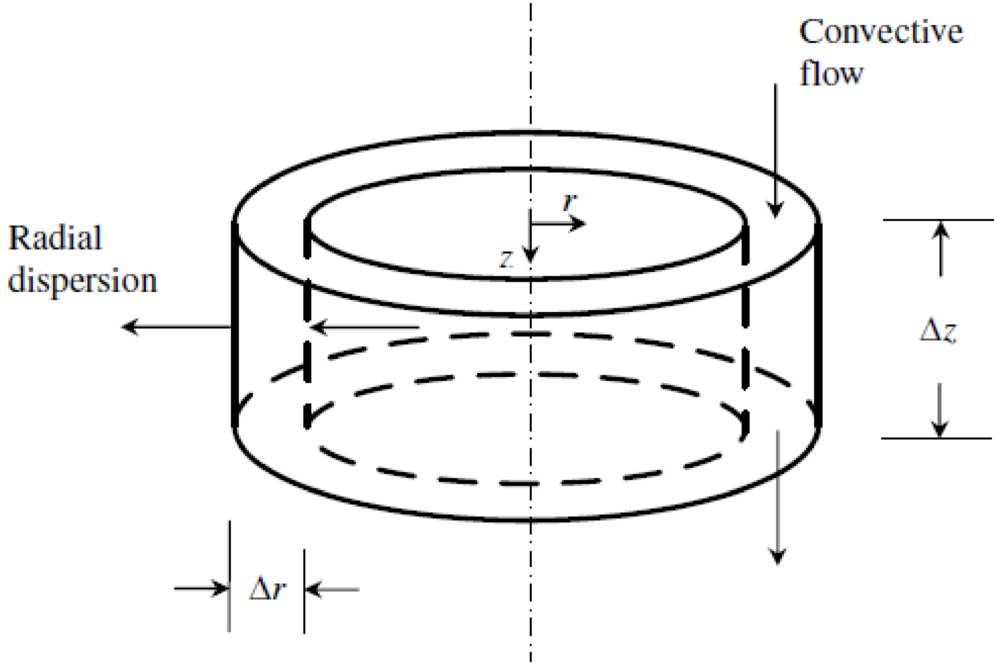
CHE 611
Advanced Chemical Reaction Engineering



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Course contents

- Homogeneous and heterogeneous reaction rate expressions. (3–4 weeks)
- Characterization of solid catalysts. (1 week)
- General characteristics of heterogeneous reactors. Simultaneous mass and heat transports with chemical reaction in porous catalysts. (3–4 weeks)
- Analysis and design of gas-liquid reactors: Mechanically agitated vessels, bubble columns, and packed columns.
- Non-catalytic reactors.
- Analysis and design of three phase reactors: Slurry reactors, trickle bed reactors, and fluidized bed reactors.

Relevant books

- Froment, G.F.; Bischoff, K.B.; De Wilde, J. 2011. Chemical reactor analysis and design. 3rd ed. John Wiley & Sons, Inc.
- Fogler, H.S. 1999. Elements of chemical reaction engineering. 3rd ed. Prentice-Hall.
- Levenspiel, O. 1999. Chemical reaction engineering. 3rd ed. Wiley & Sons, Inc., Singapore.
- Missen, R.W.; Mims, C.A.; Saville, B.A. 1999. Introduction to chemical reaction engineering and kinetics. John Wiley & Sons, Inc., New York.
- Carberry, J.J. Chemical ana catalytic reaction engineering.
- Smith, J.M. 1981. Chemical engineering kinetics. 3rd ed. McGraw-Hill Int. Book Co., Singapore.
- Hill, Jr., C.G. 1977. Introduction to chemical engineering kinetics and reactor design. John Wiley & Sons.

Basic definitions

It will be good, if we first go through some basic definitions regarding reaction engineering.

Stoichiometric coefficient

For the reaction

$$aA + bB \Leftrightarrow cC + dD$$

a, *b*, *c* and *d* are the stoichiometric coefficients.

By convention:

- A stoichiometric coefficient for a reactant is *negative*
- A stoichiometric coefficient for a product is *positive*
- A stoichiometric coefficient for an inert, solvent, or catalyst is *zero*.

Extent of a reaction

$$n_i = n_{i0} + \nu_i \cdot \xi$$

$$F_i = F_{i0} + \nu_i \cdot \xi'$$

$$\xi = \frac{n_i - n_{i0}}{\nu_i} = \frac{\text{Change in moles of a species}}{\text{stoichiometric coefficient}}$$

$$\xi' = \frac{F_i - F_{i0}}{\nu_i} = \frac{\text{Change in molar flowrate of a species}}{\text{stoichiometric coefficient}}$$

Where,

n_i	moles of *ith* reacting species
n_{i0}	initial moles of *ith* reacting species
F_i	molar flowrate of *ith* reacting species
F_{i0}	initial molar flowrate of *ith* reacting species
ξ	extent of a reaction in terms of change in moles
ξ'	extent of a reaction in terms of change in molar flowrate
ν_i	stoichiometric coefficient

Conversion or fractional conversion

It is the ratio of change in moles of a reactant (usually limiting reactant) to the moles of the reactant fed. For a reactant A:

$$\boxed{X_A = \frac{N_{A0} - N_A}{N_{A0}} = \frac{F_{A0} - F_A}{F_{A0}}}$$

Where,

N_{A0} = initial moles of the reactant “A”, mol; N_A = moles of “A” at any time t (s), mol; F_{A0} = initial molar flowrate, mol·s^{-1}, F_A = molar flowrate of A at any time t (s), mol·s^{-1}.

Conversion or fractional conversion

For an irreversible and single (no side reaction) reaction, an increase in the outlet conversion is an indication of what?

Higher rate of the reaction.

Selectivity

It is the ratio of moles of the one (usually desired) product to the moles of another (usually undesired) product.

The definition of selectivity may vary from source to source.

Yield

It is the ratio of moles of a certain product to the maximum possible moles of that product which can be formed.

Or

It is the ratio of moles of a certain product to the moles consumed of the limiting reactant.

Or

It is the ratio of moles of a certain product to the moles of the limiting reactant fed.

The definition of yield may vary from source to source. The definitions of yields defined here may be referred to as the definition of selectivity in some reference.

Limiting reactant

Usually in a reaction, one of the reactants is present in excess to that required stoichiometrically. If the reactants are added in stoichiometric amounts, there is no point using the concept of limiting reactant. The limiting reactant is the one which is consumed first and may be indicated by dividing the number of moles of each reactant in feed to the corresponding stoichiometric amount (form a balanced chemical equation) of the reactant. The reactant with the lowest ratio is the limiting reactant and will be the first to fully consumed in the reaction, if the reaction goes to completion.

It is important to mention that the choice of the limiting reactant is arbitrary and depends on the cost (profit) consideration.

Limiting reactant

Can you mention any example of an industrial process and indicate the limiting reactant? What are the reasons for the choice of a particular limiting reactant in your example?

Rate of a chemical reaction

The rate of a chemical reaction: The rate of consumption of a reactant species is defined as the change in number of moles of the reactant species per unit volume of the reaction mixture per unit time.

$$\boxed{(-r_A) = \frac{1}{V} \cdot \frac{dN_A}{dt}}$$

Where,

$(-r_A)$ = rate of consumption of reactant A, mol·m^{-3}·s^{-1}. The negative sign indicates that the rate is decreasing with time. V = volume of the reaction mixture, m^3. N_A = number of moles of A, mol. t = reaction time, s.

Rate of a chemical reaction

The definition of rate of a chemical reaction describing change in molar concentration with respect to time, i.e.,

$$\boxed{(-r_A) = \frac{dC_A}{dt}}$$

is not general and valid only when the volume of the mixture does not change during the course of the reaction. This may be only true for liquid phase reactions where volume changes are not significant. The volume of a gas also changes due to changes in operating conditions (temperature and pressure) in addition to changes in number of moles.

