Technological Applications of Honeycomb Monoliths in Environmental Processes: A Review

Soraya Hosseini[1,*], Houyar Moghaddas[2], Salman Masoudi Soltani[3],
Soorathep Kheawhom[1,*]

[1]Computational Process Engineering Research Laboratory, Department of Chemical Engineering
Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand

[2]Departments of Immunology and Physiology, Faculty of Arts and Science, University of Toronto, Ontario, Canada

[3]Department of Chemical Engineering, College of Engineering, Design and Physical Sciences, Brunel University London, London UB8 3PH, United Kingdom

*Corresponding author's Tel: (+66)-(0813658430)
*Corresponding author's e-mail: Soraya.H@chula.ac.th, soorathep.k@chula.ac.th

ABSTRACT

Honeycomb monoliths are carbon-based, ceramic or metallic structures, comprising a significant number of packed, small-in-diameter channels. One of the features associated with the honeycomb monoliths is the demonstrated low pressure drops in processes involving high flow rates. Honeycomb monoliths, with a range of structures, have found increasingly promising applications in various industries. Owing to their physical structures, they keep finding new applications in industrial treatment systems. They are mainly fabricated via two different techniques: extrusion and coating. Monoliths fabricated via each of these techniques demonstrate specific characteristics suitable for a certain number of applications. With the presence of cordierite substrate in the coated monoliths, higher mechanical strength of coated honeycomb monoliths is expected when compared to the integral monoliths. The coated monoliths are suitable when mechanical strength is of importance where the adhesion of the thin layer coating on monoliths is a determining factor in the performance of the entire process. The integral monoliths are most-commonly employed in gas-phase processes rather than liquid phase applications due to their high accessible surface area per total weight (or volume) of the monoliths. Embedding mesoporous carbon coating and nanoparticles into honeycomb monoliths has improved the efficiency of monoliths in comparison to the more conventional preparation methods. The new generation monoliths based on 3D printing techniques provide a well-defined structure and easily adaptable geometry.

Keywords: Honeycomb; Monolith; Catalyst; Adsorbent; Environmental

1 Introduction

Honeycomb monoliths have been produced and developed to overcome many of the existing problems in direct applications of carbon materials. They have also broadened the applicability of such materials as catalysts (Vergunst et al., 2001). The application of monoliths can result in enhanced energy efficiency and considerable cost reductions. Monoliths can offer more benefits compared to powder and pellets *e.g.* better mass transfer, reusability and a better dispersion of catalysts in addition to other physical properties.

Two different types of monoliths can be separately distinguished based on their preparation methods: integral and coated monoliths. Each type covers a specific range of applications. The fabrication of the integral monoliths is carried out *via* the extrusion of a mixture of carbon precursor (or clays) and various additives which may include both organic and inorganic materials (*e.g.* cordierite powder, cellulose fibre, polyester fibre). On the other hand, in order to fabricate a carbon coated monolith, a bare monolith is typically first dipped into a mixture comprised of carbon source (furfural alcohol, sucrose,….), low carbon yielding binders(polypyrrole, Polytetrafluoroethylene,…), pore former (polyethylene glycol, surfactant,….) and a polymerization catalyst(HNO_3,H_2SO_4). This is then followed by carbonization and activation at high temperatures. Monolith channels are fabricated in various cross-sectional shapes (*e.g.* circular, square, sinusoidal and hexagonal). It has been reported that the mass and heat transfer properties depend on the geometry of the channels. Circular and square channels have indicated better heat and mass transfer than the triangular channels in catalytic combustors. A specified size of channel, wall thickness and cell density are also selected for producing special monoliths in various supports ranging from ceramics to metallic alloys. Low surface area monoliths are generally extruded from ceramic materials which are coated by a catalyst layer as wash coat, while the high surface area monoliths are directly extruded from porous material which provides a high internal surface area. However, the mechanical strength well depends on the employed preparation method (Masoudi Soltani et al. 2013; Malekbala et al. 2015; How et al. 2014).

Honeycomb monoliths have been increasingly employed in the last decades in a wide range of applications. They have especially found practical use in environmental realms. They have demonstrated certain advantages including high thermal conductivities, very high surface to volume ratios, low pressure drops, ease of recyclability and low manufacturing costs (Sungkono et al., 1997). Consequently, they became well known for their beneficial applications in the removal of pollutants especially from automobile exhausts, in catalytic combustion processes and their use as catalysts' supports. For example, a porous alumina film may cover the surface of honeycomb monoliths in order to increase the surface area, with the catalytic material spread across the alumina layer – indicating clear advantages over the conventional ceramic-supported catalysts. With the catalyst coated on the channel walls, the monolith structure - consisting of a number of parallel passageways - will allow the gas to flow with a low pressure drop. Consequently, the low pressure drop and high geometric surface areas will result in high external mass transfer rates.

The active coatings (*e.g.* γ-Al_2O_3, zeolites, vanadium, SnO_2) are usually "washcoated" on the surface of the cordierite. This results in a larger specific surface area available to carry the metallic active components (Hashmi et al., 2011). Due to low adherence, zeolite coatings can be easily peeled off from the substrate (Beving et al., 2006). On the walls of the cells, the catalytically active material is deposited as a porous washcoat thin layer having a thickness between 10 and 200 μm (Bhattacharya et al., 2004). It has been proven that cordierite ($2Al_2O_3$, 2MgO, $5SiO_2$) has a very low thermal expansion coefficient over a wide range of temperatures. This significant feature has made cordierite to be preferable and advantageous over support-free carbons when some metallic actives are coated on the surface of the cordierite (Heck et al., 2002).

Catalysts in form of monoliths are expensive compared to fixed-bed systems. On the other hand, replacement of monoliths does not normally require any additional labor costs (Groppi et al., 2000). They are being widely used in automotive and stationary emission control systems; however, they have found practical applications in chemical processing industries, catalytic combustion, pollution abatement of volatile organic chemicals, oxidation of carbon monoxide and unburned hydrocarbons. The current range of applications of monoliths can be categorized as chemical process catalyst support, ultra-filtration, water filtration, industrial heat recovery, catalytic incineration, ozone abatement, indoor air purification, natural gas storage, molten metal filter, woodstove combustor, stationary emission control, diesel particulate filter and automotive emission control. In the following sections, an overview on the uses of the two types of monoliths (*i.e.* coated and integral) in environmental application will be given. While the preparation of monoliths *via* these two methods was reviewed in our previous work [Masoudi Soltani et al. 2013], the applications of monoliths in various environmental technologies will be individually studied in this work.

2 Application of the coated and integral monoliths

2.1 Removal of NO_x

The production of ground level ozone caused by the emission of NO_x, originated from diesel engines has been one of the motives in actively conducting research in lean NO_x reduction (Reynolds et al., 2004). During natural gas combustion, methane is converted into CO_2 and H_2O, with the co-generation of small quantities of CO, SO_x and NO_x. The production of the first two combustion products can be often controlled by using modified burners and the operational parameters. NO_x is a consequence of O_2/N_2 reactions in air at high flame temperatures (>1500 °C). Emissions of NO_x can be as high as 100-300 ppm. However, emissions less than 5 ppm are desired to properly cushion the emission impacts, especially for gas turbines whose future use would, in this case, increase (Tavoulareas et al., 1991).

The dominant approach in reducing nitrogen oxide emissions from stationary sources is the selective catalytic reduction (SCR) of NO_x with ammonia. Industrial operations are performed on V_2O_5 + WO_3 $(MoO_3)/TiO_2$ catalysts at 300 - 400 °C. However, catalytic efficiency considerably fades away due to the high SO_2 concentrations and the existence of ash in the flue gas. Commercially available monolithic catalysts are used in SCR at high temperatures as they have some inherent advantages over conventional fixed-bed catalytic reactors, especially when dealing with high gas flow rates requiring further treatments (Cybulski et al., 1994). A complex transport of momentum, energy, and chemical species are carried out in flow of a catalytic combustion monolith. The gaseous species is adsorbed and then diffuses on the surface of the catalytic materials coated onto the inner channel walls. After the reaction is complete, the products diffuse back into the gas flow. Since most reforming processes take place at high temperatures, homogeneous reactions in the gas phase can accompany the heterogonous reactions in the catalytic wall. Therefore, well dispersed catalysts in porous structure (washcoats) can increase the efficiency of the reactions (Santos et al. 2013).

