

CATALYSTS HAVING CATALYTIC MATERIAL APPLIED DIRECTLY TO THERMALLY-GROWN ALUMINA AND CATALYTIC METHODS USING SAME, IMPROVED METHODS OF OXIDATIVE DEHYDROGENATION

RELATED APPLICATIONS

[0001] In accordance with 35 U.S.C. sect. 119(e), this application claims priority to U.S. Provisional Application No. 60/556,014, filed Mar. 23, 2004. Also, this application is a continuation-in-part of U.S. patent application Ser. No. 10/966,162, filed Oct. 21, 2004.

GOVERNMENT RIGHTS CLAUSE

[0002] This invention was made with Government support under contract # DE-FC36-04G014154 awarded by DOE. The Government has certain rights in this invention.

FIELD OF THE INVENTION

[0003] This invention relates to microchannel apparatus, catalysts and methods of making same. The invention also relates to chemical reactions and microchannel chemical reactors.

INTRODUCTION

[0004] In recent years there has been tremendous academic and commercial interest in microchannel devices. This interest has arisen due to the advantages from micro-technology including reduced size, increased productivity, the ability to size systems of any desired capacity (i.e., "number-up"), increased heat transfer, and increased mass transfer. A review of some of the work involving microreactors (a subset of microchannel apparatus) has been provided by Gavrilidis et al., "Technology And Applications Of Microengineered Reactors," Trans. IChemE, Vol. 80, Part A, pp. 3-30 (January 2002).

[0005] Microchannel apparatus can be made of a variety of materials including ceramics, plastics, and metals. In many applications, process channels in microchannel apparatus require a coating or coatings over the structural material. The coatings can serve purposes such as absorption, adsorption, and catalysis. In some cases, microchannels are slurry coated or sol coated; for example, an oxide coat applied to a ceramic honeycomb. In some cases, sheets of a material are coated and then assembled and bonded to form a multilayer microchannel device.

[0006] Since one focus of the present invention includes aluminide coatings, reference can be made to early work described by LaCroix in U.S. Pat. No. 3,944,505. This patent describes a catalytic device made of a stack of expanded metal sheets (such as Inconel). The metal sheets carry a layer of a nickel or cobalt aluminide and a layer of alpha alumina on the aluminide, and a catalytic surface on the aluminide. LaCroix did not describe how the aluminide layer was formed on the sheets, nor did LaCroix provide any data describing the aluminide layer, nor the alumina layer, nor the catalytic surface.

[0007] Methods of forming aluminide coatings are well known and have been utilized commercially for coating certain jet engine parts. Methods of making aluminide

coatings from aluminum halides are described in, for example, U.S. Pats. Nos. 3,486,927 and 6,332,926.

[0008] There have been attempts to apply aluminide coatings on interior channels of gas turbine airfoils. Rigney et al. in U.S. Pat. No. 6,283,714 reported coating internal cooling passages of turbine blades with an aluminum coating using a slurry/pack process. Rigney et al. also stated that an aluminum halide gas could be passed through the cooling passages at high temperature so that an aluminum coating about 0.002 inch (50 μm) thick may be deposited in about 4 to 8 hours. Pfaendter et al. in U.S. Pat. No. 6,332,926 also suggests flowing an aluminum-coating precursor to deposit aluminum onto an internal airfoil surface.

[0009] Howard et al. in U.S. Pat. No. 5,928,725 entitled "Method and Apparatus for Gas Phase Coating Complex Internal Surfaces of Hollow Articles," reviewed prior art methods of gas phase coating methods for coating internal surfaces but remarked that the prior art methods were ineffective for coating multiple gas passages of modern airfoils and result in non-uniform internal coatings. In the process described in this patent, the coating gas flow rate is controlled to a different rate into at least two channels. Howard et al. state that a coating mixture including aluminum powder, aluminum oxide and aluminum flouride could be heated to deliver a coating gas. This improved method was reported to result in an aluminide coating thickness of 1.5 mils \pm 1.0 mil.

[0010] The present invention relates to catalytic processes, especially oxidative dehydrogenation to produce olefins.

[0011] Olefins find widespread utility in industrial organic chemistry. Ethylene is needed for the preparation of important polymers, such as polyethylene, vinyl plastics, and ethylene-propylene rubbers, and important basic chemicals, such as ethylene oxide, styrene, acetaldehyde, ethyl acetate, and dichloro-ethane. Propylene is needed for the preparation of polypropylene plastics, ethylene-propylene rubbers, and important basic chemicals, such as propylene oxide, cumene, and acrolein. Isobutylene is needed for the preparation of methyl tertiary butyl ether. Long chain mono-olefins find utility in the manufacture of linear alkylated benzene sulfonates, which are used in the detergent industry.

[0012] Low molecular weight olefins, such as ethylene, propylene, and butylene, are produced almost exclusively by thermal cracking (pyrolysis/steam cracking) of alkanes at elevated temperatures. An ethylene plant, for example, typically achieves an ethylene selectivity up to 85 percent calculated on a carbon atom basis at an ethane conversion of about 60 mole percent. Undesired coproducts are recycled to the shell side of the cracking furnace to be burned, so as to produce the heat necessary for the process. Disadvantageously, thermal cracking processes for olefin production are highly endothermic. Accordingly, these processes require the construction and maintenance of large, capital intensive, and complex cracking furnaces. The heat required to operate these furnaces at a temperature of about 900. degree. C. is frequently obtained from the combustion of natural gas which disadvantageously produces undesirable quantities of carbon dioxide. As a further disadvantage, the crackers must be shut down periodically to remove coke deposits on the inside of the cracking coils.

[0013] Catalytic processes are known wherein paraffinic hydrocarbons are oxidatively dehydrogenated to form