Rate of a chemical reaction

- The definition of rate usually defined in terms of change in concentration is not general and valid only for a constant density systems.
- The rate of a chemical reaction is usually based on the limiting reactant.
- On the similar basis, a rate may be defined for the formation of a product species.
- For the reaction:

$$aA + bB \rightarrow cC + dD$$

or

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

the rates of various components involved can be related as

$$\boxed{\frac{(-r_A)}{a} = \frac{(-r_B)}{b} = \frac{r_C}{c} = \frac{r_D}{d}}$$

Rate of a chemical reaction [3]

Based on unit volume
of the reaction mixture

$$r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of fluid})\,(\text{time})}$$

Based on unit mass
in fluid-solid system

$$r_i' = \frac{1}{W}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{mass of solid})\,(\text{time})}$$

Based on unit surface of solid in fluid-solid
system or unit interfacial area in two fluid systems

$$r_i'' = \frac{1}{S}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{surface})\,(\text{time})}$$

Based on unit volume of solid
in fluid-solid system

$$r_i''' = \frac{1}{V_s}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of solid})\,(\text{time})}$$

Based on unit volume of reactor when different
from unit volume of the reaction mixture

$$r_i'''' = \frac{1}{V_r}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of reactor})\,(\text{time})}$$

Rate of a chemical reaction

Rates defined on various basis are interchangeable and the following may be shown [3]:

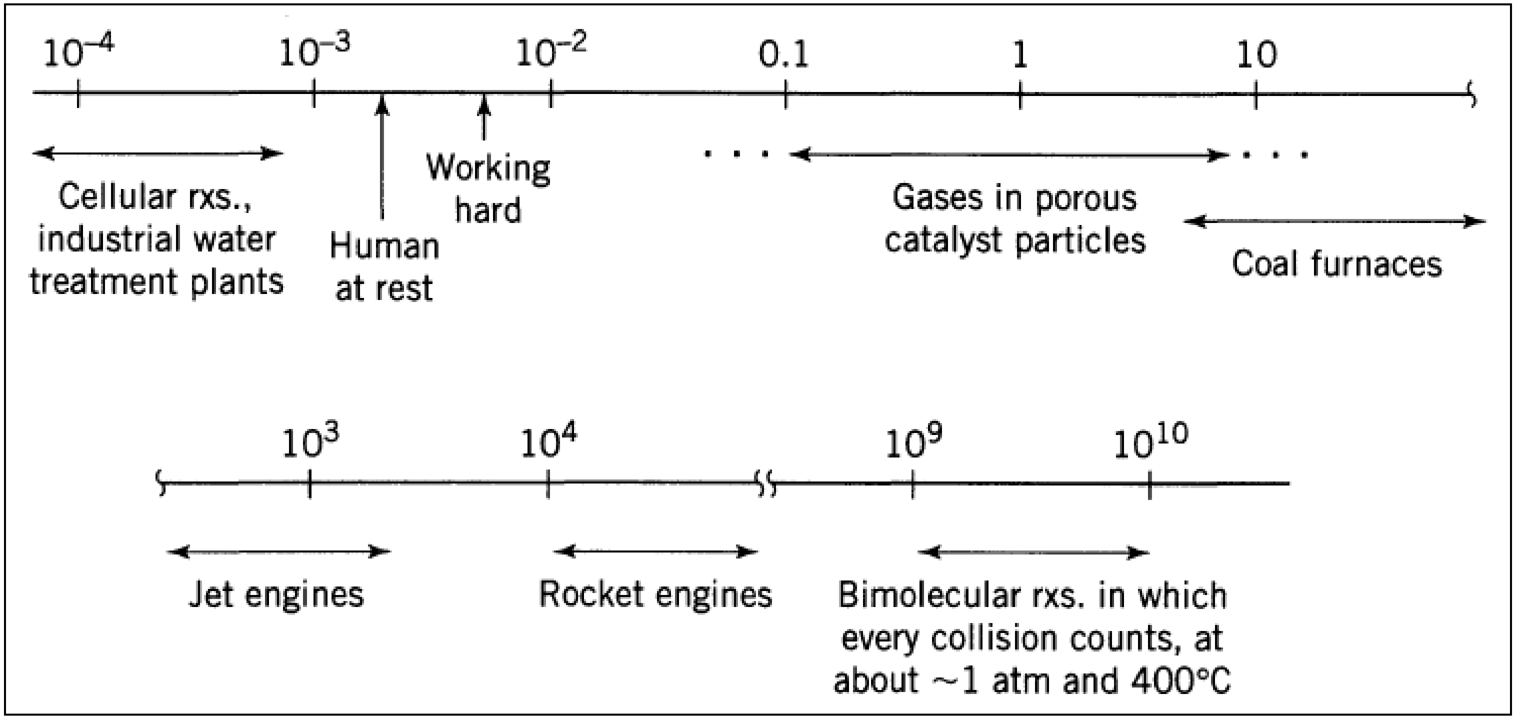
$$\boxed{\begin{pmatrix}\text{volume}\\ \text{of fluid}\end{pmatrix} r_i = \begin{pmatrix}\text{mass of}\\ \text{solid}\end{pmatrix} r_i' = \begin{pmatrix}\text{surface}\\ \text{of solid}\end{pmatrix} r_i'' = \begin{pmatrix}\text{volume}\\ \text{of solid}\end{pmatrix} r_i''' = \begin{pmatrix}\text{volume}\\ \text{of reactor}\end{pmatrix} r_i''''}$$

or

$$\boxed{V r_i = W r_i' = S r_i'' = V_s r_i''' = V_r r_i''''}$$

Rate of a chemical reaction

Rates of reactions varies in a wide range. Some reaction are very fast and some reactions are extremely slow. The figure shows an idea of variation of rates in different reaction systems [3]:



Temperature dependence of the rate of a chemical reaction

Arrhenius equation is frequently applied to approximate the temperature dependency of reaction rate and the rate constant or velocity constant, *k*, is related to temperature, *T*, by the following expression:

$$\boxed{\frac{d\ln k}{dT} = \frac{E_a}{R \cdot T^2}}$$

$$\boxed{k = k_0 \cdot e^{-\frac{E_a}{RT}}}$$

Where,

k_0 = pre-exponential factor and has units similar to that of k.

E_a = activation energy, J·mol^{-1}.

Temperature dependence of the rate of a chemical reaction

- A plot of ln$k$ vs 1/T will be straight line, the slope of which is E_a/R. The units of the slope are K. A large slope of Arrhenius plot means large value of E_a and vice versa.
- Reactions having large value of E_a are more temperature sensitive while with low value of E_a are less temperature dependent.
- Arrhenius equation may be written in terms of two rate constants and two temperatures. It is then equal to:

$$\boxed{\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

Temperature dependence of the rate of a chemical reaction

E_a and k_0 are called Arrhenius parameters. To estimate the effect of temperature on the rate of a chemical reaction, the values of Arrhenius parameters are to be known, otherwise experimental data of rate vs temperature can be used to calculate the parameters.

Rate of a chemical reaction

Why are we interested in rate? A higher rate of reaction means less processing time in a batch reactor and smaller size of reactor vessel in a continuous flow reactor (CSTR and plug flow reactor). If the residence time is dependent upon the rate, the knowledge of rate is of utmost importance for the design of a reactor. Bring to mind the basic design (performance) equations for batch and flow reactors. I hope bells are ringing!!!

Now, if the knowledge of rate is so important, question is how can we find rate? Of course we need an expression (rate equation) that describes the rate of a given reaction (to occur in a given reactor) to be used with our basic reactor design equations. Unfortunately, rate equation cannot be found from the reaction stoichiometry or by any other theoretical means and therefore rate expressions are always to be empirical, i.e., to be discovered through experiments.

Rate of a chemical reaction

The reaction for which the rate equation is to be determined is either a homogeneous (single phase) or heterogeneous (more than one phase is involved). Each of the homogenous and heterogeneous reactions may either by catalytic or non-catalytic (or autocatalytic). Nearly 90% of all industrial reactions involve heterogeneous catalysis.

In the present course, we will study the reaction engineering principles and develop rate expressions based on gas-solid reactions mostly in a tubular reactor of fixed bed of catalysts. The principles would remain the same and may be employed for the other types of reactor systems.

Space time and space velocity

Space velocity: It is the reciprocal of space time and applied in the analysis of continuous flow reactors such as plug flow reactor and CSTR. It is defined as the number of rector volumes of a feed at specified conditions which can be treated in unit time. A space velocity of 10 h^{-1} means that ten reactor volumes of the feed at specified conditions are treated in a reactor per hour.

Definitions of space time and space velocity [3]

Space-time:

$$\tau = \frac{1}{s} = \left(\begin{array}{c} \text{time required to process one} \\ \text{reactor volume of feed measured} \\ \text{at specified conditions} \end{array} \right) = [\text{time}]$$

Space-velocity:

$$s = \frac{1}{\tau} = \left(\begin{array}{c} \text{number of reactor volumes of} \\ \text{feed at specified conditions which} \\ \text{can be treated in unit time} \end{array} \right) = [\text{time}^{-1}]$$

Space time and space velocity

Gas hourly space velocity (GHSV):

In chemical reaction engineering, space velocity is sometimes reported in terms of gas hourly space velocity, which is the ratio of volume per time in hours of the gaseous feed to the volume of the reactor. It is abbreviated as GHSV.

$$GHSV = \frac{volumetric\ flowrate\ of\ the\ gaseous\ feed\ in\ cubic\ meter\ per\ hour}{volume\ of\ reactor\ in\ cubic\ meter}$$

It is normally reported for volumes measured at temperature of 25°C and pressure of 1.013 bar.