Due to the zero (or negative) thermal expansion of titania-silica mixed oxides in the glassy state, these materials could be promising constituents to be used in monolith structures (Wolff, 1988). Mariscal et al. (1994) prepared a series of titania-silica honeycombs with various titanium profiles along the walls of the cells via impregnation and homogeneous precipitation-deposition methods. These pre-formed samples can be fabricated in two different ways: (i) by extruding a paste of the mixed oxide precursors, and (ii) by impregnating a pre-shaped SiO_2 monolith with a titanium precursor. By employing method (i) a nearly homogeneous distribution of TiO_2 across the walls of the cell can be achieved. This is true with commercial de-NO_x catalysts. However, quite different distributions across the walls have been observed upon the employment of the second procedure.

Zeolites can also be supported onto the cordierite substrate either by dip-coating or *via* in-situ hydrothermal synthesis (Ulla et al., 2003). Lachman and Patil (1989), Wang et al. (2011) and Li et al. (2004) demonstrated the successful application of ZSM-5 zeolite as catalyst coated onto honeycomb ceramic supports in order to remove NO*x* by using a simulated exhaust gas. Zeolites (ZSM-5) having different Si/Al ratios were synthesized *in-situ* on the surface of honeycomb cordierite support (Shan et al., 1999). Some studies have also been conducted to investigate the use of carbon monoliths as catalyst support in the SCR of NO at low temperatures (Valdes-Solis et al., 2001& 2003). Valdes-Solis et al. (2001 & 2003) reported the application of carbon-ceramic cellular monolith-supported manganese oxides at low-temperature SCR of NO*x* with NH_3. Valdes-Solis et al. (2001) developed a method to prepare manganese oxides, supported on carbon-ceramic monoliths for the low temperature reduction of NO_x. Furthermore, Valdes-Solis et al. (2003) used a manganese acetate solution to prepare the catalyst supported carbon coated monolith *via* equilibrium adsorption impregnation. Equilibrium adsorption impregnation of vanadium permits a high metal dispersion on the support surface. Catalysts developed by this method show a higher catalytic activity in comparison with the already-developed manganese supported carbon-ceramic monoliths. In order to support vanadium on carbon-coated monoliths, a blend of two polymers, furan resin and polyethylene glycol (6000), was utilized for coating carbon. After this, vanadium was impregnated by applying ammonium meta-vanadate as the precursor (Garcia-Bordeje et al., 2004). They used the fabricated monoliths, with different porosities, in the selective catalytic reduction (SCR) removal of NO from power plants (Table 1).

Table 1 The vanadium loading carbon-coated monolith (0, 30 and 50 PEG parts per hundred parts of resin) in the SCR removal of NO at low temperatures

Monolith support	Vanadium (wt%)	V_2O_5 coverage (μmol.m^{-2})	Conversion%		Rate constant (cm^{3}s^{-1}g^{-1})	
			150 °C	180 °C	150 °C	180 °C
0 PEG-A-N	0.7	0.19	---	6.3	---	0.6
30 PEG-A-N	2.9	0.69	59.8	68.4	8.3	12.4
50 PEG-A-N	3	0.62	72.1	78.6	11.5	15.0

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Garcıa-Bordeje et al. (2004) examined various vanadium contents on mesoporous carbon-coated monoliths in order to study the configuration and coating thickness of vanadium in the SCR of NO at low temperatures. Table 2 shows the apparent rate constants for various catalysts for the low temperature SCR of NO. A direct comparison for different catalysts is not possible because the operating conditions are different, and the loading vanadium is minimum compared to other catalysts. However, the catalyst has an activity in the same order of magnitude as most of the other catalysts for such processes at low temperatures.

Garcıa-Bordeje et al. (2005) applied the second metal to the catalyst (vanadium supported on carbon-coated monolith) and at the same time added SO_2 to the feed during the SCR of NO at low temperatures. It was realized that the SO_2 addition to the feed is a noticeably better option than adding the second metal to the catalyst. The effect of the oxidation pre-treatment on vanadium dispersion and its loading was also investigated (Garcıa-Bordeje et al. 2006). To introduce oxygen-containing groups, vanadium-supported carbon-coated monoliths have been used in different oxidation treatments. The chemical and textural characterization of the samples after different oxidation treatments showed a higher vanadium loading and dispersion. Vanadium-supported honey comb monolith was treated with HNO_3 and a gas flow containing 1.5% ozone in oxygen. HNO_3 treatment resulted in a good vanadium dispersion. However, when ozone was applied, the lowest dispersion efficiency was observed. It was understood that vanadium loading depends on the number of oxygen-containing groups and the textural features achieved after the oxidation treatment.

Zamaro et al. (2005) washcoated zeolites onto a cordierite honeycomb by applying the deposition from a slurry solution method. They studied the effects of several experimental parameters including zeolite type, suspension concentration, number of immersions, solvent type, particle size and the additives impinge on the coating quality. The effects of the slurry concentration and the frequency of immersions on the coating thickness and geometry were studied. They learnt that the high slurry concentration and number of immersions led to an increase in the viscosity which consequently, resulted in the nonhomogeneous growth of zeolite loading. It was concluded that diluted suspensions sustained with only one immersion corresponded to more homogeneous washcoatings. Ouzzine et al. (2008) applied the extrusion technique for low-temperature SCR of NOx. The monoliths were synthesized from a medium volatile bituminous coal composing of 30 wt% volatile compounds and less than 6 wt% ashes and 75 vol% vitrinite phase. The extrudable paste was prepared by using additives, 9.5% silicate clay, 2.5%

glycerine, 1.9% methylcellulose 0.3% aluminium phosphate and water. The prepared green monoliths were dried at 80 °C overnight and submitted to preoxidation (air, 250 °C, 24 h), carbonization (Ar, 840 °C, 1 h) and finally, activation (H_2O, 250 Torr/Ar, 860 °C up to a burn-off degree of 15%). The results thereafter proved promising in the industrial scale utilization of monoliths as metal supports. Various nano-catalysts such as Pd, Pt, and Au were immobilized onto the monolithic honeycomb structured cordierite for the removal of NO_x at low temperatures. The authors concluded that the catalytic activities depend mainly on the compositions of the nano-catalysts; composites of Pd/Pt have showed higher NO_x conversion and a better activity than the commercial emission catalyst (Go et al. 2009).

Table 2 The performance of several catalysts in the low temperature SCR of NO

Catalyst	Catalyst load (Wt%)	Support	Temperature (°C)	Conversion %	Rate constant $(cm^3s^{-1}g^{-1})$
Mn/TiO_2	20	Hombikat TiO_2 supported	100	82	6.19
Fe-Mn	100	Al_2O_3	100	97	14.6
Mn	15	NaY zeolite	150	82	32.5
Mn	11.6	Al_2O_3	150	55	18.90
V_2O_5/C	5	carbon	250	79.7	69.9
Fe/C	10	carbon	180	97	20.74
Mn/C	1.9	carbon	140	85	10.95
Mn/C	5.3	carbon	140	85	10.95
V/C	5.3	carbon	100	73	46.6

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Wang et al. (2011) employed a hydrothermal method to directly synthesize ZSM-5 zeolites on the surface of honeycomb cordierite substrates. Cu-ZSM-5/cordierite monolithic catalyst was prepared *via* ion-exchange and impregnation methods and used for the selective catalytic reduction (SCR) of NO by NH_3 using a simulated diesel exhaust. Cu-ZSM-5 zeolites were directly synthesized on the surface of the honeycomb cordierite substrates using hydrothermal method (Li et al., 2004). The effect of channel geometry on selective catalytic reduction of NOx was also investigated (Sadeghi et al. 2017). The conversion results were estimated using fully-developed laminar flow, plug flow and CFD models. The fully-developed laminar flow predicted a greater conversion than others while the performance of the CFD model is somewthat between the fully-developed laminar flow and the plug flow models. MnO_x-CeO_2-Al_2O_3 was synthesized *via* spray drying and was coated on the ceramic honeycombs through the vacuum-impregnation method. The catalyst was then used in NO_x conversion at various temperatures. Wang et al. (2018) stated that the catalyst was efficient at temperatures between 50 and 150 °C, demonstrating a conversion of 97.4% and an N_2 selectivity of 94.5% at 150 °C. The catalyst also shows potentials to be used in stationary industrial installations. Controlling NO_x emission is a major factor in optimising and designing diesel engines. Nevertheless, reducing NO_x emissions is not only controlled by optimising the combustion reactions and altering fuel composition. The efficiencies of various catalysts (*e.g.* metal, bimetals, inorganic), in the form of extruded or coated monoliths, in NO_x removal have been investigated. It can be concluded that the extent of the poisoning of the active sites well depends on the catalyst type. The feasible operating parameters *e.g.* the operational temperature range of the catalyst, the flow rate of the diesel exhaust and the pre-treatments of the monoliths all can impact the actual observed performance. Other types of catalysts used in NO_x removal are listed in Table 3.

