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ROLE OF CATALYST DEVELOPMENTS ON THE SUSTAINABLE CHEMICAL PROCESSES

SIC-PSU
Sustainable Innovation Center

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PSU 2021 Virtual Visiting Professor Program

ASSOC. PROF. Ts DR HERMA DINA SETIABUDI

Profile

Position : Assoc. Prof.
Department : Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang, Malaysia
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Management Post

- Deputy Director (Rankings & Branding Division), Corporate & Quality Affairs Centre, Universiti Malaysia Pahang, 2021-present
- Deputy Dean (Research & Postgraduate Studies), FTKKP, Universiti Malaysia Pahang, 2020-2021
- Head of Reaction Intensification & Sustainable Energy Cluster, FTKKP, Universiti Malaysia Pahang, 2019-2020

Academic Qualification

- Universiti Teknologi Malaysia, Malaysia, Chemical Engineering, Bachelor Degree, 2010
- Universiti Teknologi Malaysia, Malaysia, Chemical Engineering, Doctor of Philosophy, 2013

Expertise

- **Reaction Intensification**
  Reforming; Isomerization; Cracking; Photocatalysis
- **Advanced Material**
  Metal based catalyst; Mesoporous silica; Nanosilica; Nanoparticles
- **Sustainable Energy**
  Hydrogen, Syngas
- **Wastewater Treatment**
  Adsorption; Photocatalysis

Research Outputs

| Patent: 1 | Journal : 75 | Book Chapter : 5 |
| Proceedings : 14 | Citations : 1,539 | h-index : 23 |

Editorial & Review Records

2021	Guest Editor, Chemical Engineering Research and Design. (Elsevier, IF: 3.739)
2021	Guest Editor, International Journal of Hydrogen Energy(Elsevier, IF: 5.816)
2021	Guest Editor, Material Today: proceedings (Elsevier)
2021 - 2023	Chief-Editor, Journal of Chemical Engineering and Industrial Biotechnology. (Penerbit UMP)
2021 - 2023	Associate Editor, Malaysia Journal of Catalysis. (Penerbit UTM)
2020	Guest Editor, Chemical Engineering & Processing: Process Intensification (Elsevier, IF: 4.237)
2020	Guest Editor, International Journal of Hydrogen Energy (Elsevier, IF: 5.816)
2020	Guest Editor, IOP Conference Series: Materials Science and Engineering (IOP Publishing)
2020	Guest Editor, Material Today: proceedings (Elsevier)
2019	Guest Editor, Chemical Engineering & Technology (Wiley, IF: 1.728)
2019	Guest Editor, SN Applied Sciences (Springer)
2018	Guest Editor, Industrial & Engineering Chemistry Research (ACS, IF: 3.720)
2016 - 2018	Associate Editor, Malaysia Journal of Catalysis. (Penerbit UTM)
2015 - present	> 200 Reviews for ISI Journals (published by ACS, Elsevier, RCS, Wiley, and Springer)

List of Selected Publication:

1. Methane dry reforming over Ni/fibrous SBA-15 catalysts: effects of support morphology (rod-liked F-SBA-15 and dendritic DFSBA-15). **Catalysis Today**. (2021)
2. Greenhouse gas mitigation and hydrogen generation via enhanced ethylene glycol dry reforming on La-promoted Co/Al_2O_3 catalyst. **Process Safety and Environmental Protection**. (2021)
3. Palm Oil-Based Chemicals for Sustainable Development of Petrochemical Industries in Malaysia: Progress, Prospect, and Challenges. **ACS Sustainable Chemistry & Engineering**. (2021)
4. Coke-resistant Y_2O_3-promoted cobalt supported on mesoporous alumina for enhanced hydrogen production. **Journal of the Energy Institute**. (2021)
5. Intensified photocatalytic degradation of 2,4–dicholorophenoxyacetic acid using size-controlled silver nanoparticles: Effect of pre-synthesis extraction. **Advanced Powder Technology**. (2021)
6. A highly competitive system for CO methanation over an active metal-free fibrous silica mordenite via in-situ ESR and FTIR studies. **Energy Conversion and Management.** (2020)
7. Facile synthesis of tunable dendritic fibrous SBA-15 (DFSBA-15) with radial wrinkle structure. ***Microporous and Mesoporous Materials***. (2020)
8. Robust Ni/Dendritic Fibrous SBA-15 (Ni/DFSBA-15) For Methane Dry Reforming: Effect of Ni Loadings. ***Applied Catalysis A: General***, 584,117174. (2019)
9. Effective removal of Pb (II) by low-cost fibrous silica KCC-1 synthesized from silica-rich rice husk ash. ***Journal of Industrial and Engineering Chemistry,*** 75, 262-270. (2019)
10. Hydrogen production via CO_2 reforming of CH_4 over low-cost Ni/SBA-15 from silica-rich palm oil fuel ash (POFA) waste. ***International Journal of Hydrogen Energy***. (2019)