Space time and space velocity

Weight hourly space velocity (WHSV):

The term is frequently used in heterogeneous reactor technology and it is defined as the ratio of mass of the feed per hour to the mass of the catalyst. Its units are h^{-1}.

$$WHSV = \frac{mass\ of\ the\ feed\ per\ hour}{mass\ of\ the\ catalyst}$$

Space time and space velocity

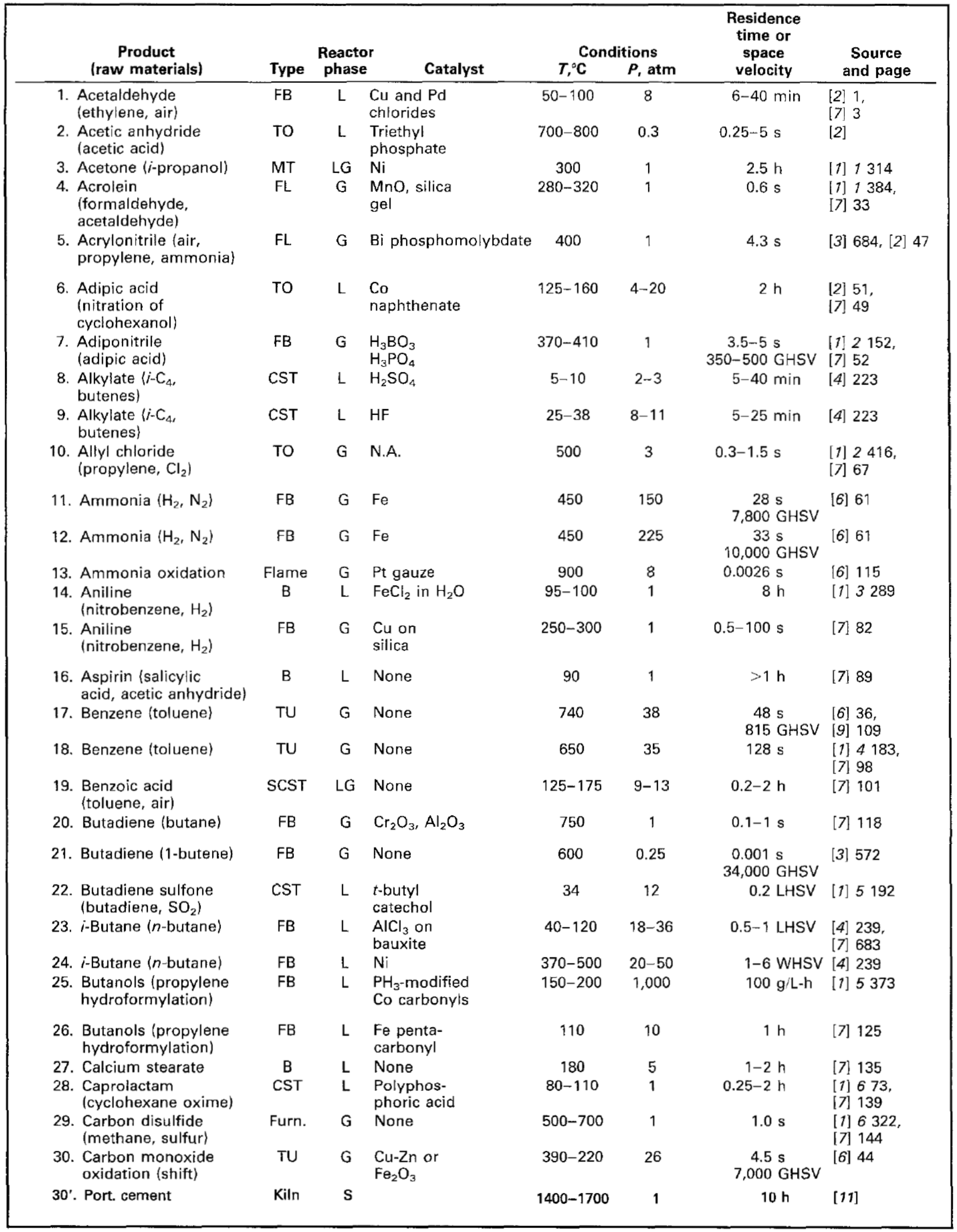
Liquid hourly space velocity (LHSV):

It is defined as the ratio of the volume of the liquid feed per hour to the volume of the reactor or catalyst required. The volume of the liquid feed is usually taken at 60°F. 60°F is not worth mentioning as volume (density) of a liquid does not appreciably change with small changes in temperature.

Space time and space velocity

Residence times and space velocities of various industrial reactors are given in Chapter 17, p. 550 of Walas (1990) and in Section 19, p. 19-5 of Perry's Chemical Engineers' Handbook. 2008. 8th ed. McGraw-Hill.

A part of the data from Walas (1990) is given on the next slide.



Product (raw materials)	Type	Reactor phase	Catalyst	Conditions		Residence time or space velocity	Source and page
				T, °C	*P*, atm		
1. Acetaldehyde (ethylene, air)	FB	L	Cu and Pd chlorides	50–100	8	6–40 min	[*2*] 1, [*7*] 3
2. Acetic anhydride (acetic acid)	TO	L	Triethyl phosphate	700–800	0.3	0.25–5 s	[*2*]
3. Acetone (*i*-propanol)	MT	LG	Ni	300	1	2.5 h	[*1*] *1* 314
4. Acrolein (formaldehyde, acetaldehyde)	FL	G	MnO, silica gel	280–320	1	0.6 s	[*1*] *1* 384, [*7*] 33
5. Acrylonitrile (air, propylene, ammonia)	FL	G	Bi phosphomolybdate	400	1	4.3 s	[*3*] 684, [*2*] 47
6. Adipic acid (nitration of cyclohexanol)	TO	L	Co naphthenate	125–160	4–20	2 h	[*2*] 51, [*7*] 49
7. Adiponitrile (adipic acid)	FB	G	H_3BO_3 H_3PO_4	370–410	1	3.5–5 s 350–500 GHSV	[*1*] *2* 152, [*7*] 52
8. Alkylate (*i*-C_4, butenes)	CST	L	H_2SO_4	5–10	2–3	5–40 min	[*4*] 223
9. Alkylate (*i*-C_4, butenes)	CST	L	HF	25–38	8–11	5–25 min	[*4*] 223
10. Allyl chloride (propylene, Cl_2)	TO	G	N.A.	500	3	0.3–1.5 s	[*1*] *2* 416, [*7*] 67
11. Ammonia (H_2, N_2)	FB	G	Fe	450	150	28 s 7,800 GHSV	[*6*] 61
12. Ammonia (H_2, N_2)	FB	G	Fe	450	225	33 s 10,000 GHSV	[*6*] 61
13. Ammonia oxidation	Flame	G	Pt gauze	900	8	0.0026 s	[*6*] 115
14. Aniline (nitrobenzene, H_2)	B	L	$FeCl_2$ in H_2O	95–100	1	8 h	[*1*] *3* 289
15. Aniline (nitrobenzene, H_2)	FB	G	Cu on silica	250–300	1	0.5–100 s	[*7*] 82
16. Aspirin (salicylic acid, acetic anhydride)	B	L	None	90	1	>1 h	[*7*] 89
17. Benzene (toluene)	TU	G	None	740	38	48 s 815 GHSV	[*6*] 36, [*9*] 109
18. Benzene (toluene)	TU	G	None	650	35	128 s	[*1*] *4* 183, [*7*] 98
19. Benzoic acid (toluene, air)	SCST	LG	None	125–175	9–13	0.2–2 h	[*7*] 101
20. Butadiene (butane)	FB	G	Cr_2O_3, Al_2O_3	750	1	0.1–1 s	[*7*] 118
21. Butadiene (1-butene)	FB	G	None	600	0.25	0.001 s 34,000 GHSV	[*3*] 572
22. Butadiene sulfone (butadiene, SO_2)	CST	L	*t*-butyl catechol	34	12	0.2 LHSV	[*1*] *5* 192
23. *i*-Butane (*n*-butane)	FB	L	$AlCl_3$ on bauxite	40–120	18–36	0.5–1 LHSV	[*4*] 239, [*7*] 683
24. *i*-Butane (*n*-butane)	FB	L	Ni	370–500	20–50	1–6 WHSV	[*4*] 239
25. Butanols (propylene hydroformylation)	FB	L	PH_3-modified Co carbonyls	150–200	1,000	100 g/L-h	[*1*] *5* 373
26. Butanols (propylene hydroformylation)	FB	L	Fe pentacarbonyl	110	10	1 h	[*7*] 125
27. Calcium stearate	B	L	None	180	5	1–2 h	[*7*] 135
28. Caprolactam (cyclohexane oxime)	CST	L	Polyphosphoric acid	80–110	1	0.25–2 h	[*1*] *6* 73, [*7*] 139
29. Carbon disulfide (methane, sulfur)	Furn.	G	None	500–700	1	1.0 s	[*1*] *6* 322, [*7*] 144
30. Carbon monoxide oxidation (shift)	TU	G	Cu-Zn or Fe_2O_3	390–220	26	4.5 s 7,000 GHSV	[*6*] 44
30′. Port. cement	Kiln	S		1400–1700	1	10 h	[*11*]