Table 3 The performance of various catalysts in NO_x removal

Catalyst	Support	Application	Remarkable Results	Ref
$LaCoO_3$	Cordierites monolith	N_2O Decomposition	50% N_2O conversion performance	Russo et al. 2007
$Rh/Ce_{0.9}Pr_{0.1}O_2$	Cordierites monolith	N_2O Decomposition	Improvement of catalytic activity	Rico-Perez et al. 2011
Pt/beta zeolite & RhO_x/ceria	Cordierites monolith	NOx reduction to N_2	100% N_2 selectivity	Rico-Pérez et al. 2013
Pt/beta zeolite	Cordierites monolith	SCR of NO_x in a real diesel engine exhaust	Optimum THC concentration of 3000 ppm	Valencia et al. 2014
M(Fe, Co)/ BEA zeolites	Cordierites monolith	N_2O direct decomposition	The optimum loading amount for M(Fe, Co)-BEA powder is ~40 wt%.	Zhang et al. 2016
ZnO/ Pt:$La_{0.8}Sr_{0.2}MnO_3$	Cordierites monolith	NOx reduction	Higher performance commercial benchmark and powder-form catalysts	Du et al. 2018
Ni, Rh, Pt on CeO_2	Cordierites monolith	Syngas production	Rh > Pt > Ni for biogas SR and Rh > Pt = Ni for biogas OSR	Vita et al.2018
Co_3O_4/C	Carbon coated Cordierites monolith	SO_2, NOx removal	123.1 and 130.2 mg/g for SO_2 and NOx	Silas et al. 2018
α-Al_2O_3/ K-$Zn_{0.4}Co_{2.6}O_4$	cordierite monolith	low-temperature N_2O decomposition	high performance (X > 90% at T < 400 °C)	Wójcik et al. 2018
Zn & P dopt Pt/Ba/Al_2O_3	cordierite monolith	NOx storage	P contributes to considerably more severe deactivation of	Jonsson et all.2019

			the catalyst than Zn	

2.2 Abatement of Volatile Organic Compounds

The use of monoliths in adsorption processes is relatively new and only a few applications have been reported on the bulk removal of the contaminants. Volatile organic compounds (VOCs) are one of the most significant classes of chemicals with a considerable contribution to atmospheric pollution. These organic compounds, with a vapor pressure greater than 133.3 Pa (1 mmHg) at room temperature and inheriting low boiling points, are environmentally of concern when emitted into the air. Once released into the atmosphere, they react with NO_x to produce O_3, a highly toxic molecule to both the environment and human health in the troposphere. Catalytic combustion, at low temperatures, is one common method to control the emission of VOCs. The formation of water vapor as a result of the combustion is the downside of this process. The water vapor can subsequently negatively impact the catalytic activity (Yang et al., 2007; Yang et al., 2011).

VOCs are emitted *via* different routes. Industrial processes can contribute to a big part of these emissions. VOCs are released in industrial processes involving solvents, polymers and resins such as those applied in painting and coating operations. Specifically, a considerable amount of xylene is released as part of the exhaust gases generated in paint factories. VOCs are also present in tobacco smoke and automobiles' exhaust gases (Pérez-Cadenas et al., 2006). Besides catalysis, adsorption on activated carbon has been a successful candidate for the removal of VOCs. Adsorption on activated carbon is a promising process when low concentrations of VOCs are involved.

VOCs are a group of industrially-significant chemicals. Nevertheless, they pose adverse impacts on the environment if discharged. Due to these facts, various processes have been designed in order to recover, reduce and control VOCs emissions into the environment. These mainly include combustion, adsorption, absorption, condensation, biofiltration and catalytic oxidation. Among these techniques, adsorption has been extensively utilized in industrial operations. Adsorption processes benefit from easy operation, low operating cost, high capacity, high selectivity and efficient recovery of most VOCs at low partial pressures. In the meantime, reversible adsorption capacity, regeneration property, and physicochemical and thermal stability are important parameters which determine the feasibility of the operation and the practicability of adsorption processes (Kim BR, 2011). Carbon-based adsorbents are mainly present in the powdered form or as granular particles in packed beds. Granular active carbon has been employed as adsorbent for the removal and recovery of organic solvents due to its low cost. It has also been used as personal protection in gas masks with relatively shallow packed beds to achieve a low pressure drop. However, the easy handling of monolithic adsorbent plus the low pressure drop along monoliths compared to that of granular or powdered adsorbents, make monoliths far better industrial candidates in comparison to the other forms (Hosseini et al. 2015).

Yu et al. (2002) used activated carbon monoliths as adsorbent to remove several VOCs such as toluene, 1-butanol and ethyl acetate. They also established the adsorption isotherms of VOCs by applying different models. Valdes-Solis et al. (2004) studied the adsorption of n-butane on carbon-coated ceramic monoliths. Shim et al. (2006) analysed the efficiency of wash-coated MCM-48 monoliths in order to adsorb VOC compounds including acetone, benzene, n-hexane, toluene and trichloroethene. Mobil researchers explored the synthesis and structure of a specific class of mesoporous materials named the M41S family. Based on the synthesis conditions applied, M41S materials are categorized into several members including MCM-41, MCM-48, MCM-50 and some other species. Their structures are different as reported MCM-41(Hexagonal (p6mm)), MCM-48 Cubic (Iad$_3$) and MCM-50 (Lamellar).

Previous studies have shown that among these mesoporous materials, MCM-48 could be a reliable adsorbent owing to its interwoven and branched porous structure that effectively favours mass transfer as well as its kinetics when compared to other materials. In order to synthesize MCM-48 mesoporous media, cethyl trimethyl ammonium bromide (CTAB) and Ludox AS-40 were used as the template and the silicon source, respectively.

Perez-Cadenas et al. (2006) synthesized a new type of VOC combustion catalysts fabricated by the combination of ceramic monoliths, carbon materials (polyfurfuryl alcohol) and noble metals (Pd and Pt). They studied the catalytic behaviour of Pd and Pt catalyst-supported carbon-coated monoliths by combusting xylene at a low temperature. In comparison to the Pd catalysts, Pt-based catalysts proved to be more active. Smaller-sized Pd catalysts showed a higher degree of reactivity in relation to the Pt catalysts. Furthermore, Perez-Cadenas et al. (2008) studied the catalytic behaviour of Pd catalysts supported on three different porous carbon-based monoliths in the gas-phase combustion of m-xylene at low temperatures. The authors investigated the role of macro as well as mesopores in the gas phase reaction. Mesopores enhance the contact surface between the Pd particles and the m-xylene molecules due to an increase in the carbon external surface area. The catalytic activities of monoliths with different porosities drop in the order of: Pd/ mesoporous >Pd/ microporous >Pd/ macroporosity.

Coal-based (as the carbon precursor) extruded monoliths were also prepared (Gatica et al. 2006). In order to obtain the appropriate dough with the desired rheological properties for the extrusion, in addition to water, some additives were used as 9.5% silicate clay, 2.5% glycerine, 1.9% methylcellulose and 0.3% aluminium phosphate were dissolved in phosphoric acid. The green monoliths were then dried in an oven at 80 °C overnight, followed by two thermal treatments: pre-oxidation (air, 250 °C, 24 h) and carbonization (Ar, 840 °C, 1 h) and finally an activation process. The coal-based monoliths were used to adsorb o-xylene, demonstrating a total adsorption capacity of 550 μmol g^{-1}. Ceramic and metallic monoliths coated with cryptomelane (manganese oxides) were applied as catalysts for VOC abatement. The results revealed that a complete conversion of VOC (ethyl acetate) into CO_2 was achieved by the as-prepared monoliths (Fig.1) at temperatures lower than 300 °C.