PART 1
FUNDAMENTAL CONCEPT OF CATALYST & CATALYSIS

Catalyst & Catalysis

Catalyst

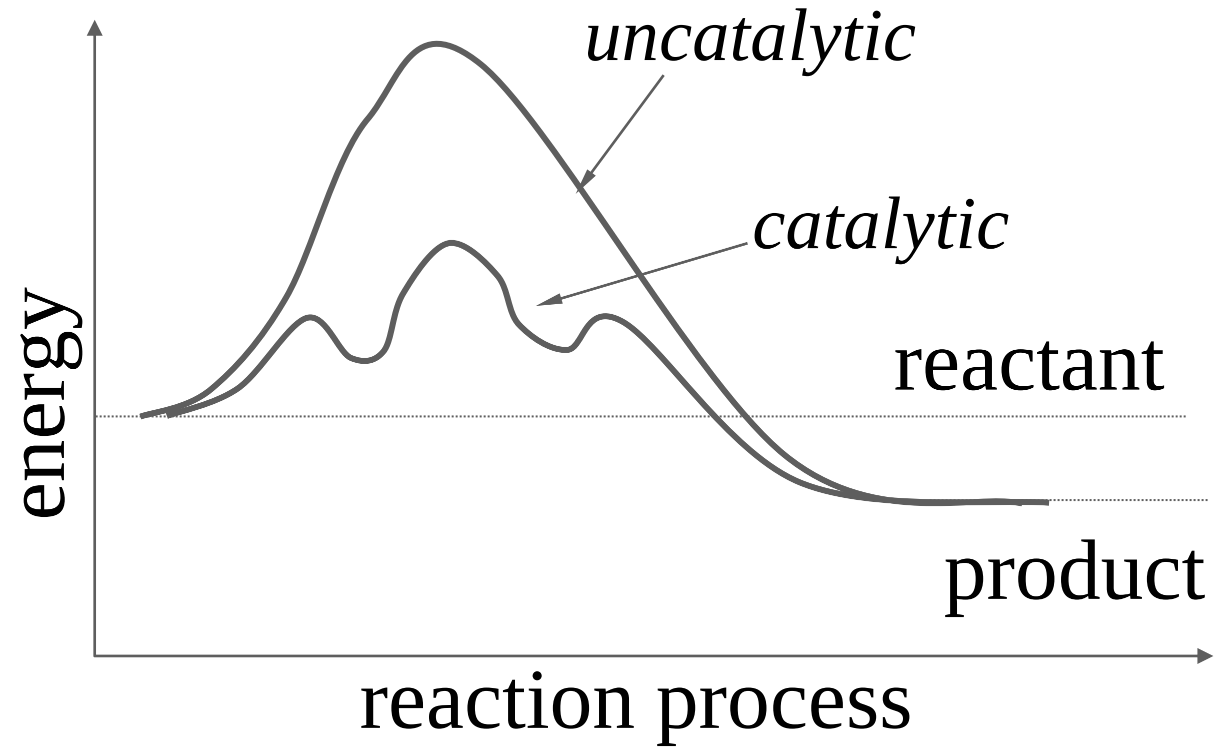
- Any substance that increases the rate of a reaction without itself being consumed.

