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Ethylene epoxidation in microwave heated structured reactors

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ABSTRACT

In the present work we show the microwave-induced heating of monolithic reactors containing a thin-layered catalyst that exhibits a strong and selective heating susceptibility under microwave irradiation. The combination of microwave radiation and structured reactors has been successfully applied for the intensification of the selective oxidation of ethylene to ethylene oxide (epoxidation) while operating at lower power consumptions and with higher energy efficiencies than in conventional heating conditions. The microwave radiation selectively heats the catalyst and the monolith walls while maintaining a relatively colder gas stream thereby creating a gas/solid temperature gradient of up to ~70 °C at a reaction temperature of 225 °C. Moreover, the influence of different parameters such as the distribution of the catalyst onto the structured monoliths or the temperature measurement techniques employed to determine the heating profiles (Optic Fibers and/or IR thermography) have been also thoroughly evaluated to justify the obtained catalytic results.

1. Introduction

Process Intensification (PI) is currently considered as one of the most important progress areas for modern chemical engineering. PI involves the development of novel reactor designs and concepts to promote safe, cost-effective and energy-efficient sustainable processes [1,2]. In this regard, the combination of microwave heating and the use of structured reactors represent a promising concept in the framework of Process Intensification. Monolithic supports provide an arrangement of straight narrow channels of well-defined sizes and shapes that can be properly coated with a thin layer of a catalytic active phase. This configuration minimizes pressure drops and mass-transfer limitations of conventional packed-bed systems [3–7]. Moreover, since the cordierite base material is essentially MW-transparent, the selective heating of the catalyst by the electromagnetic wave in gas/solid systems has additional advantages in terms of energy savings due to the specific heating of the microwave "susceptor" catalyst and the surrounding fluid. This process reduces the possibility of secondary reactions and facilitates desorption of targeted end-products into a comparatively cooler gas stream.

The use of MW heating has been largely explored to develop novel synthetic materials and organic routes of interest at significantly shorter reaction times [8,9]. Likewise, MW heating has been expected to improve the catalytic results obtained by conventional heating due to the intrinsic advantages of microwave irradiation: volumetric and selective heating with energy saving, improved conversion and product yields, reduced reaction times and rapid on-and-off action. Nevertheless, MW heating has not fully exploited its potential in heterogeneous gas-phase catalysis. One of the main reasons can be attributed to the lack of full understanding about the real effects of microwaves when interacting with the gas/solid interface of catalysts under a real reaction ambient. Other important issue deals with the number of publications available in the literature that contain contradictory results to justify the MW-induced real influence in the catalytic results. Some investigators report enhancement of the reaction selectivities or low operational temperatures due to the MW-heating [10–15] while many others do not observe such enhancements [16–20]. Recent reviews of the current state of the art [11,21] in this field have drawn an important conclusion: a non-accurate measurement of the reaction temperatures under MW irradiation can lead to a misleading interpretation of the catalytic final results.

In this work, we have evaluated the intensification of the ethylene epoxidation to generate ethylene oxide (hereafter EO), a

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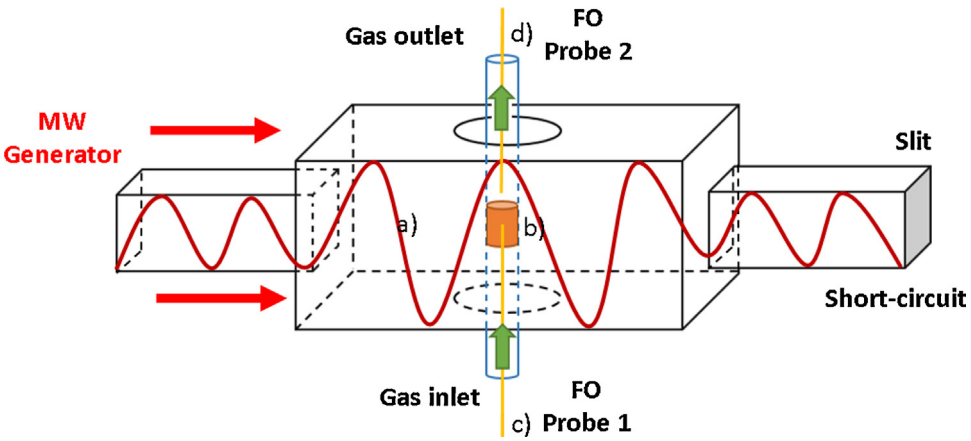

Fig. 1. Scheme of the microwave reactor: (a) monomodal cavity and MW direction of propagation; (b) location of the monolith centered at a maximum of the electric field; (c) Fiber Optic probe 1 placed in the center of the monolith in close contact with the cordierite walls to measure reaction temperature; (d) Fiber Optic probe 2 placed at the exit to measure exit gas temperature at 1 mm distance from the monolith.

chemical intermediate of paramount importance in the chemical industry that shows room for the improvement of the reaction conditions in terms of efficiency, costs, conversion and selectivity [22,23]. A novel alternative based on the synergetic advantages of combining MW dielectric heating and structured cordierite monoliths is proposed. The structured reactor contains a thin layer of catalyst [24] that simultaneously provides a selective heating upon MW irradiation and a remarkable activity for the selective conversion of ethylene to EO.