Fig. 1 Various types of monoliths coated cryptomelane as catalysts for VOC abatements; Reprinted with permission from Ref. [Santos et al. 2019]. Copyright [2019], [Elsevier].

Harti et al. (2007) used different types of Moroccan clays as the raw materials for the extrusion of monoliths. They then used the fabricated monoliths to adsorb volatile organic compounds (VOCs). The clays were collected from different regions including Tangier (UT), Nador (BENTO) and Tetuan (FARDI). The textural properties and adsorption capacities of these monoliths are shown in Table 4. In comparison, BENTO proved to have a higher adsorption capacity for o-xylene. It was shown that unlike the other two types, the BENTO sample inherited wider mesoporous pores (a great number of 9 nm pores). The schematic features of the three samples are shown in Fig. 2.

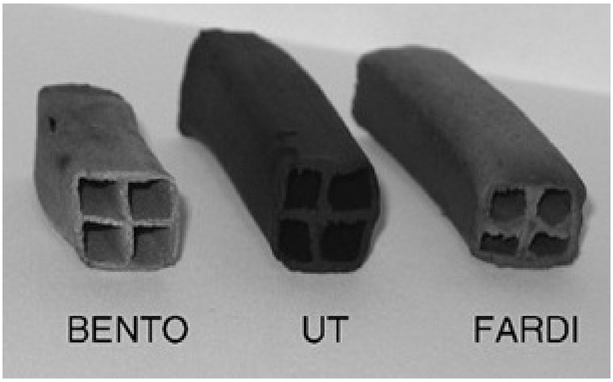

Figure 2 The three types of integral monoliths prepared using clays, sampled in Tangier (UT), Nador (BENTO) and Tetuan (FARDI) in northern Morocco, and further used as VOCs adsorbents;Reprinted with permission from Ref. [Harti et al., 2007]. Copyright [2019], [Elsevier].

Table 4 The textural properties and adsorption capacities of three types of powdered and extruded (into brackets) clay samples

Sample		Pore volume (cm^3/g)		O-xylene adsorption (µmol/g)
	S$_{BET}$ (m^2/g)	Micropores	Total (m^2/g)	
BENTO	79(80)	0.002(0.015)	0.205(0.115)	416
FARDI	23(12)	0.003(0.002)	0.039(0.037)	111
UT	29(28)	0.002(0.002)	0.054(0.06)	129

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Chafik et al. (2009) prepared monoliths using also other Moroccan natural clays. The two raw clay samples, gathered from different deposits located in the northern Morocco, were then extruded and labelled as FERA and TEFA(Fig.3). Using these natural clays, the extrusion of theses monoliths was carried out in the absence of any additional chemical binders. In this procedure, the thermal treatment step is eliminated. This allows for a significant cost reduction, both in additives and solvents as well as in energy consumption. The efficiency of the fabricated monoliths was next investigated in VOCs (*i.e.* O-xylene) adsorption processes. The textural properties and adsorption capacities of VOCs are listed in Table 5. Other types of fabricated monoliths employed in the removal of VOCs are also described in Table 6.

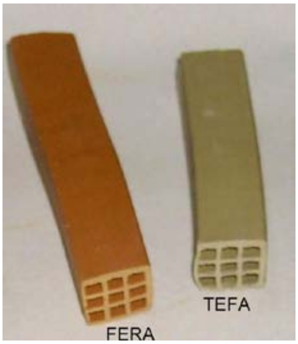

Figure 3 Monoliths extruded with FERA and TEFA clays used as adsorbents for the removal of VOCs; Reprinted with permission from Ref. [Chafik et al., 2009]. Copyright [2019], [Elsevier].

Table 5 The textural properties of the studied clays (raw clay/monolith) and the VOCs adsorption capacities of their respective monoliths.

Sample		Pore volume (cm^3/g)		O-xylene adsorption
	S_{BET} (m^2/g)	Micropores (raw clay/m)	Total (m^2/g) (raw clay/m)	(μmol/g)
FERA	38.2/37.7	0.0034/0.0026	0.0712/0.0742	144.474
TEFA	40.5/40.4	0.0031/0.0036	0.007/0.0661	140.132

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Table 6 The performance of various catalysts and their corresponding supports in VOCs removal

Catalyst	Support	Application	Remarkable Results	Ref
MnCu	FeCrAlloy metallic monoliths	Ethyl acetate Toluene Combustion	good activity ethyl acetate and toluene with detection CO_2 and H_2O	Barbero et al. 2008
$MnOx/Al_2O_3$	FeCrAlloy metallic monoliths	Combustion of volatile organic compounds	30 wt% loading indicated higher performance for Ethanol, ethyl acetate , toluene	Aguero et al. 2011
M-Clay	Extruded monolith	Oxidation air pollutants	OH groups of Brønsted acids and coordinately-unsaturated cations, such as Al^{3+}, Fe^{3+} and Fe^{2+}. Lewis acids contribute to Catalytic performance of air oxidation process.	Assebban et al. 2015
Mn, Pt, Mn/Pt	Ceramic monoliths (natural clays and gibbsite)	Removal of $CHCl_3$	Mn Pt Pt/Mn Conversion% $CHC1_3$ 82 88 75	Lerner et al. 2015

		MEK Toluene Xylene	MEK 85 95 98 Toluene 2 55 79 Xylenes 23 64 90	
Manganese	Washcoated pillared clay honeycomb monoliths	Oxidation of propane and acetone	The pillared clay allows incorporating higher amount of well distributed MnO_2	Gatica Et al. 2017
Phenolic resins and cellulosic binders	Casting method	Toluene Benzene Xylene Hexane	Monolith ctivate Carbon 18.3g/100g 22.5 g/100g 11.1 31.1 14.7 27.5 13.0 25.0	Bajwa et al. 2016
$CuO-CeO_2$	$SiO_2-Al_2O_3$ modified glass-fiber honeycomb	Oxidation Ethylacetate Isopropanol Toluene	CeO_2 increase adsorption capacity of ethyl acetate, isopropanaol and low activity in the oxidation of toluene.	Dan et al. 2017

2.3 Elimination of Bad & Pungent Smell

Ismagilov et al. (2001) applied the extrusion process to prepare TiO_2 monolith supports for Cu, Mn and Fe-containing catalysts that were fabricated by impregnation of the monolith support for high-temperature ammonia decomposition and H_2S removal. They used Mn, Fe and Cu oxides to prepare monolith catalysts based on titanium dioxide or alumina–silica precursors, followed by drying at 110 ˚C and calcination at 700 ˚C. They considered high surface area and acceptable mechanical strength of the monolith support as the experimental parameters in order to find the optimal ratio between the main oxide component, titania, silica–alumina and the calcination temperature. Their experiments led to the identification of various compositions of monolith catalysts *e.g.* Fe_2O_3/MnO_2 and CuO/MnO_2. The mixed impregnated monolith catalysts based on Fe_2O_3/MnO_2 showed the best performance due to the highest catalytic activity at lower temperatures. These monoliths are expected to be acceptable sorbents for H_2S removal. The results of ammonia conversion using a range of catalysts are described in Table 7.

