

Chemical Process Intensification
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Module 7: Process Intensification by Monolithic Reactor
Lecture 7.3: Application of monolithic catalyst

Welcome to massive open online course on Chemical Process Intensification. So we are discussing under the module, the process intensification by monolithic reactor. There are various topics on this. In this lecture, under this module, we will discuss something about application of monolithic catalyst, how the different types of monolithic catalyst are actually applied in different chemical engineering processes. So as we know that the concept of that monolithic structure is converted to the chemical engineering process based on the catalyst are being made a shape to that monolithic structure and the flow where this monolithic structured catalyst particle.

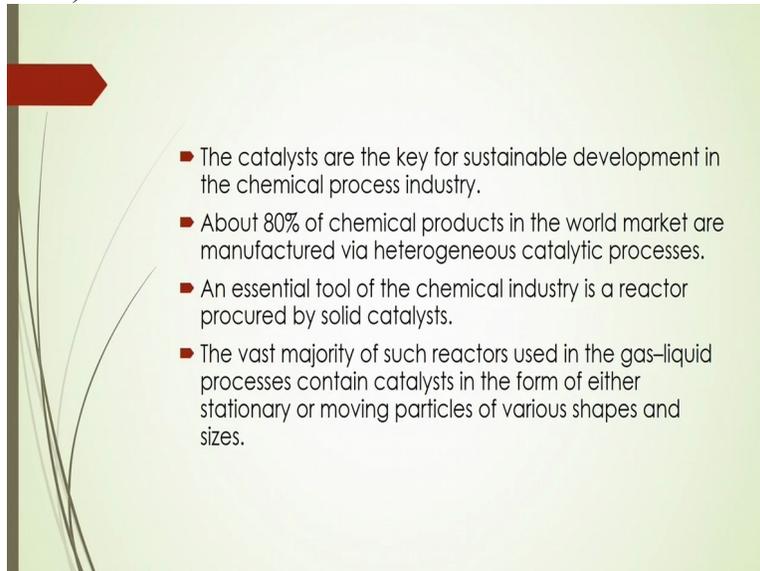
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Then how chemical engineering process can be you know that intensified that we have discussed in our earlier lectures. So there are different shapes of that monolithic structure. Maybe, honeycomb structure, even comb structure, even metallic, even sometimes ceramic materials based monolithic structures are there. And then some structures are there, honeycomb structure is there. You know, that microchannel based monolithic structures are there. And because of that we are getting that certain advantages of that flow characteristics based on how is the chemical engineering process can be intensified. So we have already discussed all those things now. Let us

discuss that several applications based on this monolithic structure catalyst in different chemical engineering processes.

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So we know that catalysts are the key for sustainable development in the chemical process industry. And also, it is reported that about 80% of chemical products in the world market are actually manufactured via heterogeneous catalytic processes. And for that, an essential tool of the chemical industry is a reactor and which is procured by the solid catalyst with a certain shape of that catalyst particles like monolithic structure. And a vast majority of such reactors used in the gas liquid processes so that contain catalyst in the form of either that stationary or moving particles of various shapes and sizes.

And as stationary like you know that the catalyst particles if it is supported by that certain metallic or ceramic monolithic structure, then it will be called as stationary. Whereas in some cases, you will see not that monolithic structure but sometimes that solid particles will be moving in a that slurry system but some other shift if like that monolithic structure but if the reactor is moving with a certain flow rate, then you can say that moving particles, that is monolithic structures may be moving in a particular processes and that can be intensified based on that moving phenomena and the Hydro phenomenon characteristics in that particular moving modes.

So these are the different that majority of such reactors are that you can use that gas liquid reactions, gas liquid solid processes, even some other processes based on that stationary and moving catalytic particles of various shapes and sizes.

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Catalyst -Recap

- Catalysts help to synthesize product in a resource protective way, with less consumption of energy and, in some cases, without any formation of byproducts and waste
- Catalysts, especially if they are applied in a structured way, play an important role in the so-called integrated approach to environmental protection,
- They include integration of various process operations such as chemical reaction, separation, heat exchange and momentum transfer.

And that catalyst help to synthesis that product in resource productive way like that with less consumption of know energy and in some cases, you can say without any formation of byproducts and ways. And also, we can say that this catalyst may integrate various process operations such as chemical reactions, separation and exchange and momentum transfer, for that integration of the process has been carried out to get the intensification of those particular processes. And in that catalyst **especially** if they are applied in a structured way, may play an important role in the so-called integrated approach to environmental protection or remediation of that unwanted particulate materials in the gaseous stream.

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And we know that different shapes of the industrial catalysts like you know, irregular or granular shapes, even spherical shapes, ring shapes, monolithic metal, pellets, extruded cylinder, trilobe type where you know that catalyst particles, monolithic foam, monolithic that ceramic particles, sometimes minilith that is shown in the figure here in the slide. Even sometimes wagon shaped wheel particles also are being used for particular chemical engineering process. And also, a MiniLessing Cross ring sometimes solid particles of this catalyst particles are being used for particular processes. So there are different shapes of industrial catalysts that are given here that you can have a look for that and also you can have idea how different shapes may act on the that industrial processes by this catalyst presence.

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Application

- The industrial application of monolithic catalysts began in 1966 with the clean-up of nitric acid tail gases, using a palladium-coated ceramic structure
- Monolithic catalysts were later used in car exhausts as three way catalysts for emission control

Some of Examples of Monolithic Structures, Materials, and Their Use

application	material	cell density/cpsi	d_h /mm	t_w /mm	ϵ or OFA%	comment
automotive	cordierite	400	1	0.10–0.18	70–80	commercial
		600	1	0.08–0.10	80–85	commercial
		900	0.8	0.05–0.08	83–88	commercial
stationary emissions (mainly oxidation and support for SCR)	cordierite	>1000				R&D
		84	2.9	0.30	82	commercial
		100	2.2	0.38	72	commercial
		230	1.5	0.18	80	commercial
		400	1	0.18	74	commercial
DeNO _x /SCR	TiO ₂ /V ₂ O ₅	8–35	3.5–8		~75	commercial, coal
		15–60	2.8–5.5		~75	commercial, oil
		35–200	1.5–3.5		70–80	commercial, gas
R&D	γ -Al ₂ O ₃ carbon Fe ₂ O ₃ /K ₂ O ₃	25–600	0.5–4	0.1–1.0	30–80	R&D, BET 200–280 m ² /g
		100–500			50–75	R&D, coated or extruded
		25–400	1–4	0.2–1.5	40–80	R&D

^a Notation: hydraulic diameter d_h , wall thickness t_w , and void fraction ϵ or OFA.

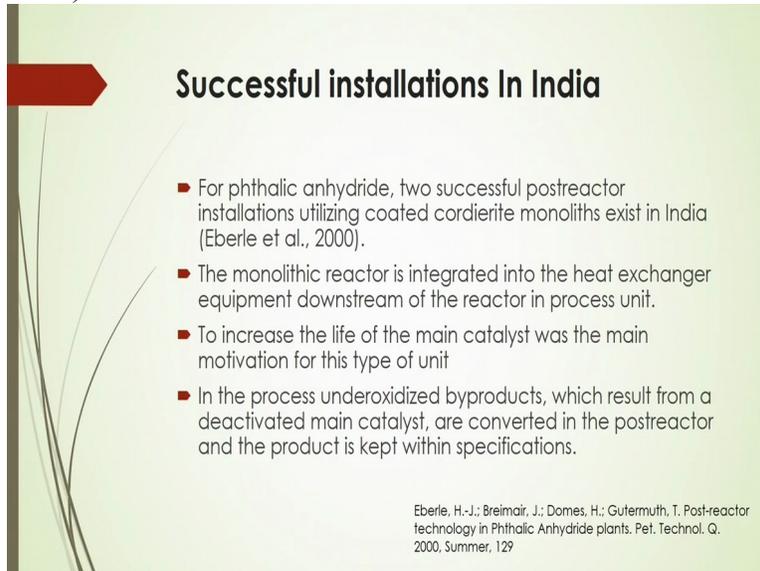
Now if we talk about that application of the monolithic catalyst, that actually you have to you know go to the earlier stage in 1966, their 1st application in industry with a clean-up of nitric acid tail gases that uses palladium coated ceramic structure. And in that case, that monolithic catalyst structures were later used in car exhausts as three-way catalysts for the emission control. So all these are the applications here where we can say that earliest days, they have actually used this monolithic catalyst for the cleanup of nitric acid tail gases. Some other applications, some examples of monolithic structures, materials and their use are given in the table here.

You know that your automotive application like material, cordierite materials for the catalyst shape and also, cell density, there it is given different cell densities applied for different hydraulic diameter. And we also width of that cell there and also you can say some commercial application and R&D applications of that automotive application for the monolithic structure. Even other different applications like stationary emissions, mainly oxidation of support for scrubbing of that particular materials from the gaseous stream. And other, in R&D also, there actually nowadays so many research is going on, based on the application of this monolithic shape catalyst in the reactor.

In this case, different materials are being synthesised and then how those materials are being made a shape and that will be monolithic different you know that shape for different structures, then how it can be applied. So researches are going on, particularly we hope that in future there

are several other applications will come based on this monolithic structure and also based on the synthesis materials of catalyst and getting the different shape for the process intensification.

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Successful installations In India

- For phthalic anhydride, two successful postreactor installations utilizing coated cordierite monoliths exist in India (Eberle et al., 2000).
- The monolithic reactor is integrated into the heat exchanger equipment downstream of the reactor in process unit.
- To increase the life of the main catalyst was the main motivation for this type of unit
- In the process underoxidized byproducts, which result from a deactivated main catalyst, are converted in the postreactor and the product is kept within specifications.