2. Experimental

2.1. Preparation of the catalytic monoliths

The structured reactor was prepared using cordierite monoliths (purchased from Corning GmbH with 400 cpsi). The dimensions of the monoliths were 12 mm of diameter and 15 mm of side length. The epoxidation catalyst was prepared according to a recently established methodology under patent licensing [24]. The catalyst loading was carried out after the immersion of the monoliths in the presence of an ethanolic suspension (1.5 g of catalyst in 50 mL) inside an ultrasonic bath for 30 min followed by calcination (2 h) at 250 °C. This process was repeated three times until the targeted catalyst loading was achieved (10% weight). Likewise, the ultrasound assisted deposition of the catalyst layer was carried out either with the monolith standing still in horizontal position within the sonication vessel or vertically suspended with the aid of tweezers. The latter approach rendered a more homogeneous dispersion of the catalyst layer.

2.2. Microwave-related equipment and characterization techniques

The microwave system (provided by Sairem Iberica) consisted of a (5, 1, 0) monomodal waveguide and a magnetron with a maximum working power of 150 W and a frequency of 2.45 GHz. Temperature distributions were registered by IR-thermography and using Fiber Optic probes. The thermographic camera is a NEC InfRec R300 which operates over 8–14 μm and allows temperature measurement between −40 °C and +500 °C. The emissivity of each material needs to be calibrated and it can be defined as the radiation emitted by a certain body in comparison with the radiation emitted by a black body. The hotter an object is, the higher fraction of infrared radiation emitted. Emissivity values range from 0 (mirror) to 1.0 (black body).

The Fiber Optic is a Neoptix Fiber Optic sensor which is based on a well-known semiconductor phenomenon: the band-gap variation in the absorption spectrum of gallium arsenide (GaAs) with temperature. The Fiber Optic is connected to a multichannel Fiber Optic signal conditioner Neoptix™ Reflex™. The temperature measured by the Fiber Optic probe was recorded by Neoptix NeoLink™ software. The temperature range is between −270 to +250 °C. The morphology of the catalysts was characterized by scanning electron microscopy, SEM (FEI-Inspect S50) at the Laboratory of Advanced Microscopies, LMA, University of Zaragoza. The dielectric properties of the materials were measured at 2.45 GHz with a network analyzer (Agilent E5061B 5Hz–3 GHz) using the 8570E dielectric probe kit). The probe was inserted into a Teflon cup (20 mm high and 10 mm diameter) covered with a lid and the powders were compacted manually, using always the same amount of powder inside the container. Dielectric constant and loss factor data were reported as the average of 20 measurements.

2.3. Microwave dielectric heating and catalytic tests

The experimental set-up is described in Fig. 1. Microwave-induced heating was supplied by a mono-modal microwave applicator operating at 2.45 GHz. The monolith (in orange) is placed inside a quartz tube (12 mm inner diameter) located in the middle of the microwave cavity, where the electric field is maximized. The temperature was measured with the aid of two Fiber Optics placed inside the central channel of the monolith (labelled as probe 1), and at the outlet gas/solid interphase at 1 mm of the monolith (labelled as probe 2), respectively. Temperature and power thresholds were limited to 225 °C and 40 W, respectively. The reaction temperature was increased from 125 to 225 °C in steps of 25 °C, varying the microwave power and measuring the composition of the outlet flow for each temperature. The inlet flow had a composition of 6% of ethylene, 12% oxygen and 82% helium, and the flow rate was set to obtain a WHSV of 0.2 mL/min mg_{cat}. The outlet composition was analyzed by a gas chromatograph (Agilent 490 Micro GC) equipped with thermal conductivity detectors and two gas separation columns, CP17970 and CP17971. It should be noted that no traces of acetaldehyde could be detected under the employed reaction conditions. For conventional heating, the same quartz tube was placed inside an electrical oven. Temperature profiles were measured with a thermocouple located either in the center of the monolith or at 1 mm of distance in the gas outlet section and connected to a PID controlled electrical furnace to maintain the desired temperature.