Definition of a catalyst

Catalyst: A catalyst is a substance that modifies (accelerates or decelerates) the rate of a chemical reaction without itself being used up. However, the term catalyst is usually employed when the objective is to increase the rate of the desired reaction. The term inhibitor is used when the rate of the desired reaction is required to decrease. A catalyst can only alter the rate of a chemical reaction and cannot affect the thermodynamics associated with the reaction. It is, therefore, cannot affect equilibrium and energy changes per mole during the reaction. A number of catalysts both homogeneous and heterogeneous are employed in the industry. Sulfuric acid, hydrofluoric acid, vanadium pentaoxide, platinum over alumina, and zeolites with and without loading of metals or oxides are common examples.

Variety of catalysts [7]

Variety of catalysts

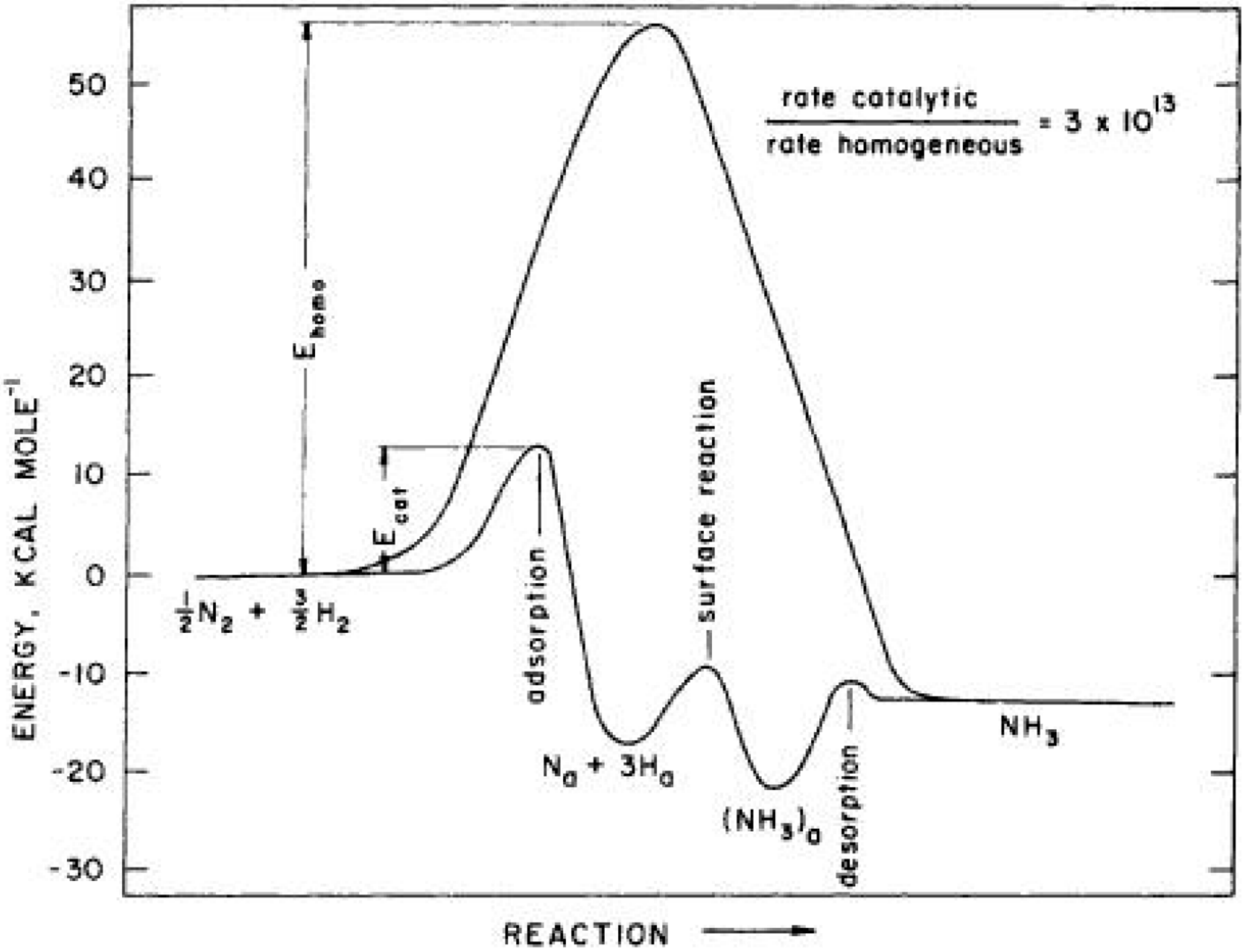
http://www.sud-chemie-india.com/prod.htm

Definition of a catalyst

For a thermodynamically possible reaction, a catalyst modifies the path of the reaction and lowers the activation energy. This results in increasing the rate of the corresponding reaction.

The reaction of ammonia synthesis from N_2 and H_2 is favorable thermodynamically but in the absence of a catalyst it occurs at extremely low pace. The activation energy, 238.5 kJ/mol (Richardson, 1999), associated with the homogenous reaction is quite high, however, the presence of a typical catalyst decreases the activation energy of the rate controlling step (adsorption of hydrogen) to only 50.2 kJ/mol (Richardson, 1999).

Catalytic reaction path for ammonia synthesis [6]



Possibility of a reaction

For a thermodynamically possible reaction means that a catalyst works only for those reactions for which Gibbs free energy of reaction ΔG_{rxn} is less than zero, i.e., the reactants have higher free energy than the products. A useful criterion (although not exact) for knowing the possibility of reaction occurrence is to know the standard state Gibbs free energy of reaction, ΔG_{rxn}^{o}. A reaction, however, may be not feasible at the standard conditions but may occur at the other conditions.

What is the reason for using ΔG_{rxn}^{o} and not ΔG_{rxn}?

Possibility of a reaction [6]

Value of ΔG_{rxn}^{o}	Possibility of reaction occurrence
< –10 kcal/mol (–41.8 kJ/mol)	Reaction is possible with very high equilibrium conversions
0 to –10 kcal/mol (–41.8 kJ/mol)	Reaction is possible with moderately high equilibrium conversions
0 to 10 kcal/mol (41.8 kJ/mol)	Reaction is possible at the other process operating conditions but usually with low equilibrium conversions
> 10 kcal/mol (41.8 kJ/mol)	Reaction may be possible at the other process operating conditions and if possible occurs with generally very low equilibrium conversions

Definition of a catalyst

As the equilibrium constant is a ratio of forward rate to the reverse rate constants, increasing forward rate of reaction also increases the rate of the reverse reaction (as equilibrium constant is to be unaffected). Principally, the same catalyst is used for forward reaction and reverse reaction. Pt/Al_2O_3 is a good catalyst for dehydrogenation of methylcyclohexane to toluene (an important reforming reaction) as well as for hydrogenation of toluene to methylcyclohexane (reverse reaction). Only the condition of operations has to be changed. At higher pressures and lower temperature Pt/Al_2O_3 catalyses hydrogenation of toluene while at lower pressures and higher temperatures it catalyses dehydrogenation. This fact can be used to discover a catalyst for a reaction at mild reaction which can be used for its counter reaction [6].

Definition of a catalyst

Supported catalyst: Usually an active component is dispersed over a relatively inactive or less active material which usually has a high surface area. Pt/alumina is a well known example of a supported catalyst. See support.

Structured catalyst:

A structured catalyst is a regular structure free of randomness in reference to the reactor. It is unlike the discrete catalyst particles such as in a conventional fixed bed reactor. Bring to mind the random packing and structured packing in a packed bed.