Eberle, H.-J.; Breimair, J.; Domes, H.; Gutermuth, T. Post-reactor technology in Phthalic Anhydride plants. *Pet. Technol.* Q. 2000, Summer, 129

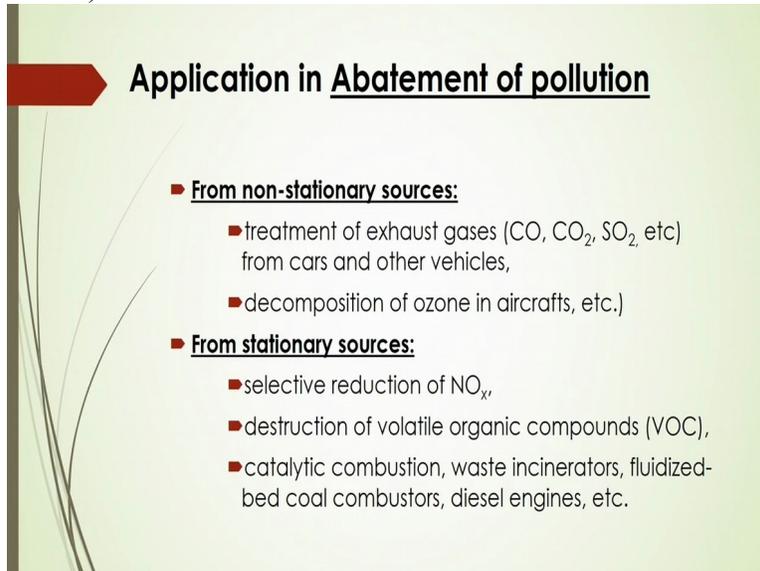
Now in India, we have that some successful installation of that monolithic reactor where some chemical engineering processes are being carried out. For phthalic anhydride, two successful post-reactor installations that utilizes coated cordierite monoliths that exist in India, that is given by Eberle et al. (2000) and they told that a monolithic structure can be used for the intensification of these reactions for production of phthalic anhydride for this cordierite monolithic structure.

And in that case, the monolithic reactor is integrated into the heat exchanger equipment downstream of the reactor in process unit. And in that case why actually they have used this monolithic reactor and why they have integrated into the heat exchanger equipment and they have reported that to increase the life of the main catalyst was the main motivation for this type of unit. So they are they are looking for that the increase of life of main catalyst. And in that case, they have used this type of monolithic structure and they also successfully that installed to carry out this chemical reactions for this particular processes.

And in the process, it is seen that under oxidised byproducts, which results from a deactivated main catalyst and those are converted in the post-reactor and the product is kept within the specifications there. So here so we can say that this is that how commercially these monolithic

catalysts are being used for that particular reactions for the chemical engineering process that we can have.

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Application in Abatement of pollution

- **From non-stationary sources:**
 - treatment of exhaust gases (CO, CO₂, SO₂, etc) from cars and other vehicles,
 - decomposition of ozone in aircrafts, etc.)
- **From stationary sources:**
 - selective reduction of NO_x,
 - destruction of volatile organic compounds (VOC),
 - catalytic combustion, waste incinerators, fluidized-bed coal combustors, diesel engines, etc.

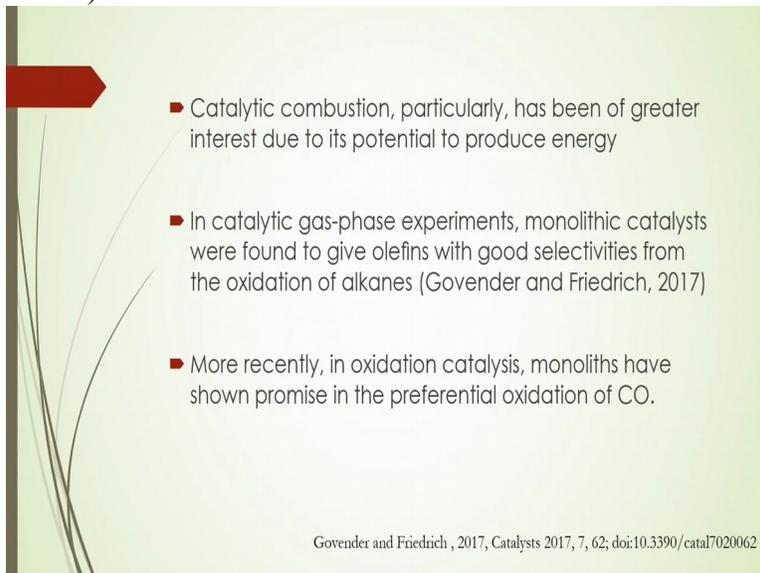
And also, there are several other applications, not only these chemical reactions of this phthalic anhydride production, there are other applications, mainly in **our**, that abatement of pollution. That is the main application there. You know from non-stationary sources, if we talk about that some exhaust gases there, you have to treat those exhaust gases for the removal of carbon monoxide, carbon dioxide, sulphur dioxide, et cetera, that is coming out from cars or other vehicles. So it is huge amount, every day there is you know that ton of gases are coming out.

So you have to treat those exhaust gases and in that case that some intensification of the process is required to remove all those gases that is **CO_x, NO_x or SO_x** gases that is coming out from the cars. So another important that for non-stationary sources like decomposition of ozone in aircrafts, that also very important. There you have to abate those ozone gases in aircraft that is coming out. So you have to decompose those ozone gases by catalytic based on that some intensified process. So that is why, this monolithic structures are nowadays giving that the best way to convert this ozone into that other derivatives and also abatement of that you know ozone from the aircraft that is coming out.

And also, stationary sources in that case selective reduction of **NO_x** is there and destruction of volatile organic compounds, catalytic combustion, waste incinerators, fluidized-bed coal

combustion and diesel engines, et cetera. So there are several you know applications that based on that monolithic structures is for the abatement of the pollution is going on.

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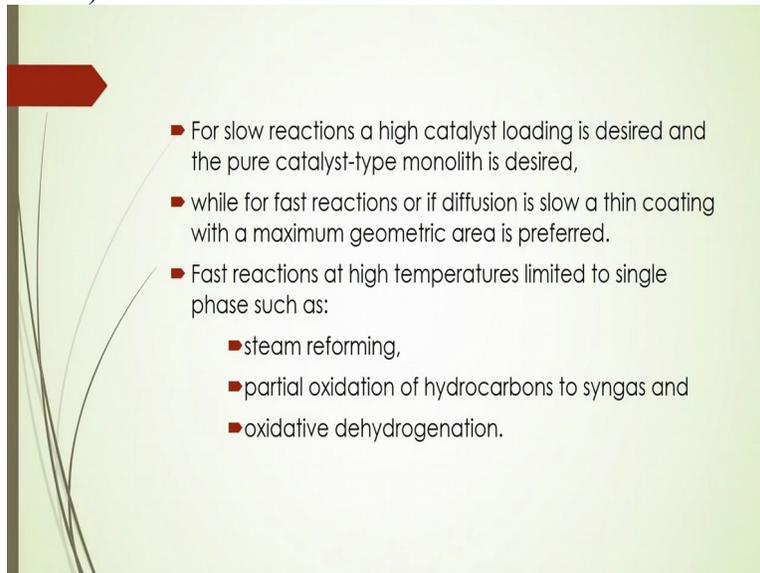


- Catalytic combustion, particularly, has been of greater interest due to its potential to produce energy
- In catalytic gas-phase experiments, monolithic catalysts were found to give olefins with good selectivities from the oxidation of alkanes (Govender and Friedrich, 2017)
- More recently, in oxidation catalysis, monoliths have shown promise in the preferential oxidation of CO.

Govender and Friedrich, 2017, Catalysts 2017, 7, 62; doi:10.3390/catal7020062

And in case of catalytic combustion, you will see that particularly it has been of greater interest due to its potential to produce energy there. So in that case, that catalytic gas phase experiments, monolithic catalysts were found to give olefins with good **selectivity** from the oxidation of alkanes. That is reported by Govender and Friedrich, in 2017. And more recently, they have stated that in oxidation catalysis, monoliths have that shown promise in the preferential oxidation of carbon monoxide. So this is the application for this monolithic structure.

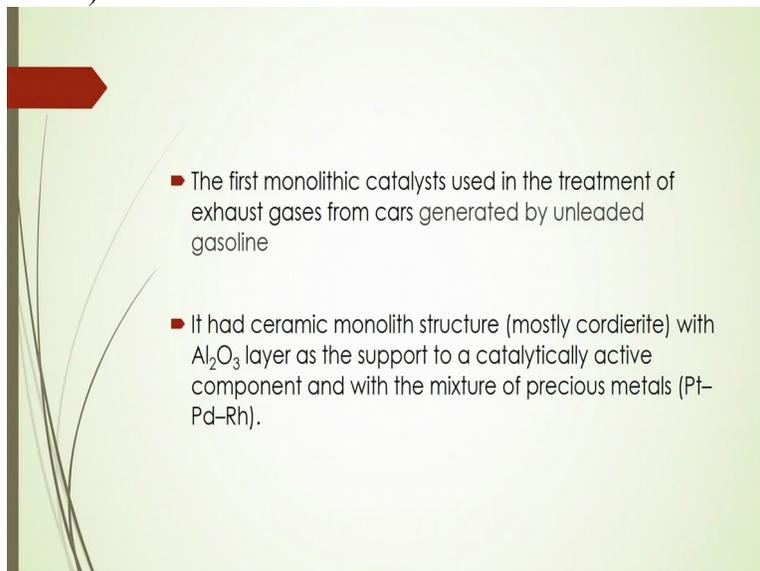
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A slide with a light green background and a dark green vertical bar on the left. A red arrow points to the right. The text is as follows:

- For slow reactions a high catalyst loading is desired and the pure catalyst-type monolith is desired,
- while for fast reactions or if diffusion is slow a thin coating with a maximum geometric area is preferred.
- Fast reactions at high temperatures limited to single phase such as:
 - steam reforming,
 - partial oxidation of hydrocarbons to syngas and
 - oxidative dehydrogenation.