Catalysis

- Catalysis is an action by catalyst which takes part in a chemical reaction process and can alter the rate of reactions, and yet itself will return to its original form without being consumed or destroyed at the end of the reactions
- Three key aspects of catalyst action
  - ✓ taking part in the reaction - *it will change itself during the process by interacting with other reactant/product molecules*
  - ✓ altering the rates of reactions - *in most cases the rates of reactions are increased by the action of catalysts; however, in some situations the rates of undesired reactions are selectively suppressed*
  - ✓ Returning to its original form - *After reaction cycles a catalyst with exactly the same nature is 'reborn'*

Action of Catalysts

- Catalyst action leads to the rate of a reaction to change.
- Reactions proceed under less demanding conditions. Allow reactions occur under a milder conditions, e.g. at lower temperatures for those heat sensitive materials
- It is important to remember that the use of catalyst DOES NOT vary ΔG & K_{eq} values of the reaction concerned, it merely change the PACE of the process
- This is realised by changing the course of reaction (compared to non-catalytic reaction). This is evidenced by the facts that
  - ✓ The reaction activation energy is altered
  - ✓ The intermediates formed are different from those formed in non-catalytic reaction
  - ✓ The rates of reactions are altered (both desired and undesired ones)



Types of Catalysts

- Classification based on the its physical state, a catalyst can be
  - gas
  - liquid
  - solid
- Classification based on the substances from which a catalyst is made
  - Inorganic (gases, metals, metal oxides, inorganic acids, bases etc.)
  - Organic (organic acids, enzymes etc.)
- Classification based on the ways catalysts work
  - Homogeneous - both catalyst and all reactants/products are in the same phase (gas or liq)
  - Heterogeneous - reaction system involves multi-phase (catalysts + reactants/products)
- Classification based on the catalysts' action
  - Acid-base catalysts
  - Enzymatic
  - Photocatalysis
  - Electrocatalysis, etc.

Applications of Catalysis

Industrial applications

- Almost all chemical industries have one or more steps employing catalysts
- Achieving better process economics and productivity
  - Increase reaction rates - fast
  - Simplify the reaction steps - low investment cost
  - Carry out reaction under mild conditions (e.g. low T, P) - low energy consumption
- Reducing wastes
  - Improving selectivity toward desired products - less raw materials required, less unwanted wastes
  - Replacing harmful/toxic materials with readily available ones
- Producing certain products that may not be possible without catalysts
- Having better control of process (safety, flexible etc.)
- Encouraging application and advancement of new technologies and materials

Applications of Catalysis

Environmental applications

- Example 1: Pollution controls in combination with industrial processes
  - ✓ Pre-treatment - reduce the amount waste/change the composition of emissions
  - ✓ Post-treatments - once formed, reduce and convert emissions
  - ✓ Using alternative materials
- Example 2: Pollution reduction
  - ✓ gas - converting harmful gases to non-harmful ones
  - ✓ liquid - de-pollution, de-odder, de-colour etc
  - ✓ solid - landfill, factory wastes

Other applications

- Catalysis and catalysts play one of the key roles in new technology development.