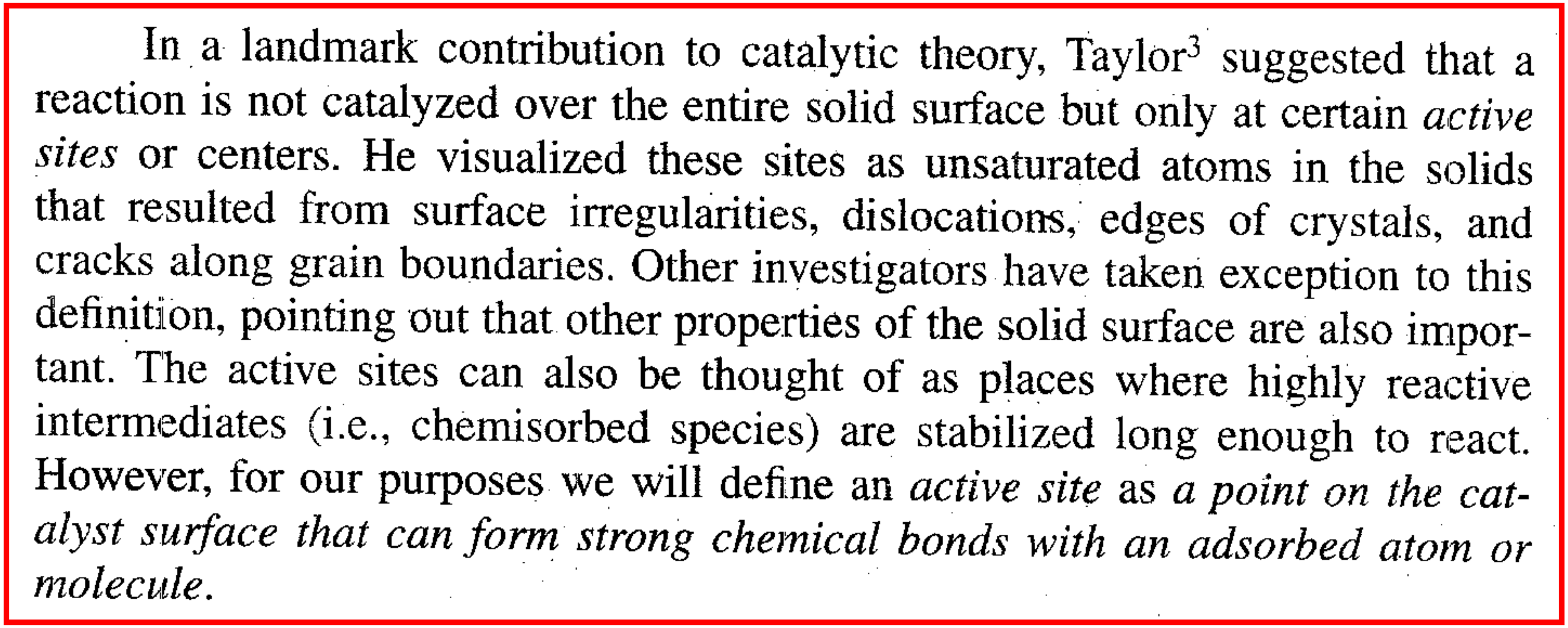
Definition of a catalyst [5]

Catalyst support: Also called as catalyst carrier. Catalyst support provides surface to the active component of a catalyst. A support is usually a high surface area porous material on which the active component is dispersed and that the support, itself, may be active or inert. A support gives strength, shape, and size to a catalyst. As an example, in 1.0 wt% Pt over alumina, Pt metal is the active component dispersed over the alumina support. The same active component when supported on a different support may greatly change the activity, selectivity, regenerability, and life of the catalyst. Examples of catalyst supports are alumina, silica, titania, and carbon.

Definition of TOF

Bifunctional catalyst: A bifunctional catalyst catalyzes two types of catalytic transformations. For example, Pt metal loaded on an acid support such as silica-alumina or zeolite is a bifunctional catalyst. The Pt metal cares for the dehydrogenation and hydrogenation reactions while acid support facilitates cracking and isomerization reactions.

Active sites or active centers [2]



In a landmark contribution to catalytic theory, Taylor[3] suggested that a reaction is not catalyzed over the entire solid surface but only at certain *active sites* or centers. He visualized these sites as unsaturated atoms in the solids that resulted from surface irregularities, dislocations, edges of crystals, and cracks along grain boundaries. Other investigators have taken exception to this definition, pointing out that other properties of the solid surface are also important. The active sites can also be thought of as places where highly reactive intermediates (i.e., chemisorbed species) are stabilized long enough to react. However, for our purposes we will define an *active site* as *a point on the catalyst surface that can form strong chemical bonds with an adsorbed atom or molecule.*

Definition of TOF

Turnover frequency (TOF):

It is the number of molecules converted per unit time per active site.

Advanced Chemical Reaction Engineering

Catalyst screening for a given process

Activity, selectivity, stability, and regenerability of a catalyst

The selection of a suitable catalyst for a process usually demands the knowledge regarding

- Activity
- Selectivity
- Stability, and
- Regenerability

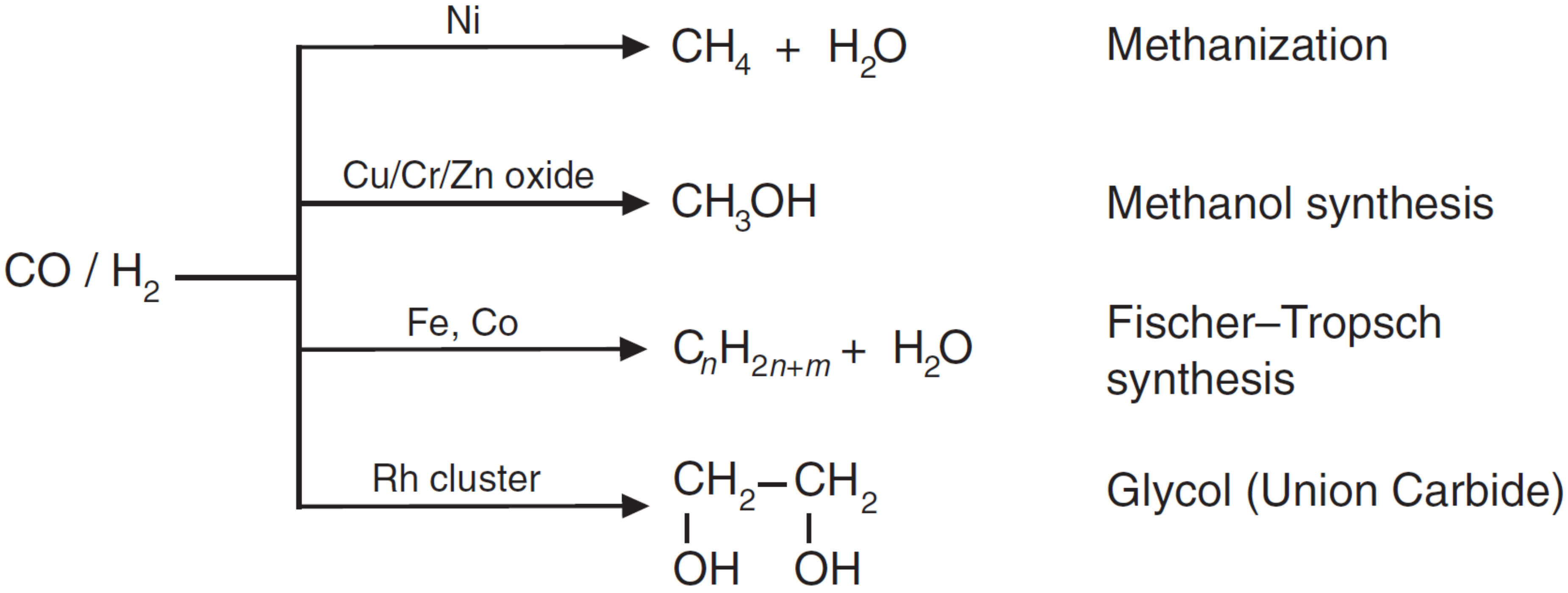
of a catalyst.

Activity, selectivity, stability, and regenerability of a catalyst

Activity: Activity of a catalyst controls the extent of a chemical reaction involved and describes the effectiveness of a catalyst towards the rate of the chemical reaction and conversion of the reactant. It has no concern with the product distribution (selectivity).