Table 7 Ammonia conversion rates and the applied temperature ranges corresponding to different catalysts

Samples	NH_3 Conversion%	Conversion temperature, °C
14%CuO(64%TiO_2 +36%Ca-f)/500	95%	780–800
8%Fe_2O_3(64%TiO_2 +36%Ca-f)/500	95%	780–800
20%MnO_2(64%TiO_2 +36%Ca-f)/500	80%	800–880
8% Fe_2O_3 + 15% MnO_2 [(64%TiO_2 +36%Ca-f)/500]	98%	750
7.5% CuO+15% MnO_2 [(64%TiO_2 +36%Ca-f)/500]	90%	800

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Atmospheric ammonia (NH_3) is a toxic inorganic gas which has a sharp odour at ambient conditions and is potentially harmful to human health (Geng et al., 2008). NH_3 is released from the ammonium nitrate and nitric acid production industries, livestock feedlots, urea manufacturing plants, the nitrogen fertilizer application industries, biomass combustion and petroleum refineries as well as the refrigeration industries. In order to overcome the polluting emission of NH_3, the selective catalytic oxidation process of ammonia (NH_3-SCO) in a stream to N_2 and

H_2O was investigated (Dravell et al., 2003). Hung et al. (2010) used honeycomb platinum-palladium-rhodium (Pt-Pd-Rh) ternary composite cordierite catalysts to oxidize NH_3. The catalysts were prepared by the incipient wetness impregnation method involving aqueous H_2PtCl_6, $Pd(NO_3)_3$ and $Rh(NO_3)_3$. The platinum-palladium-rhodium ternary composite was coated on a honeycomb cordierite cellular ceramic substrate. Based on the experimental data, it was concluded that the SCO process was potentially capable of treating highly concentrated streams of NH_3, suggesting a practical route to meet discharge standards.

Lim et al. (2010) prepared monoliths using three different types of activated carbon as an air purification filter. They used the extrusion method in order to prepare integral monoliths. The authors implemented a simple method in which the extrusion of a composite consisting of activated carbon, organic polymer binder, organic lubricant and inorganic additives without drying or calcination processes was readily performed. The results of the two different methods - namely pressurized forming and extrusion - is shown in Fig. 4. In order to optimize the manufacturing process, the viscosity, barrel temperature, the ratio of activated carbon, the binder and the adjuvant were carefully measured. The authors studied the impacts of the surface morphology, surface area and the mechanical features of the filter as well as the particle size.

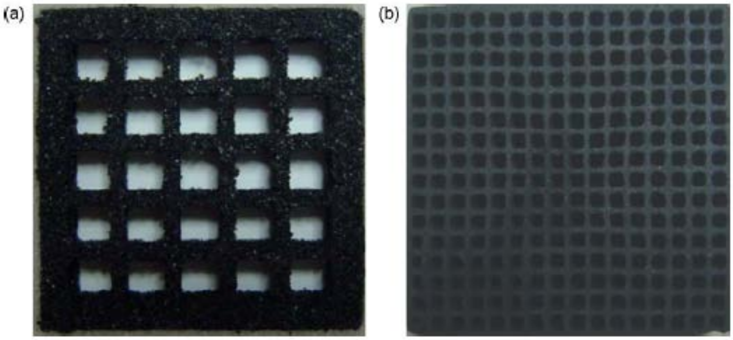

Figure 4 Filters manufactured by (a) pressurized forming (25 cell) and (b) extrusion through the 256-cell die; Reprinted with permission from Ref. [Lim et al., 2010]. Copyright [2019], [Elsevier].

2.4 Adsorbent for dehumidification process

A monolithic adsorbent comprised of NaA zeolite over honeycomb ceramic matrix was applied as adsorbent in a humidification process (Fang et al., 2018). The influence of various factors *e.g.* $CaCl_2$ concentration, seed coating, microwave temperature and contact time during the synthesis process (*in-situ* microwave hydrothermal synthesis) was investigated. The authors concluded that the new preparation method corresponded to a higher capacity for the adsorption water vapour (*i.e.* 23.3%) compared to the traditional impregnation method (*i.e.* 20.9%), using water glass and silica sol.

2.5 CO_2 capture/separation

The rise in the global temperature is widely attributed to an increase in the concentration of greenhouse gases (*e.g.* CO_2) in the atmosphere. CO_2 is mainly emitted *via* the combustion of fossil fuels such as coal, natural gas or petroleum and through industrial processes such as oil refinement and the production of cement, iron and steel. Capturing and storing CO_2 is known to be a key method in reducing the total atmospheric greenhouse gas emissions. There has been a considerable number of studies on CO_2 capture *via* adsorption processes. More recently, a significant attention has been paid toward optimising the adsorbents for CO_2 capture under different operating conditions and high flow rates. These studies have been mostly focused on adsorption processes in packed beds. Although most of these adsorbents have been realised to be inexpensive and adaptable to the process (*e.g.* silica and activated carbon), these processes are generally associated with high mass transfer resistance and high pressure drop at high flow rates in packed beds. Honeycombs monoliths have a potential to overcome such operational challenges. Carbon monoliths are characterized by straight parallel channels separated by thin walls, a high void fraction and large surface and contact areas, resulting in a low pressure drop under high flow rates. These properties suggest that carbon monoliths have some advantages in CO_2 capture. Ribeiro et al. (2008) investigated the adsorption equilibria of carbon dioxide, methane and nitrogen on activated carbon monoliths. The adsorption capacity of activated carbon monoliths is highest for CO_2, followed by CH_4 and N_2. Such experimental data is then used in the modelling of adsorption processes such as pressure swing adsorption (PSA) and temperature swing adsorption (TSA) for the separation of gas mixtures. Hosseini et al. (2015) investigated CO_2 adsorption on modified carbon-coated monoliths using alkaline solutions (NH_3 and KOH). The surface properties of the carbon-coated monoliths/activated carbon monoliths were enhanced with the addition of functional groups and hence, improving CO_2 adsorption. The presence of nitrogen- and oxygen-containing functional groups on modified carbon-coated monoliths showed an increase of approximately 12 and 27% in CO_2 adsorption, respectively, as compared to unmodified carbon-coated monoliths. An adsorbent, based on clay monolith from a natural montmorillonite, was fabricated and used in CO_2 adsorption (Yeste et al., 2017). The results demonstrated that the monoliths adequately maintained the adsorptive properties (*i.e.* around 15 mg/g), suggesting a promising potential of the monolithic design from the clays as low-cost CO_2 filters (Fig. 5). The relatively large pressure drop in processes with high flow rates leads to mass transfer limitations and slow diffusion of molecules into the particles. Many researches have well highlighted the advantages of monolithic structures in CO_2 captures processes involving high flow rates. Various types of monoliths were also applied in order to remove CO_2 that were listed in Table 8.

Figure 5 Typical image of the integral clay honeycomb monoliths from natural montmorillonite used as CO_2 adsorbents; Reprinted with permission from Ref. [Yeste et al., 2017]. Copyright [2019], [Elsevier].

Table 8 The performance of various catalysts in CO_2 removal

Catalyst	Support	Application	Remarkable Results	Ref
Zeolite 13X	Cordierites monolith	Capture CO_2 from flue gases	Increase CO_2 adsorption around two times (18% zeolite).	Ribeiro Et al.2013

MOF monoliths (40% Cr/BDC)	Extruded monolith	CO_2 adsorption	Adsorption capacity 11.57 mmol/g	Hong et al. 2015
Petroleum tar pitch & powdered coal	Extruded monolith	adsorption of CO_2, CH_4 and N_2	Adsorption capacity 7.398, 5.049 and 3.516 mol/kg CO_2, CH_4 and N_2.	Arami-Niya et al. 2016
Amine-Functionalized (Mg, Mn)	Cordierites monolith wash-coated α-Alumina	CO_2 Capture	uptake of 2.37 and 2.88 mmol/g	Darunte Et al. 2017
Fe/TiO$_2$	Cordierites monolith	Photocatalytic carbon dioxide reduction	Selectivity 99.70%	Tahir et al. 2018
SAPO-34 zeolite	3D-printed	CO_2 adsorption	very high selectivity for CO_2 in mixture CO_2/N_2	Couck et al. 2018
Ni/GDC	Cordierites monolith	CO_2 methanation	The highest CH_4 productivity of 10.7 LCH_4/g h was obtained at 400 °C and 50,000/h	Vita et al. 2018
zeolite NaUSY/ activated carbon	Extruded monolith	CO_2 capture/ ESA	the electrical efficiency increased from 18 to 73%	Zhao et al. 2018
H-ZSM5/activated carbon	Extruded monolith	CO_2 capture vacuum & ESA	CO_2 purity of 33% recovery of 72% electrification time of 30 s	Zhao et al. 2019
zeolite 13X, activated carbon	3D-printed monolith	CO_2 adsorption ESA	Adsorption capacity 3.49 mol/kg	Regufe et al. 2019
Ni-MMT/TiO$_2$	Cordierites monolith	Conversion of (CO_2) and (CH_4) to fuels	CO_2 750 mmol/ h. g H_2 1126 mmol/ h. g C_2H_6 6.3 mmol /h. g	Tahir et al. 2019