Now for slower reactions, if we consider that high catalyst loading, it is of course sometimes desired and the pure catalyst type of monoliths should be you know used there. So while for fast reactions or if diffusion is slow, so in that case you have to consider a thin coating with a maximum geometric area there. So in that case, so you have to use that monolithic catalytic reactor based on the criteria of slow or fast reactions. And in case of fast reactions at high temperature, it is limited to single phase such as steam reforming, partial oxidation of hydrocarbons to syngas and oxidative dehydrogenation there.

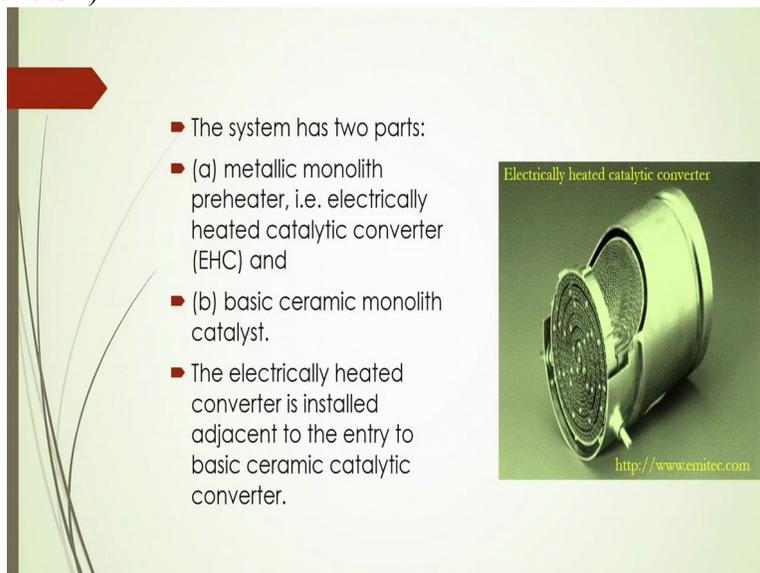
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A slide with a light green background and a dark green vertical bar on the left. A red arrow points to the right. The text is as follows:

- The first monolithic catalysts used in the treatment of exhaust gases from cars generated by unleaded gasoline
- It had ceramic monolith structure (mostly cordierite) with Al_2O_3 layer as the support to a catalytically active component and with the mixture of precious metals (Pt-Pd-Rh).

And the first monolithic catalyst used in the treatment of exhaust gases from the cars generated by unleaded gasoline. So this is also important applications there in monolithic structure catalyst for that particular particulate materials removal from the exhaust gases. And also, it is seen that the ceramic monolith structure with aluminium oxide layer as a support to a catalytically active component and the mixture of precious metals like platinum, rhodium, palladium, those materials will give you that you know that intensified way of that remove of that exhaust gases from the cars that is generated by gasoline.

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- The system has two parts:
- (a) metallic monolith preheater, i.e. electrically heated catalytic converter (EHC) and
- (b) basic ceramic monolith catalyst.
- The electrically heated converter is installed adjacent to the entry to basic ceramic catalytic converter.

Electrically heated catalytic converter

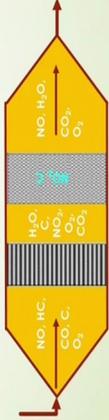
<http://www.emitec.com>

And the system has that **two** parts of that you know that catalytic converter, mainly the metallic monolith preheater, electrically that is heated catalytic converter and also basic ceramic monolith catalyst shown in here in the picture, the electrically heated converter is installed adjacent to the entry to basic ceramic catalytic converter here as shown in the figure. This actually, figure is taken from that website is given in the slide. **So**, that is why, the catalytic converter is actually widely used for that removal of gases from the that is coming out from the car by combustion of gasoline in there. So that is why, what type of actually that monolithic structure should be used? That metallic monolithic preheater and also ceramic monolithic catalyst also, both can be used in that particular catalytic converter. And electrically heated converter is installed adjacent to the entry to basic ceramic catalytic converter there you have to remember.

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Monolithic catalytic system of car

- Simultaneous removal of solid particles and nitrogen oxides from the exhaust gases generated by diesel fuel combustion and regeneration of a catalytic system
- The first part of the system has a ceramic monolith catalyst (Pt as a catalytically active component) that enables oxidation of CO and hydrocarbon into CO₂ and H₂O, respectively.
- Simultaneously, nitrogen oxides (present in flue gases mostly as NO) oxidize to NO₂, while the remaining gas mixture passes through other part of the system where solid particles accumulate.

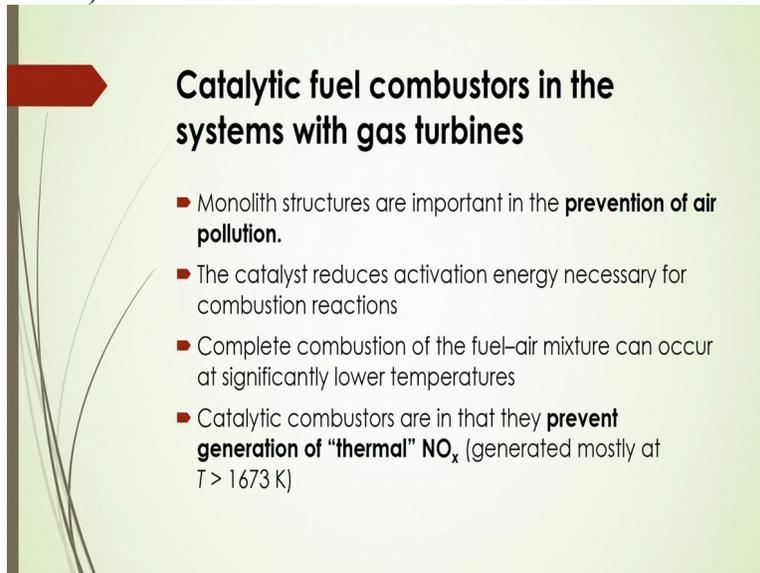


And monolithic catalytic system of car, here see in the figure it is shown that this converter from the bottom that there will be you know simultaneous removal of solid particles and the nitrogen oxide that is from the exhaust gases generated by diesel fuel combustion and generation of the catalytic system there. This is the function of this catalytic converter. And in this case, the 1st part of the system has a ceramic monolithic catalyst that is platinum as a catalytically active component is being used and which actually enables oxidation of carbon monoxide and hydrocarbon into carbon dioxide and also water respectively.

So it is to be actually remembered that there are **two** parts of this catalytic converter. In the 1st part system, that is ceramic monolithic catalyst are being used to enable the oxidation of carbon monoxide and also hydrocarbon to its carbon dioxide. That is carbon monoxide to carbon dioxide and hydrocarbon to water. And there also, you will see simultaneously, nitrogen oxides that is present in the few gases mostly as **NO_x**, that is nitrous oxide, they are that oxidize to nitrogen dioxide. While remaining gaseous mixture may pass through other part of the system where solid particles are being accumulated.

So that is why, when the 1st part and the 2nd part, that is totally then the 1st part that is carbon monoxide is converted to carbon dioxide and hydrocarbon is converted to water whereas the 2nd part it will be nitrous oxide to be treated and to give you nitrogen dioxide and also other mixtures through this part of the system where solid particles are accumulated.

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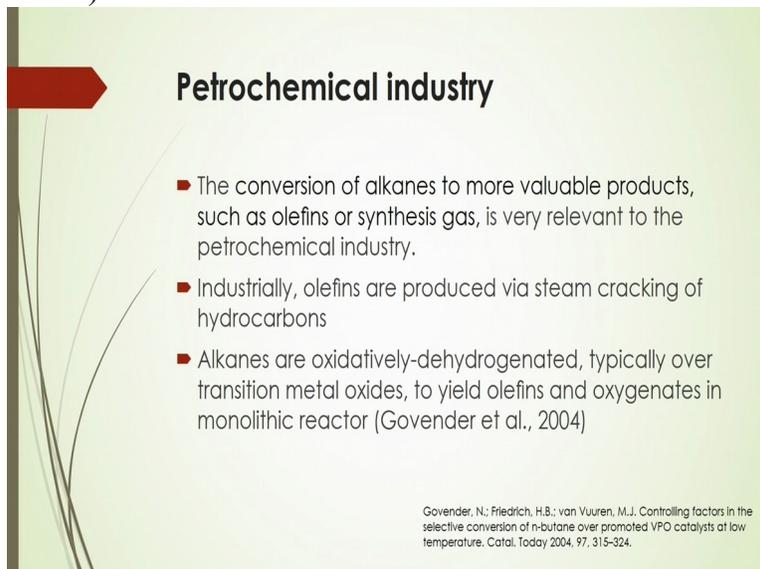


Catalytic fuel combustors in the systems with gas turbines

- Monolith structures are important in the **prevention of air pollution**.
- The catalyst reduces activation energy necessary for combustion reactions
- Complete combustion of the fuel-air mixture can occur at significantly lower temperatures
- Catalytic combustors are in that they **prevent generation of "thermal" NO_x** (generated mostly at $T > 1673$ K)

And in case of catalytic fuel combustors in the system with gas turbines, in that case you will see monolith structures are important in prevention of air pollution. In that case, the catalyst reduces activation energy which are actually required for the combustion reactions. And in that case, complete combustion of the fuel-air mixture that may occur at significantly lower temperature. But in this case, you have to remember that catalytic combustors are in that they are prevent generation of thermal **NO_x** generally generated at temperature greater than 1673 Kelvin.