Selectivity: Selectivity refers to the efficacy of a catalyst towards producing the desired product. For both the parallel and consecutive reactions, the selectivity is important and a catalyst is required to produce the desired product in greater amounts (increased selectivity).

Selectivity: Synthesis gas reactions [Hagen, 2006]



$CO / H_2 \xrightarrow{Ni} CH_4 + H_2O$ Methanization

$CO / H_2 \xrightarrow{Cu/Cr/Zn\ oxide} CH_3OH$ Methanol synthesis

$CO / H_2 \xrightarrow{Fe,\ Co} C_nH_{2n+m} + H_2O$ Fischer–Tropsch synthesis

$CO / H_2 \xrightarrow{Rh\ cluster} \underset{OH}{CH_2}-\underset{OH}{CH_2}$ Glycol (Union Carbide)

Activity, selectivity, stability, and regenerability of a catalyst

Stability: For a catalyst, it refers to the life of the catalyst. If the activity and selectivity of a catalytic system remains unchanged during the course of a given period of time, under the same conditions of temperature, pressure, and space time, the catalyst gives the same product composition for the same feed composition, the catalyst is said to have stable characteristics for that period of time.

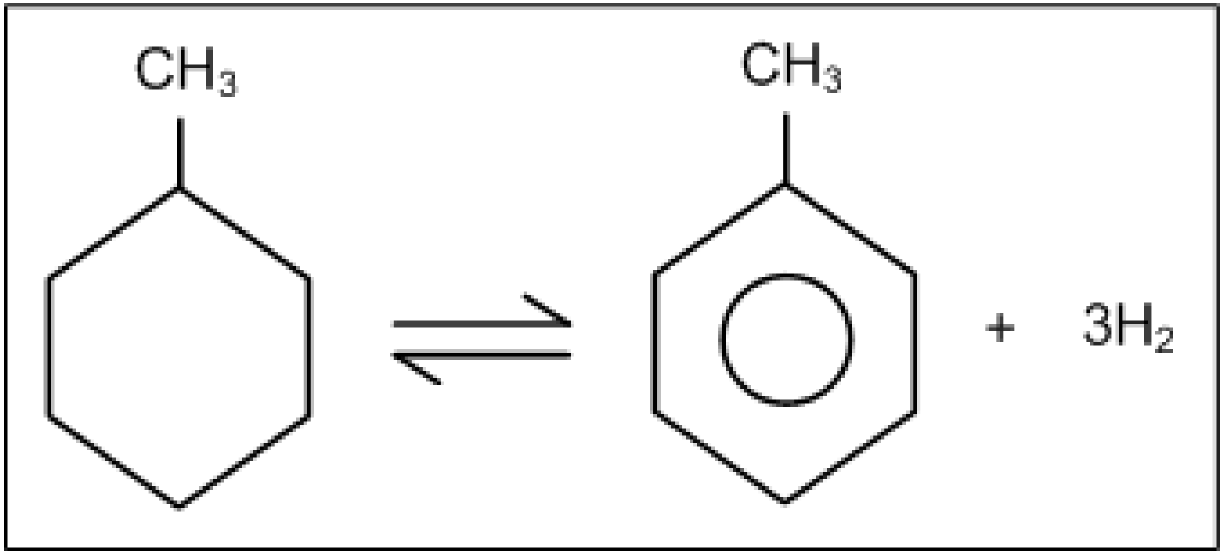
Regenerability: It refers the ability of a catalyst to be reactivated to more or less to its original conditions.

Activity, selectivity, stability, and regenerability of a catalyst

Richardson [6] suggests the order of importance of the activity, selectivity, and stability as:

1. Selectivity
2. Stability
3. Activity.

The dehydrogenation of methylcyclohexane: Example reaction



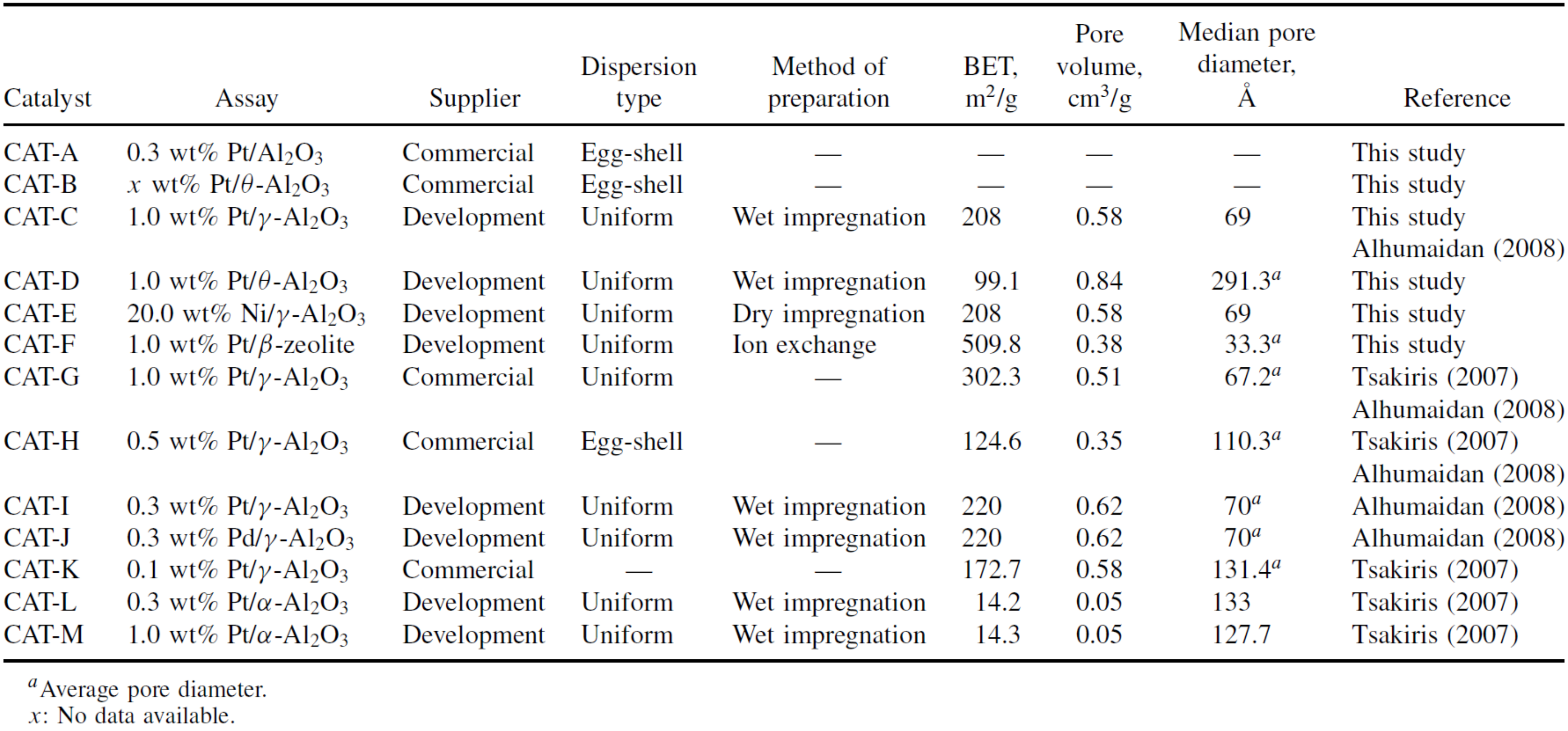
$$C_7H_{14} \rightleftharpoons C_7H_8 + 3H_2$$

Methylcyclohexane	Toluene	Hydrogen

Importance of the example

- Dehydrogenation of methylcyclohexane is an important reforming reaction.
- Dehydrogenation of methylcyclohexane may be useful in the conversion of naphthenic base heavy oils.
- Dehydrogenation of methylcyclohexane is involved in the hydrogen storage applications in the MTH (methylcyclohexane-toluene-hydrogen) system.
- Dehydrogenation of methylcyclohexane may be used as a fuel to absorb energy in high speed air craft engines.