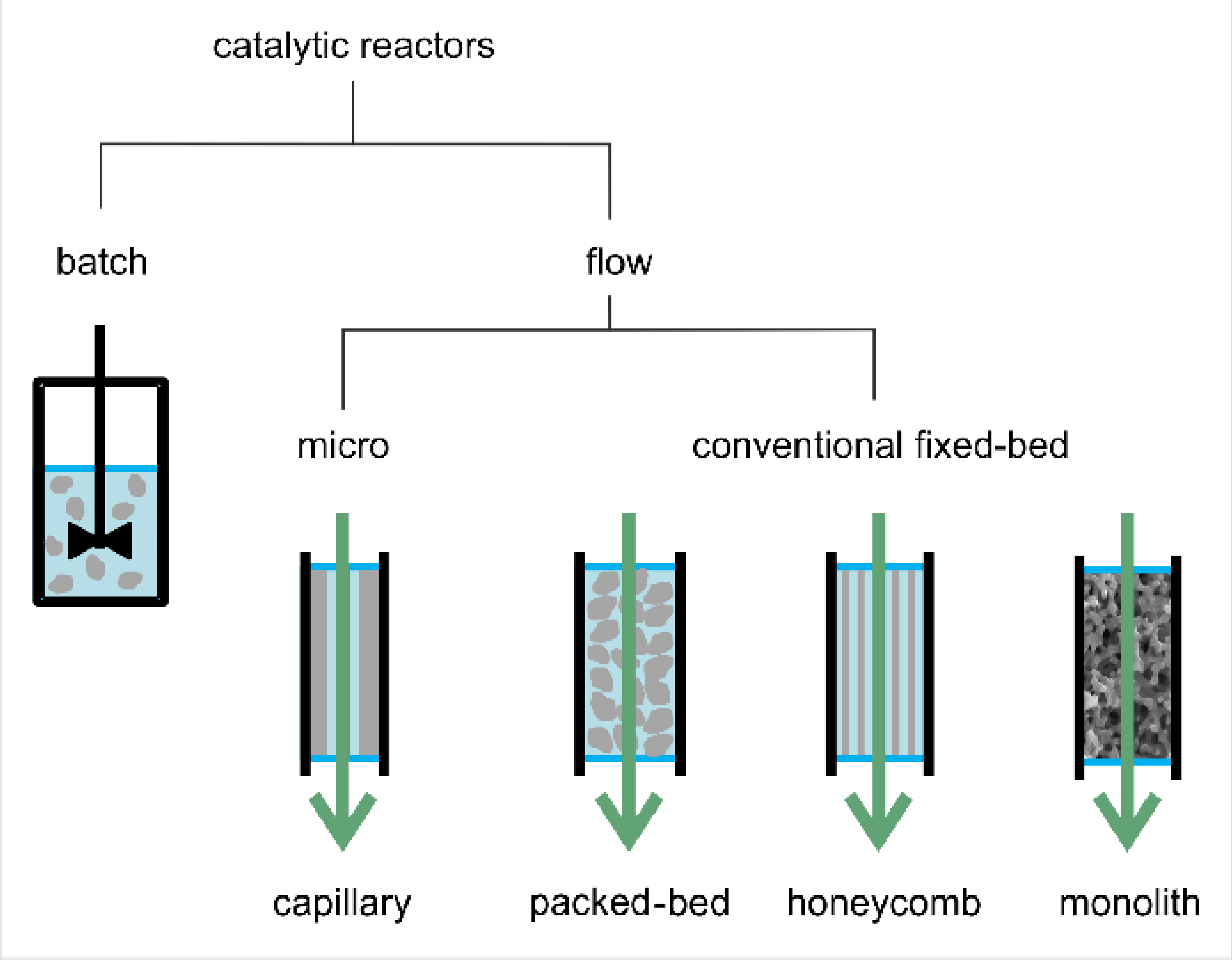
Research in Catalysis

Research in catalysis involve a multi-discipline approach

- Reaction kinetics and mechanism - *Reaction paths, intermediate formation & action, interpretation of results obtained under various conditions, generalising reaction types & schemes, predict catalyst performance*
- Catalyst development - *Material synthesis, structure properties, catalyst stability, compatibility*
- Analysis techniques - *Detection limits in terms of dimension of time & size and under extreme conditions (T, P) and accuracy of measurements, microscopic techniques, sample preparation techniques*
- Reaction modelling - *Elementary reactions and rates, quantum mechanics/chemistry, physical chemistry*
- Reactor modelling - *Mathematical interpretation and representation, the numerical method, micro-kinetics, structure and efficiency of heat and mass transfer in relation to reactor design*
- Catalytic process - *Heat and mass transfers, energy balance and efficiency of process*

Catalytic Reaction Processes

- A catalytic reaction can be operated in a *batch* manner
  - Reactants and catalysts are loaded together in reactor and catalytic reactions (homo- or heterogeneous) take place in pre-determined temperature and pressure for a desired time / desired conversion
  - Type of reactor is usually simple, basic requirements
    - ✓ Withstand required temperature & pressure
    - ✓ Some stirring to encourage mass and heat transfers
    - ✓ Provide sufficient heating or cooling



- Catalytic reactions are commonly operated in a *continuous* manner
  - Reactants, which are usually in gas or liquid phase, are fed to reactor in *steady* rate (e.g. mol/h, kg/h, m^3/h)
  - Usually a *target conversion* is set for the reaction, based on this target
    - ✓ required quantities of catalyst is added
    - ✓ required heating or cooling is provided
    - ✓ required reactor dimension and characteristics are designed accordingly.

Catalytic Reaction Processes

Continuous **catalytic system**

- Catalysts are pre-loaded, when using a solid catalyst, or fed together with reactants when catalyst & reactants are in the same phase and pre-mixed
  - ✓ It is common to use solid catalyst because of its easiness to separate catalyst from unreacted reactants and products. (*Note: In a chemical process separation usually accounts for ~80% of cost. That is why engineers always try to put a liquid catalyst on to a solid carrier)*
  - ✓ With pre-loaded solid catalyst, there is no need to transport catalyst which is then more economic and less attrition of solid catalyst (Catalysts do not change before and after a reaction and can be used for number cycles, months or years),
  - ✓ In some cases catalysts has to be transported because of need of *regeneration*
- In most cases, catalytic reactions are carried out with catalyst in a fixed-bed reactor (fluidised-bed in case of regeneration being needed), with the reactant being gases or liquids