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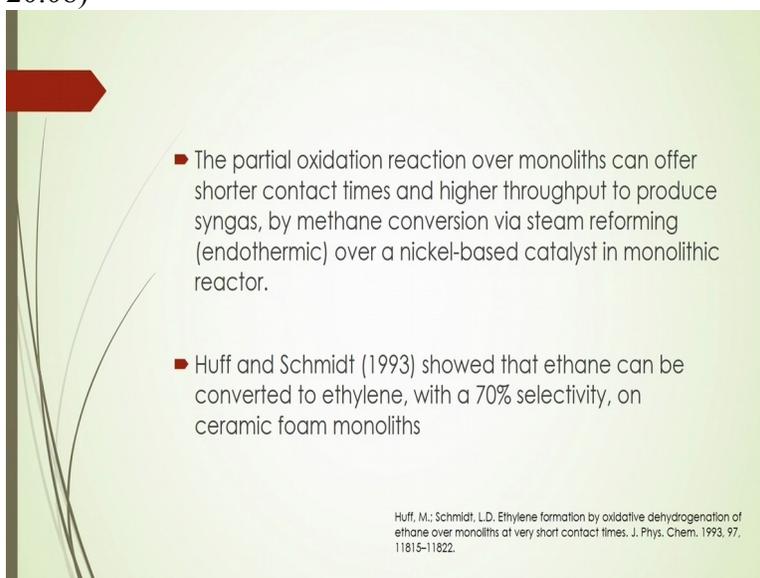
Petrochemical industry

- The conversion of alkanes to more valuable products, such as olefins or synthesis gas, is very relevant to the petrochemical industry.
- Industrially, olefins are produced via steam cracking of hydrocarbons
- Alkanes are oxidatively-dehydrogenated, typically over transition metal oxides, to yield olefins and oxygenates in monolithic reactor (Govender et al., 2004)

Govender, N.; Friedrich, H.B.; van Vuuren, M.J. Controlling factors in the selective conversion of n-butane over promoted VPO catalysts at low temperature. *Catal. Today* 2004, 97, 315-324.

And there are other applications of this monolithic catalyst that is in petrochemical industry. In that case, that conversion of alkanes, alkenes and other organic compounds decomposing into that other products by catalyst, in presence of catalyst. So in that case, the conversion of alkanes to more valuable products such as olefins or synthesis gases is very relevant to this petrochemical industry and in that case, olefins are produced via steam cracking of hydrocarbons and that is being actually occurred in that monolithic structure. Also, that alkanes are oxidatively dehydrogenated in this monolithic reactor, typically over transition metal oxides, to yield olefins and oxygenates in that monolithic reactor. That is reported by Govender et al., 2004.

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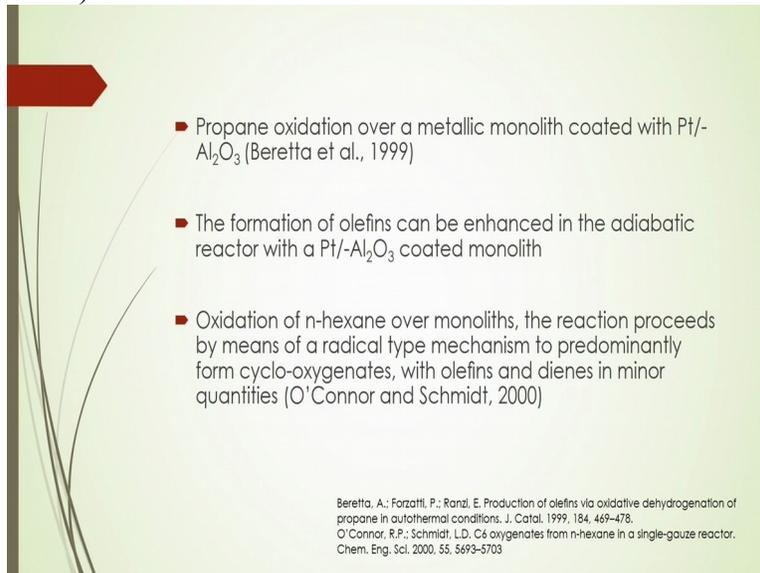


- The partial oxidation reaction over monoliths can offer shorter contact times and higher throughput to produce syngas, by methane conversion via steam reforming (endothermic) over a nickel-based catalyst in monolithic reactor.
- Huff and Schmidt (1993) showed that ethane can be converted to ethylene, with a 70% selectivity, on ceramic foam monoliths

Huff, M.; Schmidt, L.D. Ethylene formation by oxidative dehydrogenation of ethane over monoliths at very short contact times. *J. Phys. Chem.* 1993, 97, 11815-11822.

And the partial oxidation reaction over monoliths can also offer shorter contact times, that is why it is advantageous and also you will see whenever we are actually use or carry out that partial oxidation reaction in that monolithic structures, it is seen that there will be higher throughput to produce that syngas with a very shorter contact times. In that case, methane conversion is very important because this gives that you know that different hydrocarbons via steam reforming, that is the reaction is at lower temperatures, that is endothermic reaction is there over a nickel-based catalyst. And in this case, you have to remember that it is seen that and also reported by Huff and Schmidt that Ethane can be converted to ethylene with a 70 percent selectivity on ceramic foam monolith structures there.

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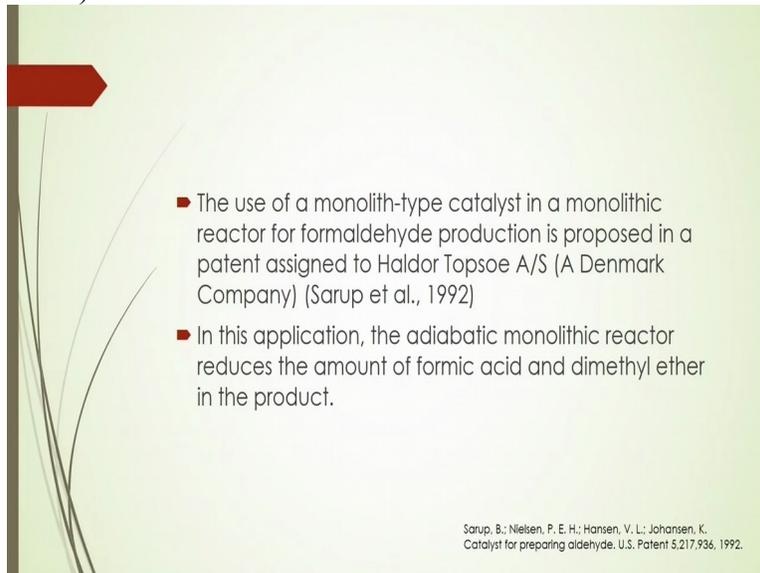


- Propane oxidation over a metallic monolith coated with Pt/ Al_2O_3 (Beretta et al., 1999)
- The formation of olefins can be enhanced in the adiabatic reactor with a Pt/ Al_2O_3 coated monolith
- Oxidation of n-hexane over monoliths, the reaction proceeds by means of a radical type mechanism to predominantly form cyclo-oxygenates, with olefins and dienes in minor quantities (O'Connor and Schmidt, 2000)

Beretta, A.; Forzatti, P.; Ranzì, E. Production of olefins via oxidative dehydrogenation of propane in autothermal conditions. *J. Catal.* 1999, 184, 469–478.
O'Connor, R.P.; Schmidt, L.D. C₆ oxygenates from n-hexane in a single-gauze reactor. *Chem. Eng. Sci.* 2000, 55, 5693–5703

And propane oxidation over a metallic monolith coated with platinum aluminium oxide is very important in the case of monolithic structure which are made in metal like you know that stainless steel and others. And the formation of olefins can be enhanced in the adiabatic reactor with a platinum aluminium oxide coated monoliths there. And in the petrochemical industries, they are normal hexane over monoliths, in that case, the reaction proceeds by means of a radical type of mechanism to predominantly form cyclo-oxygenates with that olefins and also dienes in minor quantities where you can get this oxidation of this normal hexane over this monoliths. So it is reported to by O'Connor and Schmidt in 2000 there.

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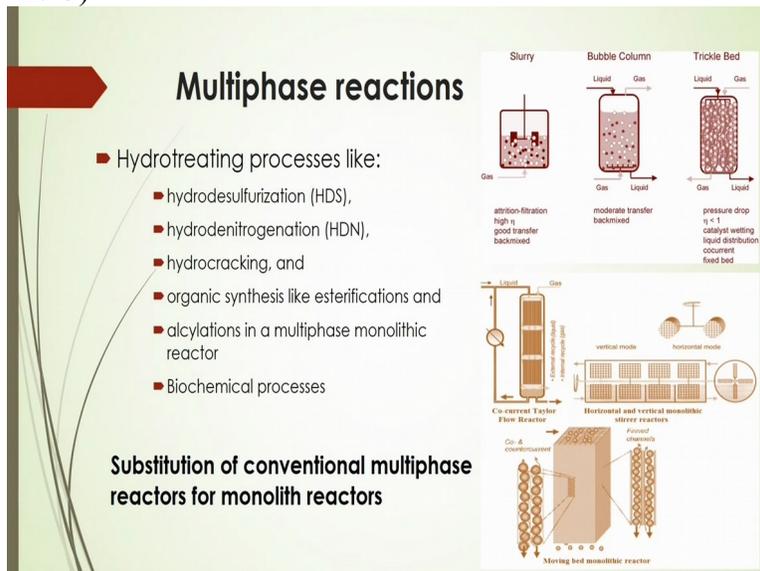
■ The use of a monolith-type catalyst in a monolithic reactor for formaldehyde production is proposed in a patent assigned to Haldor Topsoe A/S (A Denmark Company) (Sarup et al., 1992)

■ In this application, the adiabatic monolithic reactor reduces the amount of formic acid and dimethyl ether in the product.

Sarup, B.; Nielsen, P. E. H.; Hansen, V. L.; Johansen, K. Catalyst for preparing aldehyde. U.S. Patent 5,217,936, 1992.