2.6 Dye and heavy metals retention in liquid phase

The application of carbonaceous adsorbents in the liquid phase is well limited to conventional particle forms such as powders. Various types of monoliths were utilized in removal of pollutants (heavy metals, dyes, organic chemicals and etc.). Gatica et al. (2010) used coal-based monoliths in the treatment of non-gaseous polluted effluents. Carbon-based monoliths have been prepared following the previously described procedures and were later patented (ES Patent P200202334, 2002). Integral carbon monoliths were prepared by using a natural coal to adsorb methylene blue and p-nitrophenol from dilute aqueous solutions under dynamic conditions. The monoliths were subjected to three different kinds of treatment after drying and prior to any application. These treatment steps consisted of simple carbonization in Ar flow at 840 °C for 1 h (sample C), carbonization as before followed by activation at 860 °C using an Ar flow saturated with water vapour (sample CA, carbonization and activation) and pre-oxidation in air flow at 250 °C during 24 h (sample PCA, preoxidation , carbonization and activation). Table 9 shows the data with the degree of retention reached for each experiment after 24 h as a function of the pollutant and its concentration. Table 10 demonstrates the application of various types of monoliths for removal of liquids (dye, heavy metals, organic compounds…..).

Table 9 Dye adsorption on the carbon-based monoliths (24h) for methylene blue (MB) and p-nitrophenol (PNP)

Sample	Adsorption%		
	MB (C_o=100ppm)	MB (C_o=100ppm)	PNP (C_o=100ppm)
C	41	48	13
CA	100	10	89
PCA	100	27	100

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Table 10 The performance of various types of monolith in liquid phase application

Catalyst	Support	Application	Remarkable Results	Ref
3D $C_6H_7MgO_9P$ graphene-based monolith	Extruded monolith	Bisphenol A	Adsorption capacity 324 mg/g	Fang et al. 2018
Acid modified carbon (FA& PEG)	Cordierites monolith	Methyl orange adsorption	88 mg/g at pH 6	Cheah et al. 2013
Graphene oxide (GO)/ carbon nanotube	Extruded monolith	Adsorption of anionic methyl orange, cationic	Good affinity of the hybridized monolith toward hydrophilic and	Wu et al. 2019

		rhodamine, and silicon oil	hydrophobic molecules	
Fe_2O_3/TiO_2	Mold	Industrial dye (remazol brilliant red X-3BS) and pesticide (Fipronil)	Dye removal & degradation for RbX 98.83% and 90.57% . Degradation efficiency of 8.71% for Fipronil	Singh et al. 2019
Porous Graphene Monoliths with induce Glycol, Lactic acid, succinic acid	Extruded monolith	Lead removal	well structural stability and plasticity Gl-RGO > La-RGO > Su-RGO	Fang et al. 2017
carbon coated monolith (FA& PEG 600 and 8000)	Cordierites monolith	lead adsorption	Adsorption capacity 50 mg/L(600) to 250 mg/L(800)	Teoh Et al. 2017
Polymeric porous monoliths based on Glycidyl methacrylate	Mold	oil/water separation	pH-switchable monoliths suitable for practical applications in the large-scale	Guo et al. 2019
Nitrogen-doped carbon monoliths (urea, hexaketocyclohexaneoctahydrate, chitosan)	Mold	Adsorption dye (Rhodamine B)	Rhodamine B adsorption capacity of 63 mg/g	Jordan et al. 2018
Powdered active carbon /silica	Mold	Methylene blue from wastewater	215.1 mg/g at adsorbent dosage of 0.25 g and 154.2 mg/g at adsorbent dosage of 0.35 g	Li et al. 2017
natural Moroccan clays	Extruded monolith	Lead adsorption	2 mg of Pb(II) per gram of clay	Ahrouch et al.2019

Hosseini et al. (2011) prepared carbon-coated monoliths using furfuryl/PEG8000/pyrrole in order to remove methyl orange (MO) from aqueous solutions. The maximum adsorption capacity was found to be 102.04 mg/g. The studies showed that the maximum recovery of MO was achieved in an alkaline medium. An increase in desorption was observed by increasing MO concentration. Regeneration studies showed a 35% to 12% drop in the adsorption capacity after the first three adsorption-desorption cycles. The adsorption efficiency remained almost constant for the subsequent experiments (Fig.6). Yu et al. (2017) studied a new design of honeycomb/cobweb fabricated from graphene oxide (GO)/chitosan (CS) and aerogel microspheres (GCAMs) by combining electro-spraying with freeze-casting methods in order to optimize the adsorption of heavy metal ions and soluble organic pollutants in water. Significant uptakes were observed in a very short timespan (i.e. 5 min) with capacities corresponding to 82% and 89% of the equilibrium adsorption capacities for Cr (VI) (292.8 mg/g) and MB (584.6 mg/g), respectively.

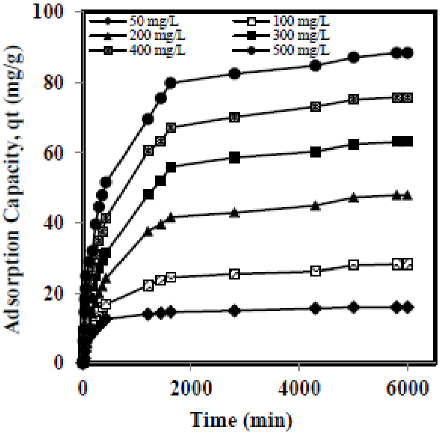

Figure 6 Effect of contact time for methyl orange adsorption at different initial dye concentration (50 to 500 mg/l), 200 rpm using carbon coated honeycomb monolith(0.7g carbon); Reprinted with permission from Ref. [Hosseini et al., 2011]. Copyright [2019], [Elsevier].

2.7 Applications in biotechnology

Potential utilization of monolithic reactors in a biological process has been experimentally studied. Enzyme carriers need to have certain criteria; the support should prove to inherit good adsorption efficiency and it must be capable of firmly maintaining the enzyme on the monolithic surface. The capability of the immobilized matter for the stabilization and retaining of the biological activity is a critical parameter (de Lathouder et al., 2008). Finally, the operational characteristics (*i.e.* mechanical strength, hydrodynamics and the resistance to degradation) must be acceptable while the process should at the same time remain economical. Typically, the use of a porous support is preferred over a non-porous media as the enzyme will not only be adsorbed at the outer surface of the material but also it will reside within the pores (de Lathouder et al., 2006).

Physical adsorption is advantageous processes, owing to the associated high degree of reversibility. However, desorption can also be a limiting downside if it occurs during the adsorption reaction. Enzyme adsorption has been studied through physical adsorption in combination with different types of particulate carrier materials such as polymers, molecular sieves, silica and silica-alumina composites (Koops et al., 1999; Gonqalves et al., 1996) and carbonaceous materials. The adversely affecting scenario of these adsorbents is the limitation in diffusion which results in a considerable fraction of unused enzymatic activity.

De Lathouder et al. (2006) employed carbon-coated monoliths as carriers in the adsorption of enzymes. They used three different carbon sources including sucrose, furfuryl alcohol and carbon nano-fibres (CNFs), grown over deposited Ni. The results showed that carbon can be employed as the support material for a lactase from Aspergillus oryzae. Due to the microporous nature of the carbons from sucrose and polyfurfuryl alcohol, these coated monoliths proved to be enzyme carriers with a low enzyme adsorption capacity. On the other hand, the CNF-based supports showed a good degree of adsorption capacity due to 1) the open structure between the fibres, 2) the regular structures and 3) a homogeneous diameter/length distribution. Furthermore, de Lathouder et al. (2007) used carbon-nanofibres, grown on two different types of monoliths with different microstructures for the physical adsorption of enzymes (Fig. 7). The monoliths were compared to novel acicular mullite monoliths (ACM) with a more open wall structure. ACM monoliths can yield a higher carbon loading compared to the classical cordierite monoliths, which results in a higher enzyme loading. Due to the more open structure between the fibres and the open walls in the ACM monoliths, the CNFs on the ACM are more readily accessible for lactase adsorption in comparison with the cordierite carriers. A comparison of lactase adsorption using three different carbon sources including nanocarbon, sucrose and furfuryl alcohol on the two monolith types are listed in Table 11.