Catalysts studied [5]



Catalyst	Assay	Supplier	Dispersion type	Method of preparation	BET, m^2/g	Pore volume, cm^3/g	Median pore diameter, Å	Reference
CAT-A	0.3 wt% Pt/Al_2O_3	Commercial	Egg-shell	—	—	—	—	This study
CAT-B	x wt% $Pt/\theta\text{-}Al_2O_3$	Commercial	Egg-shell	—	—	—	—	This study
CAT-C	1.0 wt% $Pt/\gamma\text{-}Al_2O_3$	Development	Uniform	Wet impregnation	208	0.58	69	This study Alhumaidan (2008)
CAT-D	1.0 wt% $Pt/\theta\text{-}Al_2O_3$	Development	Uniform	Wet impregnation	99.1	0.84	291.3[a]	This study
CAT-E	20.0 wt% $Ni/\gamma\text{-}Al_2O_3$	Development	Uniform	Dry impregnation	208	0.58	69	This study
CAT-F	1.0 wt% Pt/β-zeolite	Development	Uniform	Ion exchange	509.8	0.38	33.3[a]	This study
CAT-G	1.0 wt% $Pt/\gamma\text{-}Al_2O_3$	Commercial	Uniform	—	302.3	0.51	67.2[a]	Tsakiris (2007) Alhumaidan (2008)
CAT-H	0.5 wt% $Pt/\gamma\text{-}Al_2O_3$	Commercial	Egg-shell	—	124.6	0.35	110.3[a]	Tsakiris (2007) Alhumaidan (2008)
CAT-I	0.3 wt% $Pt/\gamma\text{-}Al_2O_3$	Development	Uniform	Wet impregnation	220	0.62	70[a]	Alhumaidan (2008)
CAT-J	0.3 wt% $Pd/\gamma\text{-}Al_2O_3$	Development	Uniform	Wet impregnation	220	0.62	70[a]	Alhumaidan (2008)
CAT-K	0.1 wt% $Pt/\gamma\text{-}Al_2O_3$	Commercial	—	—	172.7	0.58	131.4[a]	Tsakiris (2007)
CAT-L	0.3 wt% $Pt/\alpha\text{-}Al_2O_3$	Development	Uniform	Wet impregnation	14.2	0.05	133	Tsakiris (2007)
CAT-M	1.0 wt% $Pt/\alpha\text{-}Al_2O_3$	Development	Uniform	Wet impregnation	14.3	0.05	127.7	Tsakiris (2007)

[a] Average pore diameter.

x: No data available.

Activity results [5]

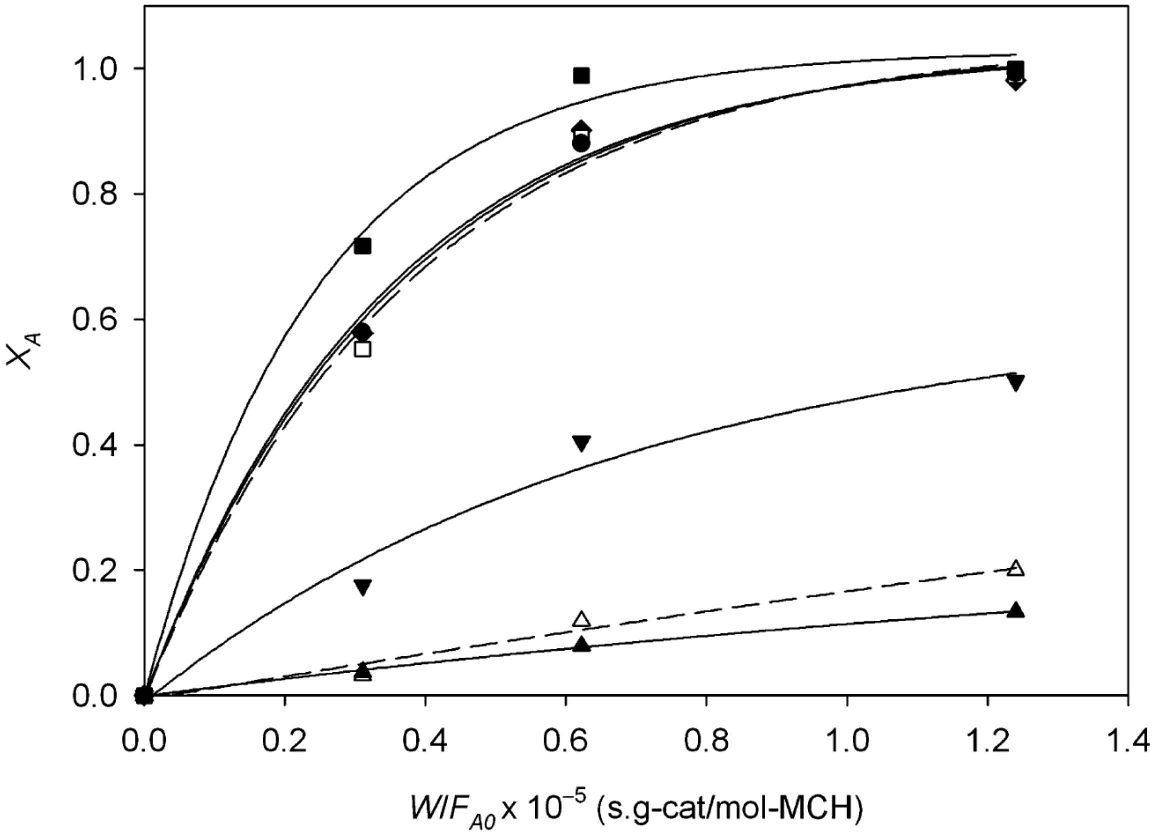


Figure 1. Comparative study of the effect of space time on the conversion of MCH for the range of in-house development and commercial catalysts. $T_w = 380°C$, $p = 1.013$ bar, H_2 to MCH ratio = 8.4 (CAT-A: △; CAT-B: ▲; CAT-J: ▼; CAT-I: ■; CAT-H: ◆; CAT-G: □; CAT-C: ●).

Selectivity results [5]

