading) per monolith (diameter and length, 15 mm).

MW reaction setup

The experimental system used provides direct heating of the solid support in a monomodal MW cavity using a MW-transparent quartz wall reactor while allowing real-time reading of the solid temperature using a

pyrometer and a thermal camera (Fig. 1C and fig. S5). Reactions under MWH were performed in a TE101 monomodal cavity equipped with a solid-state generator operating between 2.43 and 2.47 GHz (maximum power, 150 W). The SiC monolith was placed inside a MW-transparent quartz tube with an internal diameter of 12 mm, introduced in the MW cavity at a nodal position where the electric field reaches a maximum. The gas feed ($50 \text{ ml}/\text{min}^{-1}$; 20% isobutane, 10% CO_2 , and 70% helium) was introduced from the bottom of the reactor. The monolith temperature was increased in steps of 50°C, varying the MW power from 50 to 80 W. The reactor was pretreated under the reaction atmosphere at 550°C for 2 hours. The composition of the outlet gas was analyzed by online gas chromatography (Agilent 490 Micro GC equipped with three separation columns). Mass balance closures were better than 3%. Catalyst regeneration was performed with an air flow of $50 \text{ ml}/\text{min}^{-1}$ for 5 min. Reactions under CH were carried out using exactly the same catalytic monolith used for MWH. In this case, the quartz tube containing the SiC monolith was placed inside an electrical oven, and temperature profiles were measured with the pyrometer and with a thermocouple inserted in a central position of the monolith, connected to a PID (proportional-integral-derivative)-controlled electrical furnace to maintain the desired temperature. To evaluate isoconversion conditions and the influence of contact times, gas hourly space velocities were systematically varied from 30,000 to 45,000 $\text{ml}/\text{g}^{-1} \text{ hour}^{-1}$ at three different reaction temperatures under both CH and MWH conditions (Fig. 3C and fig. S6).

Solid temperature measurements under MWH

In this work, it was essential to ensure an accurate reading of temperatures and especially to minimize the possibility of undetected hot spots that are deemed responsible for many outstanding (and difficult to reproduce) results obtained under MWH. To this end, an extensive effort was devoted to continuous temperature monitoring of the catalyst. In particular, the temperature of the monolith surface was measured: (i) with a pyrometer located in the upper part of the tube (monolith surface corresponding to the exit gas side) and (ii) with an external thermographic camera that had a direct view of the monolith surface through the quartz wall (see Fig. 1C and fig. S5). The thermal camera was an OPTRIS PI 1M thermographic camera, which operates at $1 \mu\text{m}$ and allows temperature measurement between 450° and 1800°C. Since, at a wavelength of $1 \mu\text{m}$, quartz is nearly transparent to IR radiation (37, 38), a direct reading of the solid temperature inside the reactor through the quartz wall was possible during reaction (see Fig. 1C and fig. S5). The pyrometer was an OPTRIS CL 2MH1 pyrometer (temperature range, 490° to 2000°C; spectral range, $1.6 \mu\text{m}$) and was used to measure the top surface temperature, which is not accessible with the thermal camera that only gives a lateral view. This dual-temperature reading system was used to address one of the main problems related with the design of the MW reactors (39), where conventional probes (e.g., thermocouples) cannot be used and optical fibers face severe temperature limitations. Temperatures were continuously recorded using commercial software, after calibrating the emissivity (17) of the surface as a function of temperature (see Supplementary Materials and Methods).

Gas-phase temperature measurement/estimation under MWH

As explained above, solid temperatures were read directly on the top and lateral monolith surfaces throughout the experiment. However, to measure gas temperatures under MWH (to obtain solid-gas

temperature differences), a more complex procedure had to be followed. Up to the working limit of the optical fiber ($\sim 250^\circ\text{C}$), the temperature of the gas exiting the reactor was directly measured by locating an optical fiber 1 mm downstream of the monolith. Above 250°C , the gas-phase temperature was estimated indirectly from the exit gas composition. Since, in this system, methane is only formed in the gas phase, the average gas-phase temperature could be obtained from the observed production rate of methane obtained from the analysis of the product gas. Our detailed kinetic model was able to accurately predict methane formation rates (see theoretical calculations and goodness of model predictions in the Supplementary Materials), and from this, the corresponding gas temperature could be calculated.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/5/3/eaau9000/DC1>

Supplementary Materials and Methods

Fig. S1. Product yields at the reactor outlet during blank reaction tests with a catalyst-free monolith for isobutane CODH.

Fig. S2. Validation of the gas-phase kinetic model simulations.

Fig. S3. Additional characterization of the $\text{V}/\text{Al}_2\text{O}_3$ catalyst.

Fig. S4. Scanning electron microscopy images and EDX mapping corresponding to SiC monoliths after deposition of the $\text{V}/\text{Al}_2\text{O}_3$ catalyst.

Fig. S5. General view and scheme of the experimental setup.

Fig. S6. Influence of contact times on the isobutane CODH reaction under CH and MWH conditions.

Fig. S7. Deactivation and regeneration of the $\text{V}/\text{Al}_2\text{O}_3/\text{SiC}$ catalyst after five consecutive cycles.

Table S1. Product distribution for the isobutane CODH reaction under MW and CH.

Table S2. Molar fluxes (in mol/s^{-1}) for the different species, conversion, and selectivity (overall, gas phase, catalyst phase) during isobutane CODH.

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