And the use of monolith type catalyst in a monolithic reactor or formaldehyde production is actually proposed in a patent that is assigned to Haldor Topsoe in that company, that is, this is a Denmark company that is reported by Sarup et al., 1992. This company also is using this monolithic type catalyst **for that production** of formaldehyde there. So in this case, the adiabatic monolithic reactor reduces the amount of formic acid and also dimethyl ether in the product.

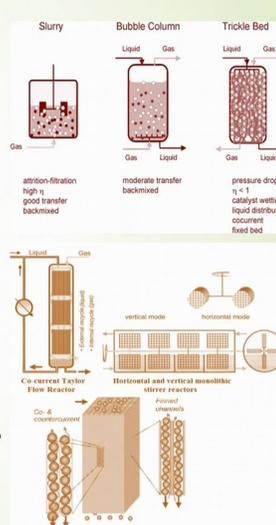
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Multiphase reactions

- Hydrotreating processes like:
 - hydrosulfurization (HDS),
 - hydrodenitrogenation (HDN),
 - hydrocracking, and
 - organic synthesis like esterifications and
 - alcylation in a multiphase monolithic reactor
 - Biochemical processes

Substitution of conventional multiphase reactors for monolith reactors



The diagrams illustrate different reactor configurations. The top row shows Slurry, Bubble Column, and Trickle Bed reactors with their respective flow patterns and characteristics. The middle row shows a Cu-current Taylor Flow Reactor and Horizontal and vertical monolithic stirred reactors. The bottom row shows a Moving bed monolithic reactor.

Now except this multiphase petrochemical you know that conversion of different alkanes or alkenes into several products, you can have this monolithic structures applied in multiphase

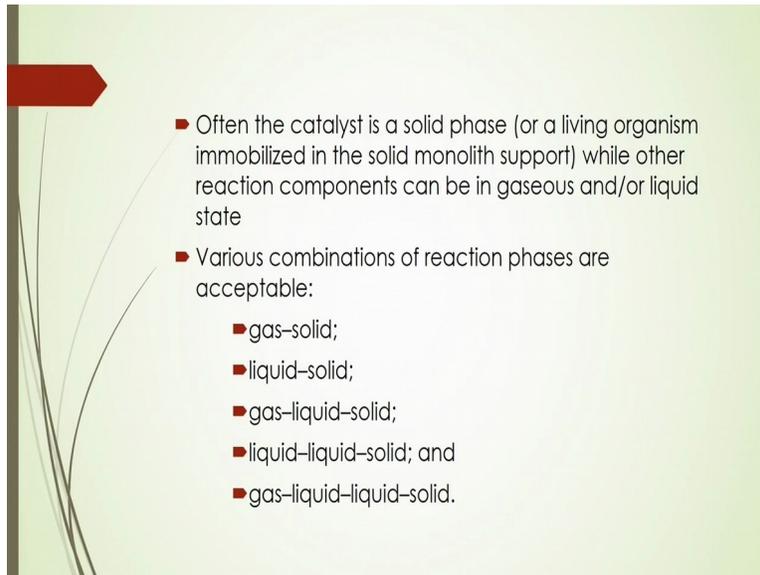
reactions also like hydrotreating processes, there you know hydrodesulphurization, hydrodenitrogenation, even hydrocracking, sometimes that biochemical processes, alkylation in multiphase monolithic reactor, sometimes organic synthesis like Esterifications, those are actually applied in monolithic structures or catalyst there.

So in the monolithic reactor, they are using this multiphase different type of reactions and in this case, the conventional multiphase reactors are being actually substituted by this monolithic reactors because of some advantages for this you know that getting the more contact, even the more residence time, and also lower pressure drop, there are several hydrodynamic aspects are actually involved in this particular monolithic structures when these multiphase reactions are being carried out. So conventional reactions like slurry, column, bubble column reactor, trickle bed reactors are there.

That is gas liquid reactions. There also, there are several advantages like backmixing, even that backmixing can be reduced by that structure of that conventional slurry bubble column in a two-dimensional column and also that trickle bed reactors may not be up-flow trickle bed reactor, that will be down flow reactors. They are also, that channeling of that liquid and gas flow, they may give that intensification of the process but still, there for the reactions that we can further intensify the process by this monolithic structure where catalyst particles are actively take part for that particular multiphase reactions there.

So in this case, whenever you are analysing these multiphase reactions in this monolithic structure, you have to consider the several hydrodynamic aspects of that, based on that hydrodynamic aspects that you can get the intensified way of that output of that multiphase reactions there. You have to study that what is the frictional pressure drop, what is the hold up, what will be the liquid distribution over the monolithic structure, even how you know that residence time distribution actually is there in the inside the reactor and also there are several geometry of that liquid distribution should be considered whenever you are doing or the multiphase reactions have been carried out in the monolithic reactor there.

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So often, the catalyst is a solid phase, you will see that or a living organism immobilised in the solid monolithic structure. In that case that reaction components can be gaseous or liquid state. So there are several combinations of the reactions in the multiphase systems like you know gas-solid reactions, liquid-solid reactions, gas-liquid-solid reactions, gas-liquid-liquid-solid, even gas-liquid-liquid-solid also there. So in that case, there are several you know that multiphase operations should be considered and for the particular chemical engineering process like gas-solid, there are several applications of gas-solid reactions.

Maybe sometimes, drying process is gas and solid. Even you know that, sometimes you know that catalytic cracking in the gaseous medium, coal combustions to get the several hydrocarbons when you know that to produce power there. Liquid-solid, there are leaching operations. You have to extract some that liquid from the solid materials like that you are extracting oil from the seeds like this. Gas, liquid and solids, they are catalytic reactions in a slurry reactor in monolithic reactor gas liquid reactions. Even liquid-liquid-solid, sometimes in presence of that solid particles, catalytic extraction is there. So liquid-liquid extraction in presence of solid particles there.

When gas-liquid-liquid-solid sometimes that liquid-liquid extraction in gas induced operations, via that you can get the mixing phenomena, even intense mixing may you know that result the more yield of the extraction process is there.

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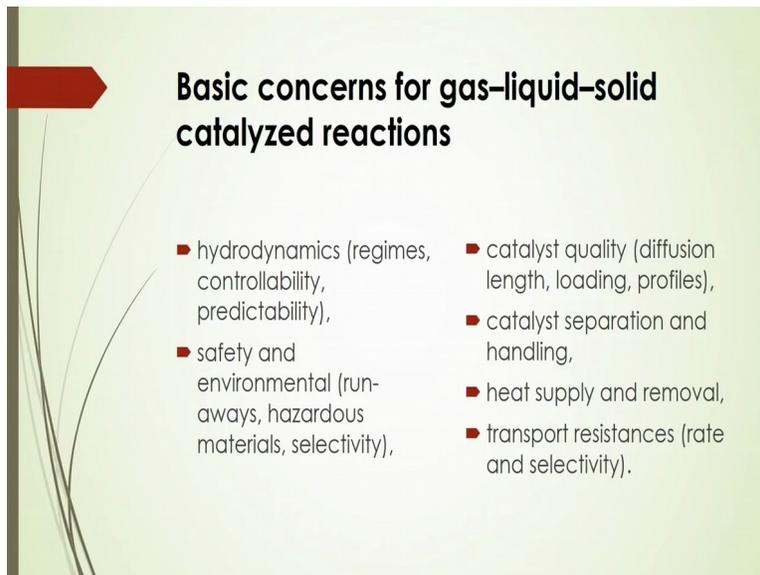


And there are several other, that operations that in presence of monolithic structures based on this combination of that gas-liquid-solid reactions there. So you have to you supply those gas on liquid through that monolithic reactor. In that case, it may be co-current, it may be countercurrent operation.

So with respect to the relatively small channel diameter, you can use this the monolithic structure. And for countercurrent operations, maybe in monolithic structure will be very limited because it is very difficult to get that countercurrent operations and get liquid in the monolithic structure because this channel size is very low. So it is actually very convenient to get that co-current operations of gas and liquid. Whereas, that in most cases, solid-phase is immovable but there are designs with the moving bed applications also.

You know, that moving packed bed or monolithic reactor is there, movable monolithic reactors for that centrifugal action by which you can separate that some liquid particles from the solid or extraction or absorption processes also by this that centrifugal action of this monolithic structure. So in that case you can think about that how moving bed can be applied for that particular chemical engineering processes based on that monolithic structure.

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Basic concerns for gas-liquid-solid catalyzed reactions

- hydrodynamics (regimes, controllability, predictability),
- safety and environmental (run-aways, hazardous materials, selectivity),
- catalyst quality (diffusion length, loading, profiles),
- catalyst separation and handling,
- heat supply and removal,
- transport resistances (rate and selectivity).

Now you have to remember some basic things for this gas-liquid-solid catalytic reactions there. So in that case what should be the hydrodynamics, like regimes? If it is gas-liquid reactions, then what would be the size of the gas slug, what would be the size of the liquid slug is there. So you have to control all those things to get that intensified way of process output. And also, safety and environmental aspects is very important that you have to consider for that catalytic reaction whether it is giving that hazardous materials as output or not. So you have to select the solvent in such a way that you can minimise that hazardous materials to be coming out as output byproduct.

And also, you have to use that catalyst which will be selective, that may be qualified with that diffusion link, loading and also profiles there. And also that how to handle that catalyst in the monolithic structure that you have to consider, how to distribute the liquid through that catalyst particles in the monolithic structures. And also, if it is to be regenerated, then how to remove from that catalyst particles from the monolithic structure, that is also important there. And whenever you are supplying any heat for that particular chemical engineering reactions there and also how to remove those heat there, if there are that heat continues there, maybe you know that sometimes thermal properties of that material may be degraded.