Catalytic Reaction Processes

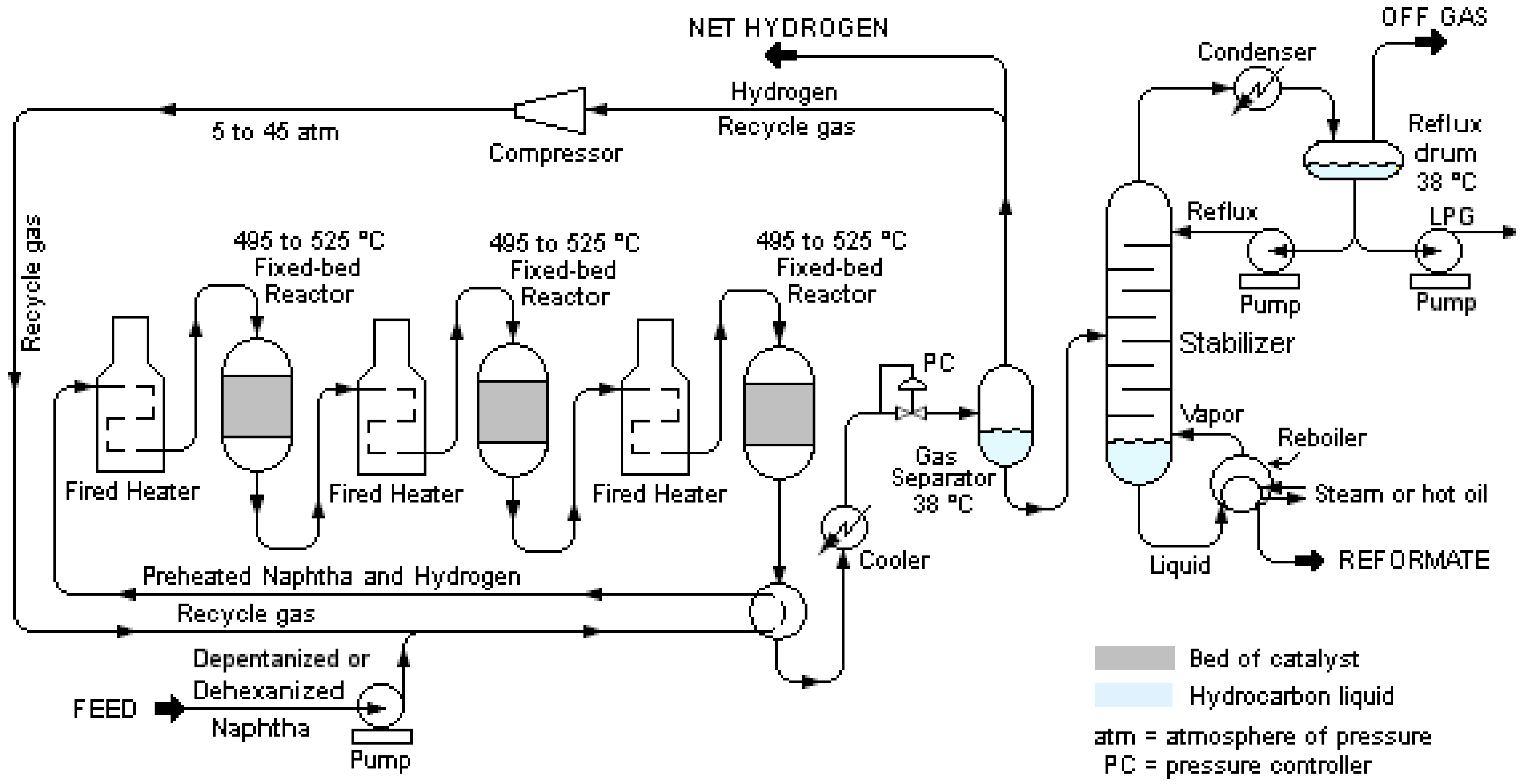
General requirements for a good catalyst

- Activity - being able to promote the rate of desired reactions
- Selective - being to promote only the rate of desired reaction (*Note: The selectivity is sometime considered to be more important than the activity and sometime it is more difficult to achieve*)
- Stability - a good catalyst should resist to deactivation, caused by
    i. the presence of impurities in feed (e.g. lead in petrol poison TWC.
    ii. thermal deterioration, volatility and hydrolysis of active components
    iii. attrition due to mechanical movement or pressure shock