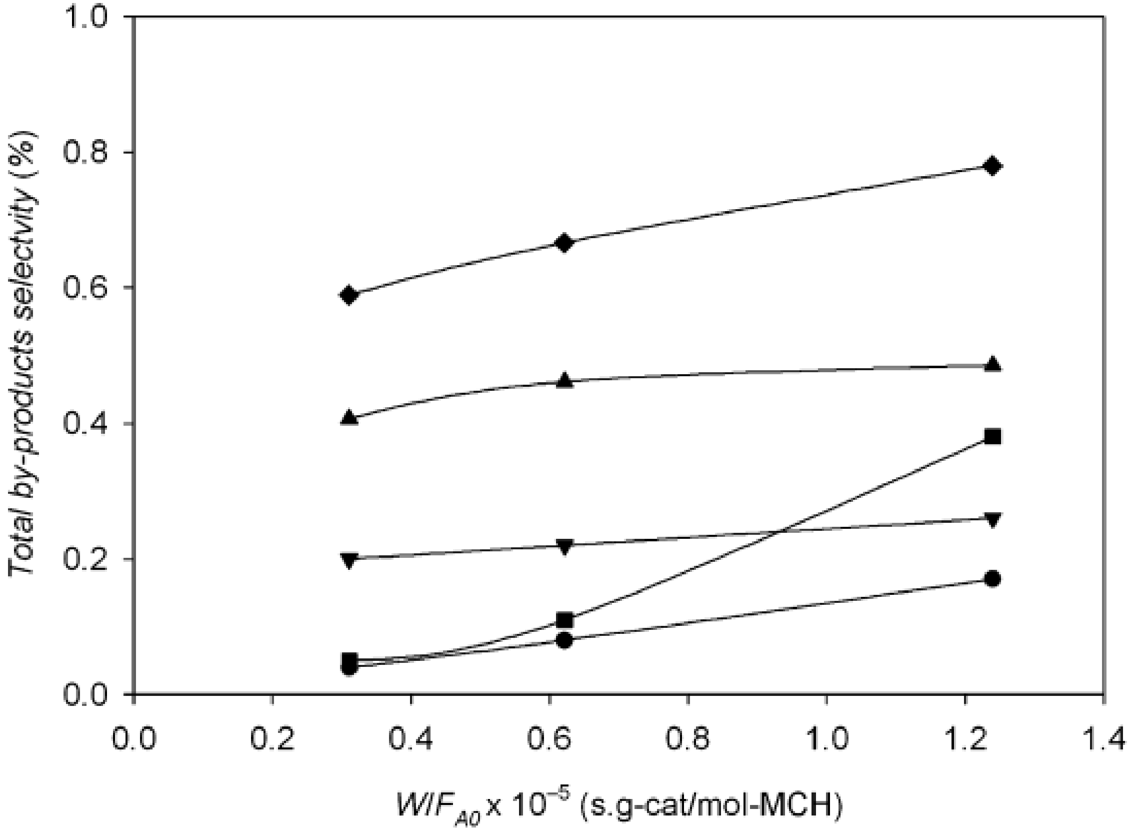
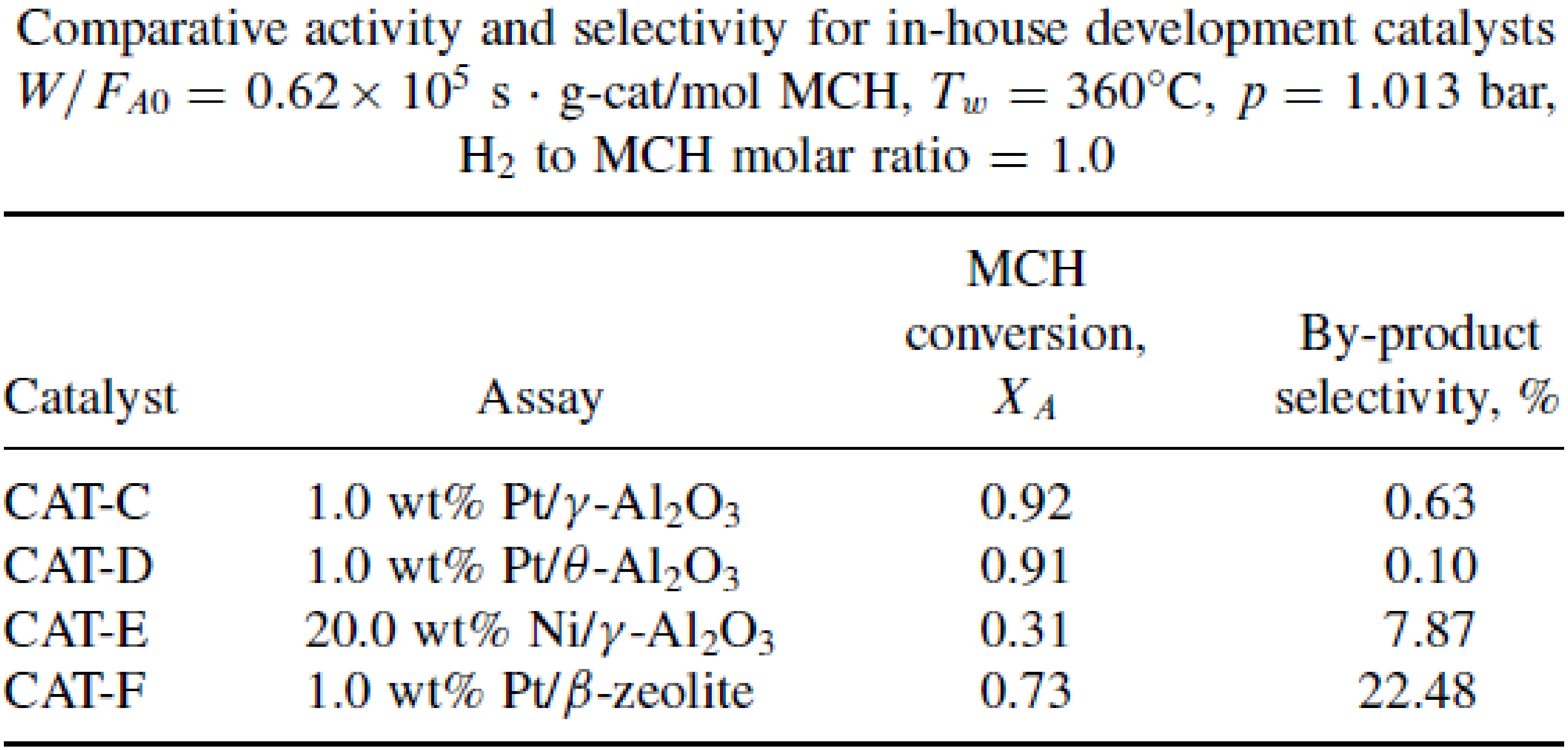


Figure 3. Effect of space time on the total selectivity of the by-products. Total selectivity of the by-products is defined as the conversion of MCH less the total toluene formed per mole of MCH fed. $T_w = 380°\text{C}$, $p = 1.013$ bar, H_2 to MCH ratio = 8.4 (CAT-B: ▲; CAT-J: ▼; CAT-I: ■; CAT-H: ●; CAT-C: ♦).

Some further tests on activity and selectivity [5]



Comparative activity and selectivity for in-house development catalysts
$W/F_{A0} = 0.62 \times 10^5$ s · g-cat/mol MCH, $T_w = 360°\mathrm{C}$, $p = 1.013$ bar,
H_2 to MCH molar ratio = 1.0

Catalyst	Assay	MCH conversion, X_A	By-product selectivity, %
CAT-C	1.0 wt% Pt/γ-Al_2O_3	0.92	0.63
CAT-D	1.0 wt% Pt/θ-Al_2O_3	0.91	0.10
CAT-E	20.0 wt% Ni/γ-Al_2O_3	0.31	7.87
CAT-F	1.0 wt% Pt/β-zeolite	0.73	22.48

Long term deactivation or stability [5]

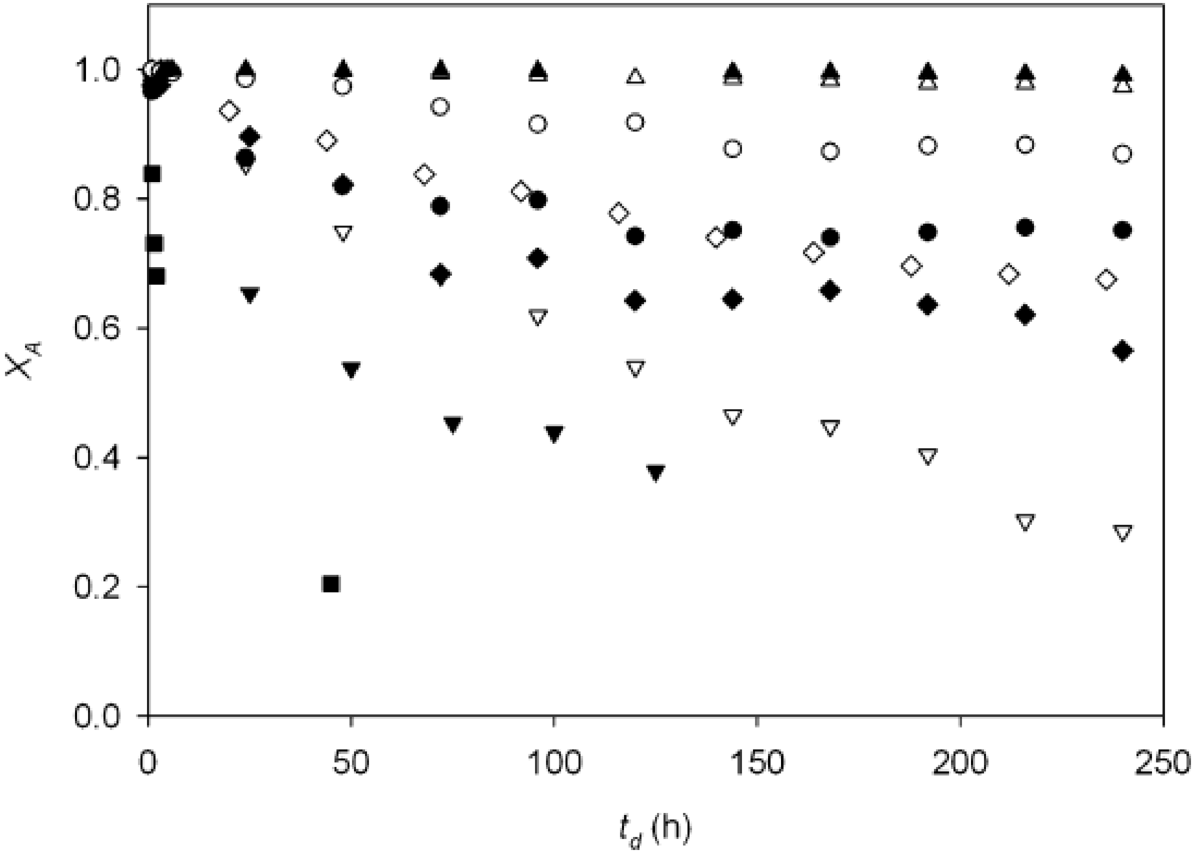


Figure 4. Effect of time on-stream on the deactivation behavior of the catalysts. $W/F_{A0} = 1.24 \times 10^5$ s · g-cat/mol MCH, $T_w = 380°\text{C}$, $p = 1.013$ bar, and pure MCH feed (CAT-M: ▽; CAT-L: ▼; CAT-H: ●; CAT-G: ◇; CAT-K: ⧫; CAT-C: △; CAT-I: ○; CAT-D: ▲; CAT-F: ■).

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