So in that case you have to wisely use that supplying of the heat and also its removal by that sometimes heat exchanger or other mechanical devices to control that heat. And also, you have to think about that transport resistances, maybe rate and selectivity there. If it is there gas-liquid

transfer or gas-solid reactions is there, how that you liquid thin film will be acting or play a role in that gas-liquid reactions and also in the solid surface, how porosity will be taking part for that particular reactions to get its that selective yield there.

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Qualitative Rating of the Technical Benefits of Monolithic Catalysts in Different Processes

type of reaction	gas/solid and liquid/solid ^a		gas/liquid/solid ^a	
	fast	slow	fast	slow
hydrodynamics	low pressure drop	+++	+++	
	low fouling potential	++	+	
	catalyst bed uniformity	++		++
	high countercurrent hydraulic capacity		N/A	+++
reactive performance	better solid irrigation/utilization		N/A	++
	high catalyst load/pressure drop ratio	++	+++	++
	high mass transfer/pressure drop ratio	+++	+	+++
	good dynamic response		++	++
	better temperature control (conductive monolith)	+++		++
structural	enables egg-shell/thin thickness catalyst system	+++	N/A	+++
	good structural integrity	+++ ^b + ^c		+++ ^b + ^c
	low catalyst attrition	++	+	++

^a+: small benefit. ++: solid benefit. +++: very significant benefit. ^b Catalyst supported on an inert monolithic backbone. ^c Bulk monolithic catalyst.

Ref.: T. Boger, A. K. Heibel and C. M. Sorensen, Ind. Eng. Chem. Res., Vol. 43, No. 16, 2004

Now in this case you have to remember these things that topology of this you know that qualitative rating of the technical benefits of this monolithic catalysts in different processes, like if you are considering that hydrodynamic aspects, then type of reactions would be that low-pressure drop based reactions, low fouling potential based reactions, even catalyst bed uniformity and also high countercurrent hydraulic capacity should be considered in that case for the particular reactions.

In this case, you can carry out that gas-solid reactions or liquid-solid reactions, that may be fast or slow. In this case, fast and slow, both you can have but sometimes that for high countercurrent hydraulic capacity based reactors you cannot consider that gas-solid or liquid-solid reactions at this hydrodynamic conditions. And for gas-liquid-solids, there you can this low-pressure, low fouling catalyst bed uniformity and also high countercurrent hydraulic capacity based reactions in considering that hydrodynamic aspects for fast and slow reactions.

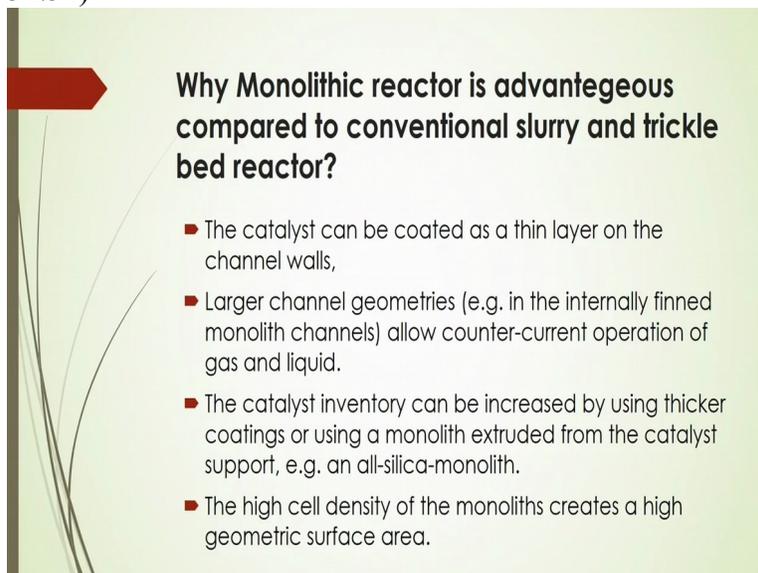
And also, reactive performance if we consider that, you will see that better solid irrigation or utilisation should be considered. Higher catalyst load or pressure drop ratio to be maintained, even high mass transfer or pressure drop ratio to be considered and good dynamic response to be that

taken care and also that better temperature control to be there for that particular reactions. In that case, you know that how fast and slow reactions have happened, you know that maximum cases in the fast reactions, you know high mass transfer or pressure drop ratio. In that case, you can get the fast reactions for the gas-solid reactions and also slow reactions also can have but be limited.

But in case of structural that in this case, enables egg-shell/thin thickness of catalyst systems and a good structural integrity, low catalyst attrition. In that case, you can have both fast and slow reactions but slow reactions would be limited. Whereas in gas-liquid-solid, in that case also you can have that fast and slow reactions. Whereas slow reactions will be limited. So here, in this case that plus indicated in this figure ABC, here plus is small benefit, double plus is solid benefit and triple plus is very significant benefit. And catalyst supported on an inert monolithic backbone, that will also be considered in the case of that catalytic structure of monolithic reactor.

And also bulk monolithic catalyst to be considered if is there, then you know that there will be a good structural integrity of their node, that should be considered for that fast or slow reactions of gas-solid or liquid-solid reactions.

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Why Monolithic reactor is advantageous compared to conventional slurry and trickle bed reactor?

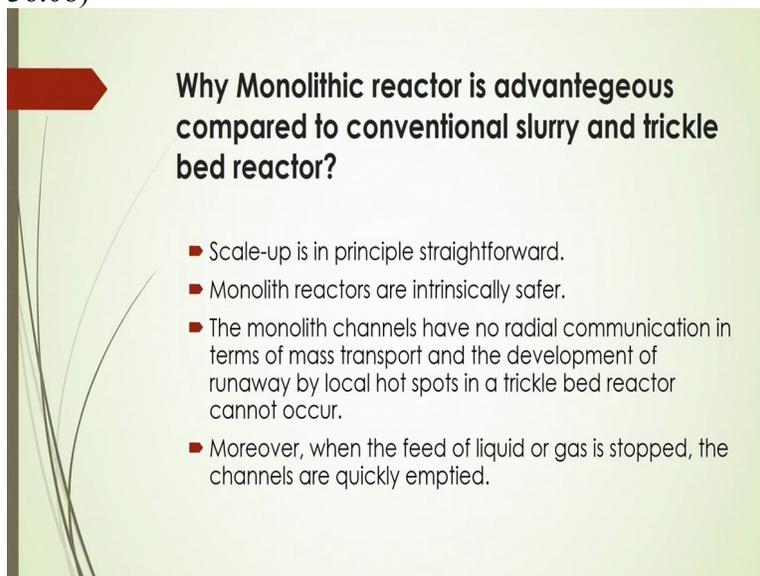
- The catalyst can be coated as a thin layer on the channel walls,
- Larger channel geometries (e.g. in the internally finned monolith channels) allow counter-current operation of gas and liquid.
- The catalyst inventory can be increased by using thicker coatings or using a monolith extruded from the catalyst support, e.g. an all-silica-monolith.
- The high cell density of the monoliths creates a high geometric surface area.

Now main question is that why this monolithic reactor is advantageous, that is compared to conventional slurry and trickle bed reactors? In this case, you will see, for monolithic reactor, the catalyst can be coated as a thin layer on the channel wall. That is advantageous, whereas it is not in that conventional slurry or trickle bed reactor. And also, in the monolithic structure, you will

see larger channel geometries that is internally finned monolithic channel allow countercurrent operation of the gas and liquid there. And in the catalyst inventory can be increased by using thicker coatings or using a monolithic extruded from the catalyst support and also other you know that structure based on that catalytic type.

So in that case, one example that an alumina silica, you know that monolithic structure can be used for this catalyst inventory to increase by its thicker coating or using a monolithic extruded from the catalyst support. And the high cell density of the monoliths creates a high geometric surface area, that is one advantages, where main advantage is that you may not get that backmixing here, maximum that slug flow, phenomena of slug flow phenomena will give you that you know that better performance of the reactions and yield.

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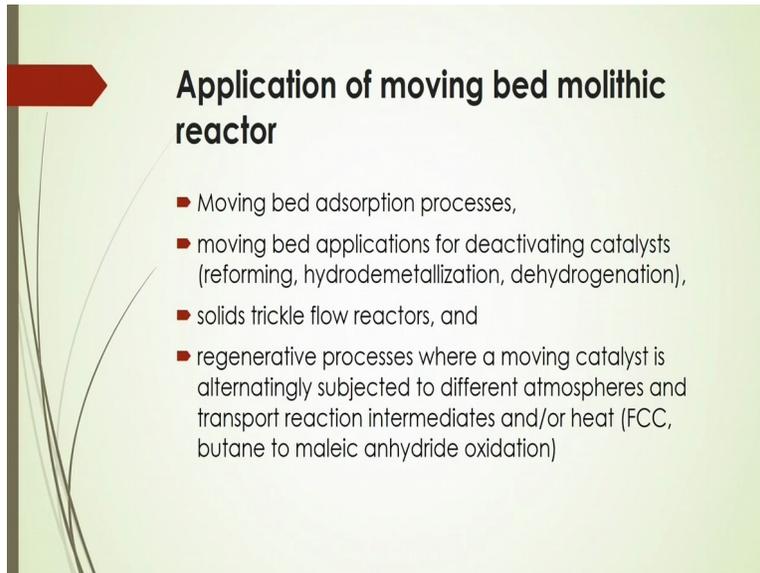


Why Monolithic reactor is advantageeous compared to conventional slurry and trickle bed reactor?

- Scale-up is in principle straightforward.
- Monolith reactors are intrinsically safer.
- The monolith channels have no radial communication in terms of mass transport and the development of runaway by local hot spots in a trickle bed reactor cannot occur.
- Moreover, when the feed of liquid or gas is stopped, the channels are quickly emptied.