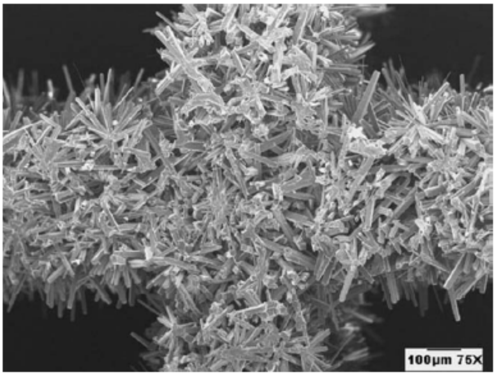

Figure 7 The SEM pattern of the microstructure of highly porous acicular mullite monoliths (ACM, 400 cpsi); Reprinted with permission from Ref. [de Lathouder et al., 2007]. Copyright [2019], [Elsevier].

Table 11 Carbon ceramic carriers for lactase immobilization: immobilization and activity

Catalyst	Total adsorption (mg protein)	Enzymatic activity (mmol $m^{-3}_{monolith}$ S^{-1})	Enzymatic activity (mmol $g^{-1}_{protein}$ S^{-1})
Free lactase			3.25×10^{-3}
C-CNF	210	8.6	2.0×10^{-3}
ACM-CNF	510	23.4	1.8×10^{-3}
C-SUC	60	1.9	1.9×10^{-3}
ACM-SUC	197	8.2	2.1×10^{-3}
C-PFA	130	3.9	2.4×10^{-3}
ACM-PFA	150	7.7	$2. 5\times10^{-3}$

CNF(Carbon Nanofiber), ACM(Acicular Mullite), SUC(Sucrose),PFA(Polyfurfuryl Alcohol); Reprinted with permission from Ref. [de Lathouder et al., 2007]. Copyright [2019], [Elsevier].

Perez-Cadenas et al. (2005) investigated the performance of two different monolithic catalysts in the hydrogenation of fatty acid methyl esters. The monolith samples were selected to have square and rounded channels. The cordierite monoliths were with α-Al_2O_3 layer using a dip-coating method in order to block the macro-porosity and to prevent the deposition of catalytic material in the wall of this monolith substrate. In order to coat polyfurfuryl alcohol (PFA) on the monolith surface, the α-Al_2O_3-coated monolith was immersed into the liquid polymer solution. Carbon was oxidized in order to establish anchoring sites for ion exchange with a tetraamminepalladium (II) nitrate solution leading to a carbon-supported Pd catalyst. The circular channels provided a uniform carbon layer. However, in the square channels a non-uniform carbon distribution was identified.

Ebrahimi et al. (2005) investigated the biofilm growth pattern in honeycomb monolith packings. Clogging due to the formation of biofilms is known to be the main potential drawback of biological monolithic reactors. An interesting phenomenon is the pattern in which biofilms develop inside the monolith channels. It was observed that the top of biofilm structure in the middle of the channel wall receives larger substrate fluxes; this eventually results in higher rates of biomass growth compared to the corners. This trend can be also observed for the biofilms formed in the experimental setup as shown in Fig. 8. The authors concluded that the biofilm patterns depended largely on the thickness of the hydrodynamic as well as on the mass transfer boundary layers.

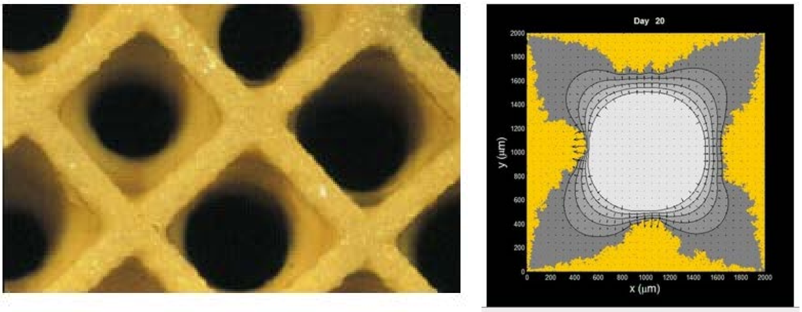

Figure 8 A biofilm developed in the square monolith channels at HRT = 30h (left), Simulated result of the developed biofilm in square monolith channels (right); Reprinted with permission from Ref. [Ebrahimi et al., 2005]. Copyright [2019], [Elsevier].

Enzyme cross-linked polyaniline-coated monoliths (*i.e.* glucose oxidase) were developed, demonstrating a high stability. The developed monoliths were employed in the bioconversion of glucose to glucolactone with a conversion of up to 83%. The stability of the enzyme-coated monolith was reported to be approximately 100% throughout the eight days of operation (Joo & Lee 2010). A sugar catalyst-supported honeycomb monolith was employed in order to produce biodiesel from palm fatty acid distillate (PFAD). A maximum methyl ester (biodiesel) content of 89% at the optimum condition (*i.e.* a methanol/oil molar ratio of 15:1, catalyst amount (2.5 wt.% with respect to PFAD), a reaction time 240 min and a temperature of 80 °C was yielded. Hosseini et al. (2015) observed that the prepared catalyst has a comparable reactivity compared with the sugar catalyst powder.

2.8 Chemical process catalyst support

Monolithic catalyst supports, promising replacements for conventional carriers, have been widely used in the synthesis of heterogeneous catalysts. The use of monolithic supports has demonstrated specific advantages (*e.g.* energy input, catalyst separation, efficiency and safety) over the fixed bed reactors and conventional slurry methods. These monoliths with various wash-coated materials were mostly used in different reactions as catalyst supports (Table 12).

3. **3D-printed honeycomb monoliths**

Successful progress has been recently made to take advantage of 3D printing in a range of applications including medicine and chemistry. There have been several reports on the application of 3D printing in the fabrication of monoliths. This method opens up new horizons for monolith fabrications with tailor-made channel networks and different catalysts' loadings. 3D printing overcomes challenges currently associated with conventional extrusion methods *i.e.* freedom of design and operation. Davó-Quiñonero et al. 2019 reported the 3D printing of monoliths with improved reaction and diffusion rates compared to conventional monoliths. This has been attributed to the ability of selecting larger inlet channels for the reactants' ease of access. Light 3D-printed pure graphene-based monoliths were fabricated based on the filament printing method. The monoliths were next applied in the treatment of wastewater using catalytic wet peroxide oxidation processes. The increasing deactivation of 3D monoliths due to the deposition of organic matter is one of major drawbacks. The applicability of thermal regeneration of these monoliths paves the way for industrial-scale applications (Quintanilla et al. 2019). Catalyst incorporation in 3D-printed templates using high-resolution digital light processing technology enables one to control the porosity, shape, size and shrinkage during thermal treatments. Deposition of ZSM-5 type zeolite on the MFI layer with a low Si/Al ratio (*i.e.* Si/Al=30) has resulted in 97-79% conversion of α-pinene (Hędrzak et al. 2019). SAPO-34 zeolite-based structured honeycomb-like monoliths were also fabricated *via* 3D printing (*i.e.* the Direct Ink writing method) and were used as adsorbent in gas separation processes (Fig.9). Due to material degradation and thermal effects, the adsorption capacity was lower than the expected capacity, however, this method was realised to be a fast, flexible and practical (Couck et al. 2018).