And also scale-up is the issue there. Scale-up is in principle straightforward in monolithic reactor. Monolithic reactors are intrinsically safer and also when the feed of liquid or gas is stopped, the channels are quickly emptied and also, the monolithic channels have no radial communication in the terms of mass transport and the development of runaway by local hot spots in a trickle bed reactor that cannot occur here. So in the trickle but reactor, we are having that local hot spots but here in this monolithic structure, we are not having that local hot spots there.

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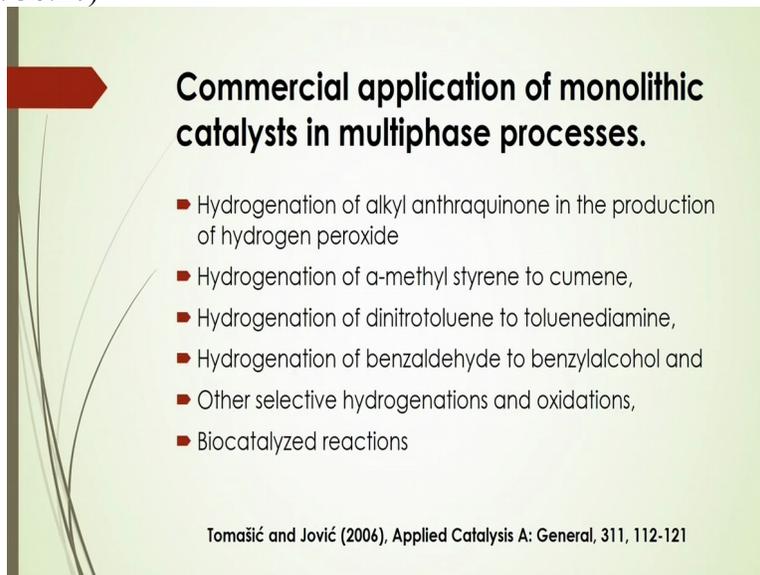
Application of moving bed molithic reactor

- Moving bed adsorption processes,
- moving bed applications for deactivating catalysts (reforming, hydrodemetallization, dehydrogenation),
- solids trickle flow reactors, and
- regenerative processes where a moving catalyst is alternately subjected to different atmospheres and transport reaction intermediates and/or heat (FCC, butane to maleic anhydride oxidation)

And also a moving bed adsorption process is one of the important application in monolithic structure moving bed reactor. In that case, deactivating catalysts, reforming, dehydrodemetalisation and also dehydrogenation, even you know that other regeneration processes of catalyst that can be done in the monolithic structure, whereas the solid trickle flow reactions, they are in the trickle bed reactors are generative process. In that case you can use that movable reactors instead of this monolithic reactors but sometimes that hydrodynamic aspects may give the disadvantage of this that trickle but reactor in this movable condition as compared to that monolithic structure because they are, you know that the transfer of that gaseous components to the solid components, it actually depends on that energy transport there.

Whereas, in trickle bed reactors, it may require more energy dissipation compared to that monolithic structures because there that channeling of that radial distribution of that gas-liquid will give you that higher energy distribution required for that trickle bed reactor.

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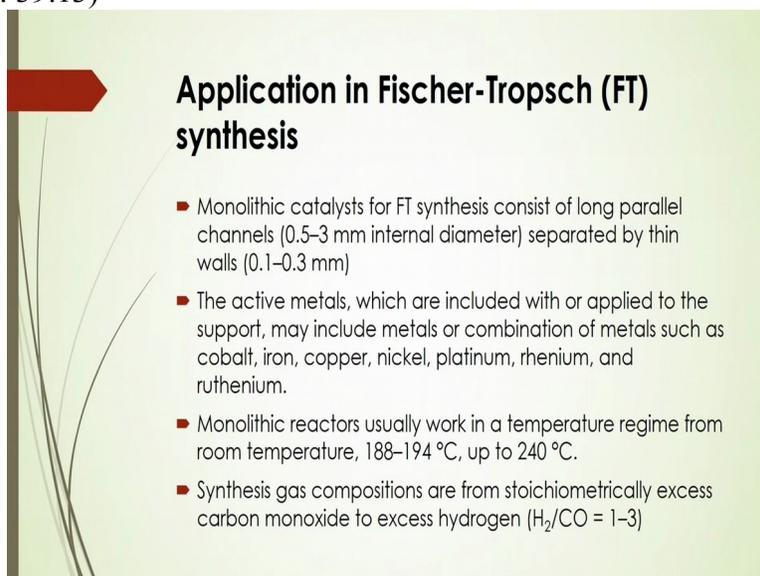
Commercial application of monolithic catalysts in multiphase processes.

- Hydrogenation of alkyl anthraquinone in the production of hydrogen peroxide
- Hydrogenation of α -methyl styrene to cumene,
- Hydrogenation of dinitrotoluene to toluenediamine,
- Hydrogenation of benzaldehyde to benzylalcohol and
- Other selective hydrogenations and oxidations,
- Biocatalyzed reactions

Tomašić and Jović (2006), *Applied Catalysis A: General*, 311, 112-121

Whereas hydrogenation of alkyl anthraquinone in the production of hydrogen peroxide are generally used in commercially, actually installed monolithic catalytic reactor. In that case, hydrogenation of methyl styrene to cumene, another example we have to remember and also that some bio-catalyst reactions are being used in this that monolithic catalyst in multiphase processes. So this hydrogenation of dinitrotoluenes to toluenediamine and hydrogenation of benzaldehyde to benzyl alcohol, so this type of that applications are being commercially available here for this multiphase reactions in monolithic reactor.

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Application in Fischer-Tropsch (FT) synthesis

- Monolithic catalysts for FT synthesis consist of long parallel channels (0.5–3 mm internal diameter) separated by thin walls (0.1–0.3 mm)
- The active metals, which are included with or applied to the support, may include metals or combination of metals such as cobalt, iron, copper, nickel, platinum, rhenium, and ruthenium.
- Monolithic reactors usually work in a temperature regime from room temperature, 188–194 °C, up to 240 °C.
- Synthesis gas compositions are from stoichiometrically excess carbon monoxide to excess hydrogen ($H_2/CO = 1-3$)

Now another important applications, it is called Fischer-Tropsch synthesis. So monolithic catalyst for Fischer-Tropsch synthesis consists of long parallel channels where this 0.5 to 3 millimeter internal diameter are being used to separate different thin walls of this monolithic structure of 0.1 to 0.3 millimeter. And then, the active metals which are included with or applied to the support may include metals or combination of metals such as cobalt, iron, copper, nickel, platinum, rubidium, even rhenium and also ruthenium, this type of metals are being used for the you know catalytic support.

And monolithic reactors usually work in a temperature ranges from 188 to 194 degrees centigrade up to 240 degree centigrade. And in that case, synthesis gas composition are from stoichiometrically excess carbon monoxide to excess hydrogen are to be maintained.

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Comparison of monolithic reactor with multiphase reactors

Property	Monolith reactor	Slurry reactor	Trickle-bed reactor
Energy input	Low	Medium, stirring	High, pressure drop
Catalyst efficiency	High, thin active layer	High, small particles	Low, large particles required due to pressure drop
Pressure drop	Insignificant	Small	High
Catalyst separation	Unnecessary	Costly filtering necessary	Easy
Catalyst loading	Medium or small	Medium or small	High
Catalyst replacement	Difficult	Easy, continuous exchange during operation	Difficult
Experience	Two phases-extensive multiphase-limited	High	High

Tomašić and Jović (2006), Applied Catalysis A: General, 311, 112-121

Now some comparison of the monolithic reactor with multiphase reactors, here are based on that energy input, catalyst efficiency, pressure drop, catalyst separation, catalyst loading, catalyst replacement and also experience. If we consider that energy input, in that case monolithic reactors are required low energy, whereas slurry reactor require medium energy for the steering generally and for the trickle bed reactor, high energy is required because their frictional pressure drop is high. And also in terms of catalyst efficiency, if we think about that, that monolithic reactor would be that high, that is thin active will be there.

That is why catalyst efficiency should be high there. Slurry reactor also, it is high if you are considering the small catalyst particles and in case of trickle bed reactors, it will be low because in the trickle bed reactor, you cannot use the small particles. It is made only large particles due to the pressure drop there. And also, if we consider that pressure drop, of course that monolithic reactors, it would be insignificant whereas in the slurry and trickle bed reactors maybe medium and high respectively.

And for that catalyst separation this monolithic reactor it is not required that criteria. And for the slurry reactors, it is of course required because to regenerate that catalyst particles you have to separate those catalyst particles from the multiphase mixer. Whereas in the trickle bed reactor, this catalyst separation is easy since the size is very high. So we can easily separate but for the slurry reactors, it is sometimes not easier because you have to invest some price for filtering those small particles there for the regeneration of that catalyst particles.

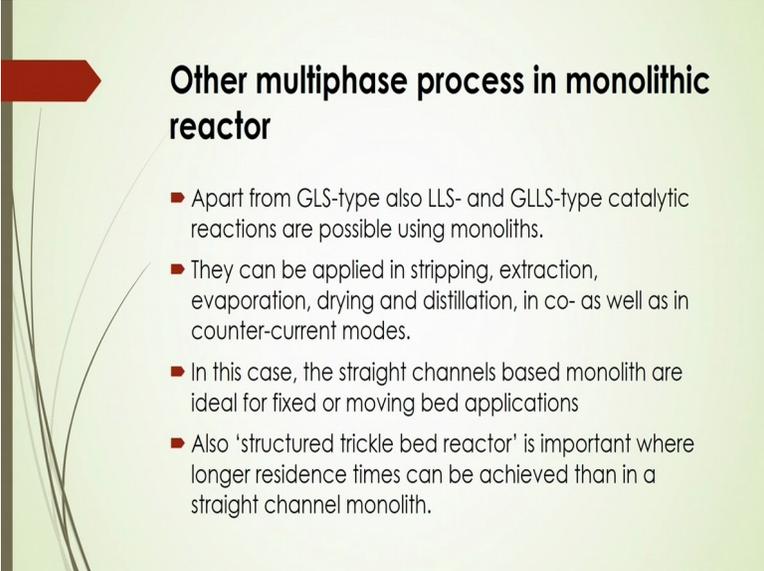
In case of monolithic reactor, you will see medium or small scale of catalyst loading is required. Whereas slurry reactors, it is medium or small scale of catalyst loading is required. Whereas in case of trickle bed reactor, it is high. And in case of catalyst replacement, monolithic reactor is very difficult whereas slurry reactor is very easy because continuous exchange during the operations can be done and also in the trickle bed reactor also this replacement of the catalyst is very difficult.