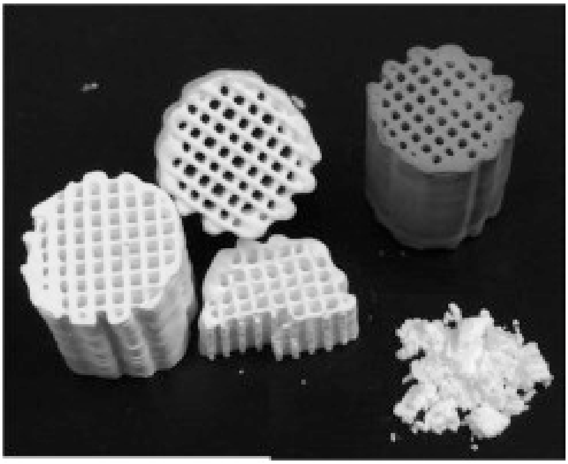

Figure 9 The 3D-printed monoliths (several SAPO-34 monolith segments (white) and one SAPO-34/graphite monolith (grey); Reprinted with permission from Ref. [Couck et al. 2018]. Copyright [2019], [Elsevier].

Table 12 Use of monoliths in different reactions as catalysts' support

Catalyst	Support	Application	Remarkable Results	Ref
Ni	Cordierites monolith	methane autothermal reforming	higher activity of foam structured at a lower average temperature	Ciambelli et al. 2010
Cobalt molybdenume-boron	Cordierites monolith	hydrolysis of sodium borohydride	well controllability of reaction and easy separation from the spent solution	Zhuang et al. 2015
ZnO, Na_2O, MgO, CaO/γ-aluminawash	Cordierites monolith/C	Fatty acid methyl ester biofuels	stabilizing catalytic activities using CaO	Kwon et al. 2015
natural medium volatile bituminous coal/ extruded		methane decomposition	higher amorphous graphite, highest activity	Gatica et al. 2015
Co_3O_4/CoO/ extruded		thermochemical heat storage	largely reduced swelling intensity	Karagiannakis et al. 2016
$Ni/MgAl_2O_4$ Ni/Al_2O_3	FeCrAlloy substrate	Hydrogen production	high activity& long-lasting stability	Koo et al. 2016
1.5%Pd/SiO_2/COR	Cordierites monolith	Synthesis of H_2O_2	space time yield (793.2 g H_2O_2 / Pd g. h	Guo et al. 2016
Nanocrystalline Pt–Ce oxides	Cordierites monolith	methane oxidation	good activity for oxygen conversion	Jin et al. 2016
2% Rh/α-Al_2O_3	Cordierites monolith	Oxidation of Iso-octane	fast, and sharp gradients of temperature and concentration	Carrera et al.2017
nickel ferrite	Cordierites monolith	H_2O splitting	High performance (compared to Ni-powder)	Lorentzou et al. 2017
HZSM-5 zeolites	Cordierites monolith	methanol to propylene reaction	Higher CH_3OH conversion (increasing 6.66 times)	Huang Et al. 2017
Mg-Sn-W composite oxides	Cordierites monolith	Baeyere-Villiger oxidation of cyclohexanone	high selectivity 86% and a conversion above 64%, significant the recycling,	Han et al. 2018
PtSnNa/g-Al_2O_3	Cordierites monolith	Propane dehydrogenation	more stable and active than classical granule catalyst	Zhao et al. 2018
Cu/SiO_2	Cordierites monolith	ethylene carbonate (EC) hydrogenation	EC (99%), ethylene glycol (97%), MeOH (50%)	Zhou et al. 2018
Sr/La_2O_3	Cordierites monolith	Oxidative coupling of CH_4	increase in methane conversion and C_2 yield	Sollier et al. 2018
Pd/Carbon	Cordierites monolith	CO oxidation	90 days 1000 m^3/h pilot experiment	Wang et al. 2014
$PdCl_2$-$CuCl_2$	Cordierites monolith	CO conversion	98% CO conversion	Yuan et al. 2016
3D$LaCoO_3$/ɤ-Al_2O_3, SiO_2, TiO_2	Cordierites monolith	Soot oxidation	the highest catalytic $LaCoO_3$/ɤ-Al_2O_3	Tang et al. 2017

4. **Regeneration processes**

A range of different methods have been recommended for the regeneration of monoliths *e.g.* washing with solvents under reflux condition, washing with water, thermal regeneration techniques, oxidation/reduction, reduction and ultrasound (Argyle; Bartholomew 2015). The ultrasound is advantageous in that it would not require an elevation in temperature. Shang et al. 2010 employed an aeration process together with an oscillating device in a washing process in order to thoroughly remove the accumulated deposits. The method was based on the regeneration of the sulfuric acid solution at a higher pH value (pH=2). The authors concluded that these processes could be considered as effective approaches for the regeneration of industrial V_2O_5–WO_3/TiO_2 catalysts. Cimino et al. 2019, investigated the thermal treatment under air (400 – 450 °C) as well as water washing at room temperature for the regeneration of V_2O_5-WO_3/TiO_2 catalyst in a tail-end SCR unit of a municipal waste incineration plant. Both of the regeneration techniques were able to remove the poisoning compounds from the used catalysts. The thermally-regenerated catalysts recovered 87% of the original rate of the SCR, whereas the washing method, was able to almost completely revive the original SCR activity.

Conclusion

In the review, the applications of honeycomb monoliths was discussed in different industrial and scientific realms. Various monoliths are used as catalyst carriers, in heat exchanger processes, in electro-chemical applications, in air purification units and in water treatment units. They are also widely used in the abatement of volatile organic compounds (VOCs), hazardous air pollutants (HAPs), carbon monoxide (CO), nitrogen oxides (NO_x), organic particulate matter (OPM), in CO_2 capture, SO_2 removal, removal of odours and other air toxics and also in dye and heavy metals removal from aqueous media. Low pressure drop, larger external surface area, low axial dispersion and back-mixing (high product selectivity), reduction of external mass transfer and internal diffusion limitations, elimination of fouling and plugging, uniform distribution of flow (gas phase), increasing catalyst lifetime and easy scale-up are the most important advantages of honeycomb monoliths' supports. Monoliths are typically produced *via* three different methods (*i.e.* coating and integration) and 3D-printing. 3D-printed monoliths are fabricated *via* layer-by-layer deposition of the constructing materials. Owing to their tailor-made designs, 3D-printed monoliths demonstrate superior mass and heat transfer properties, good architectural designs as well as higher performance in various applications. Honeycomb monoliths fabricated from natural clays have found industrial applications, especially in environmental realms, as they have proven to be good adsorbents of toxins. However, they are associated with defect formation during the extrusion processes. Paste rheology should be controlled to mitigate the formulation of the paste and additives (*i.e.* binder, catalyst and etc.) and to establish high stabilities in order to prevent phase migration. Monoliths have been developed to overcome many of the existing challenges in the direct applications of catalysts and porous carbons. Two remarkable properties of the monoliths (*i.e.* low mass transfer resistance and low pressure drop at high flow rates) well justify their prominent role in industrial and advanced applications. It is now realised that monoliths can be promising materials in different realms such as catalysis, adsorption and wastewater treatment. The prominent advantage of monoliths, produced through these methods, is the ease of application, which is attributed to lower pressure drops and the ease of regeneration. Owing to higher strengths and good uniformity, honeycomb monolith cordierites are mostly employed as catalysts' support. On the other hand, due to the issues originating from the extrusion and drying processes, the extruded monoliths are generally employed in the environmental applications. It is evident that the applications of monoliths in environmental research and large-scale technologies have well proven to be successful, with demonstrated advantages over conventional powder and granular materials.

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Nomenclature

Symbol	Description
ACM	Acicular Mullite
CFD	Computational Fluid Dynamics
CNF	Carbon Nanofiber
CO	Carbon Monoxide
CTAB	Cethyltrimethylammonium Bromide
HAP	Hazardous Air Pollutants
MCM-41	Mobil Composition of Matter No. 41
MCM-48	Mobil Composition of Matter No. 48
MCM-50	Mobil Composition of Matter No. 50
MEK	Methyl Ethyl Ketone
NOx	Nitrogen Oxides
OPM	Organic Particulate Matter
PEG	Polyethylene Glycol
PEG-A-N	A- activated and N for oxidized with nitric acid
PFA	Polyfurfuryl Alcohol
PFAD	Palm Fatty Acid Distillate
PSA	Pressure Swing Adsorption
SCO	Selective Catalytic Oxidation
SCR	Selective Catalytic Reduction
SUC	Sucrose
TSA	Temperature Swing Adsorption
VOC	Volatile Organic Compounds
ZSM	Zeolite Socony Mobil–5

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