And monolithic reactors, the two-phase extensive multiphase reactions are there. Whereas other different types of the gas-liquid-solid, even gas-liquid-liquid-solid reaction is sometimes limited whereas in the slurry reactor, it is high because that you can easily handle those you know that slurry mixer in the slurry reactors, whereas in the trickle bed also it is very high. So as per that comparison of this monolithic reactor with multiphase reactors, we can conclude that in maximum cases, that monolithic reactors are giving that better performance compared to the slurry and trickle bed reactor. But some aspects it may not be there.

So case to case, you have to use that reactors in particular which cases that energy required will be that more that you have to sometimes avoid for those reactors for that particular reactors but sometimes for pilot scale operations, sometimes the slurry reactors would be better way to do that you know multiphase reactions. Like Fischer-Tropsch synthesis, it is better that in slurry

reactors where as in monolithic reactor, it will be sometimes that less yield will be given by this monolithic reactor.

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Other multiphase process in monolithic reactor

- Apart from GLS-type also LLS- and GLLS-type catalytic reactions are possible using monoliths.
- They can be applied in stripping, extraction, evaporation, drying and distillation, in co- as well as in counter-current modes.
- In this case, the straight channels based monolith are ideal for fixed or moving bed applications
- Also 'structured trickle bed reactor' is important where longer residence times can be achieved than in a straight channel monolith.

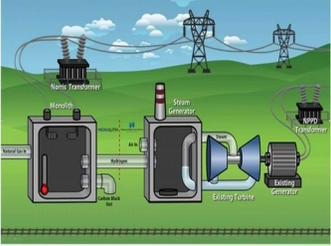
Other multiphase processes in monolithic reactor, apart from that, gas-liquid-solid, also liquid-liquid-solid and gas-liquid-liquid-solid type catalytic reactions are possible using this monoliths. Of course, there that hydrodynamic aspects to be considered during that apart from this analysis of this monolithic reactor. And they can be applied in stripping, extraction, evaporation, drying and distillation also. And also, in this case you will see that straight channels based monolith are ideal for fixed or moving bed applications. And structured trickle bed reactors are important where the longer residence time can be achieved than in a straight channel monolith is there.

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Application in Power Sector

- More recently, there has been renewed interest in the use of monoliths for reactions where energy efficiency and cost reduction are required.
- In particular, these include catalytic combustion for
- Power generation,
- The selective oxidation of alkanes and preferential oxidation (PrOx) of CO.

In the catalytic combustion approach, methane or natural gas can be converted over a noble metal-based catalyst to drive a gas-turbine for power generation



Reference: <https://www.youtube.com/watch?v=0IYLcRT18qM>

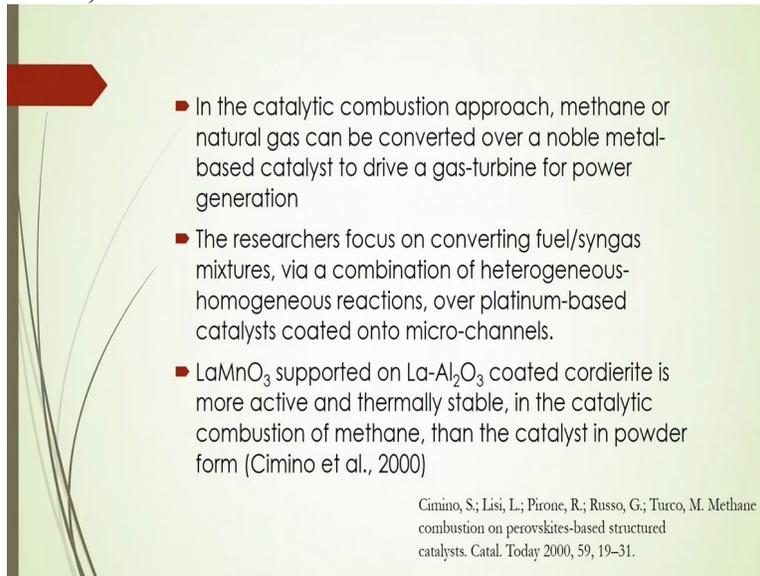
And another important applications is power sector, more recently you can say that there has been renewed interest in the use of monoliths for reactions where energy efficiency and cost reactions are required. So in particular, this include catalytic combustion for power generation, the selective oxidation of alkanes and preferential oxidations is there. Here, see this video, how this power is generated based on this monolithic reactor, how, in this case you will see that by power you have to heat this methane gases to convert it into that carbon and hydrogen.

So you will say that here this, how this cracking of this methane gas is happening in this monolithic reactors. And you will see that this monolithic, how this methane will crack into carbon and hydrogen. And then, this hydrogen gas is passing through that other that steam generator unit. By this that by hot air, with this hydrogen gases, there will be that circulation of these hot gases through the turbine of this hydrogen because this hydrogen gas will be giving that less pollution to the environment without that carbon monoxide or that other exhaust gases. In this case this hydrogen gas will with this hydrogen gas that heated up by this hot air and then that steam will be generated and then steam will, that fed that turbine and the power will be generated here.

So this is the basic process by which that power can be generated by this monolithic reactor by that catalytic cracking of this methane into hydrogen gas. So the selective oxidation of alkanes and preferential oxidation of carbon monoxides is that happened in this case. So in the catalytic

combustion approach, methane or natural gas can be converted over a noble metal-based catalyst to drive a gas turbine for power generation. So we have discussed the different aspects of application of this monolithic reactor based on that multiphase reactions and other applications also.

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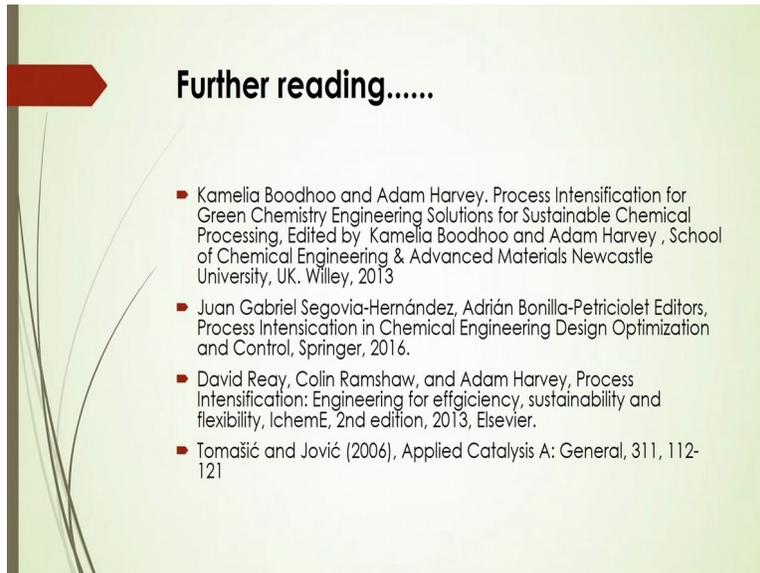
- In the catalytic combustion approach, methane or natural gas can be converted over a noble metal-based catalyst to drive a gas-turbine for power generation
- The researchers focus on converting fuel/syngas mixtures, via a combination of heterogeneous-homogeneous reactions, over platinum-based catalysts coated onto micro-channels.
- LaMnO_3 supported on $\text{La-Al}_2\text{O}_3$ coated cordierite is more active and thermally stable, in the catalytic combustion of methane, than the catalyst in powder form (Cimino et al., 2000)

Cimino, S.; Lisi, L.; Pirone, R.; Russo, G.; Turco, M. Methane combustion on perovskites-based structured catalysts. *Catal. Today* 2000, 59, 19–31.

In the catalytic combustion approach, the methane or natural gas can be converted over a noble metal-based catalyst to drive that gas turbine for power generation. And in this case, the researchers focus on converting that fuel or syngas mixtures via a combination of heterogeneous-homogeneous reactions over platinum-based catalyst coated onto micro-channels. Even other metals supported on coated cordierite is more active and thermally stable in the catalytic combustion of methane than the catalyst in powder form there. So based on which this monolithic reactor is actually giving more that environment friendly process of converting this methane to hydrogen which will convert to the power.

So this is the application in the power sector, how these monolithic reactors are being used.

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So I think we have discussed several applications of this that monolithic reactors for single phase reactions, multiphase reactions; in petrochemical industry how these monolithic reactors are being used for different chemical reactions; in multiphase reactions how it is actually compared with that slurry reactors, flat bed reactors or trickle bed reactors; then monolithic reactors, how actually for that gas-liquid reactions, gas-liquid-solid reactions are being carried out in this particular microchannel based monolithic reactors and how it will be giving the better performance that we have discussed.

Even based on that hydrodynamic aspects, how these monolithic reactors can be actually analysed for the better performance, that also we have discussed to some extent. In the next lecture, we will discuss some hydrodynamic aspects of that monolithic structures, how that monolithic structures can be assessed by that hydrodynamic aspects. So I would suggest you to go further for better understanding of those that different applications of monolithic reactors for different chemical engineering processes. Here some references are given. So, thank you.