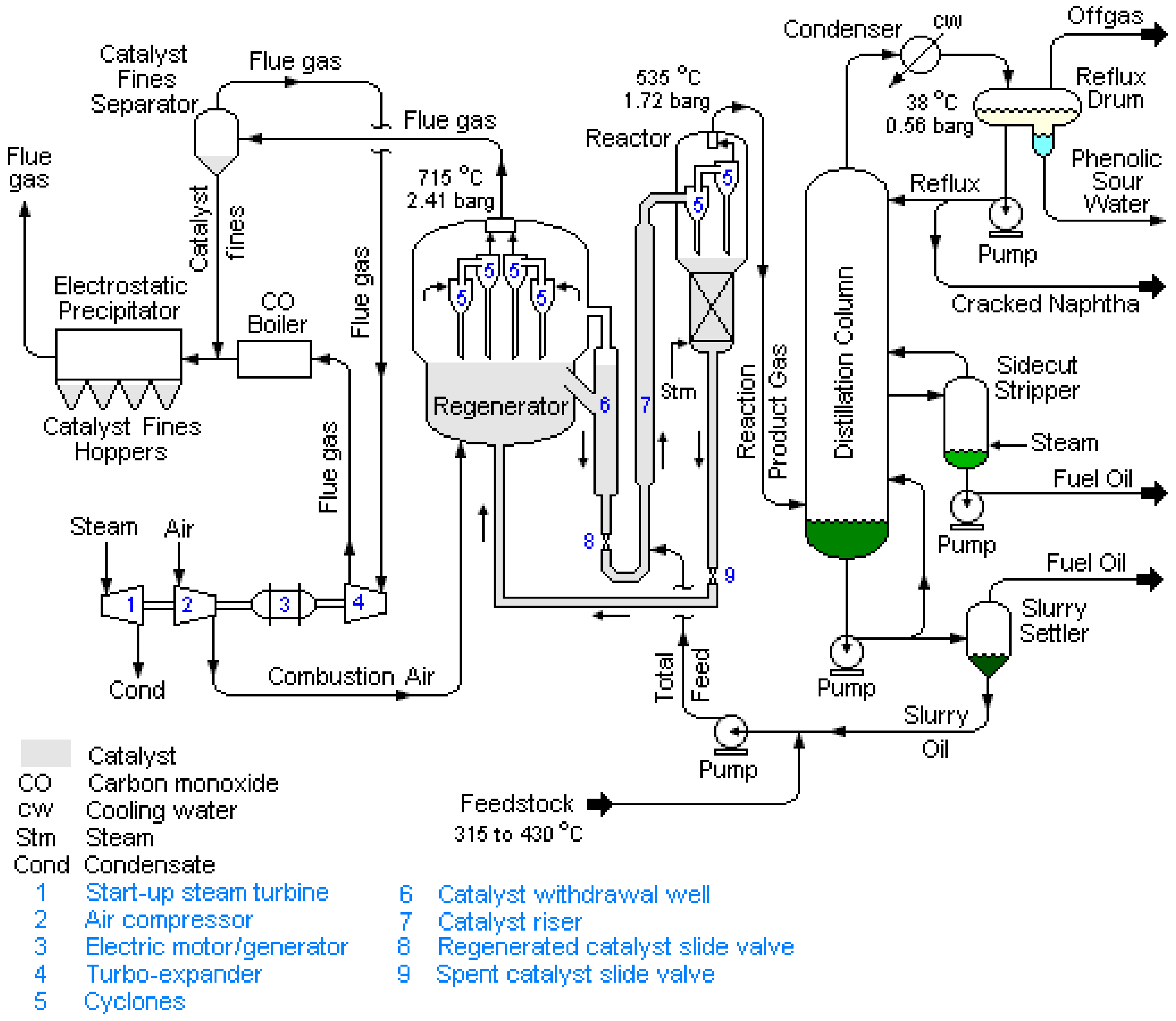
Catalytic Reaction Processes

Example Applications

- Catalytic reforming: This is an important process in the petroleum refinery. It is the chemical process of converting petroleum refinery naphtha distilled from crude oil into reformates which have a higher octane number in the presence of a platinum-containing catalyst.



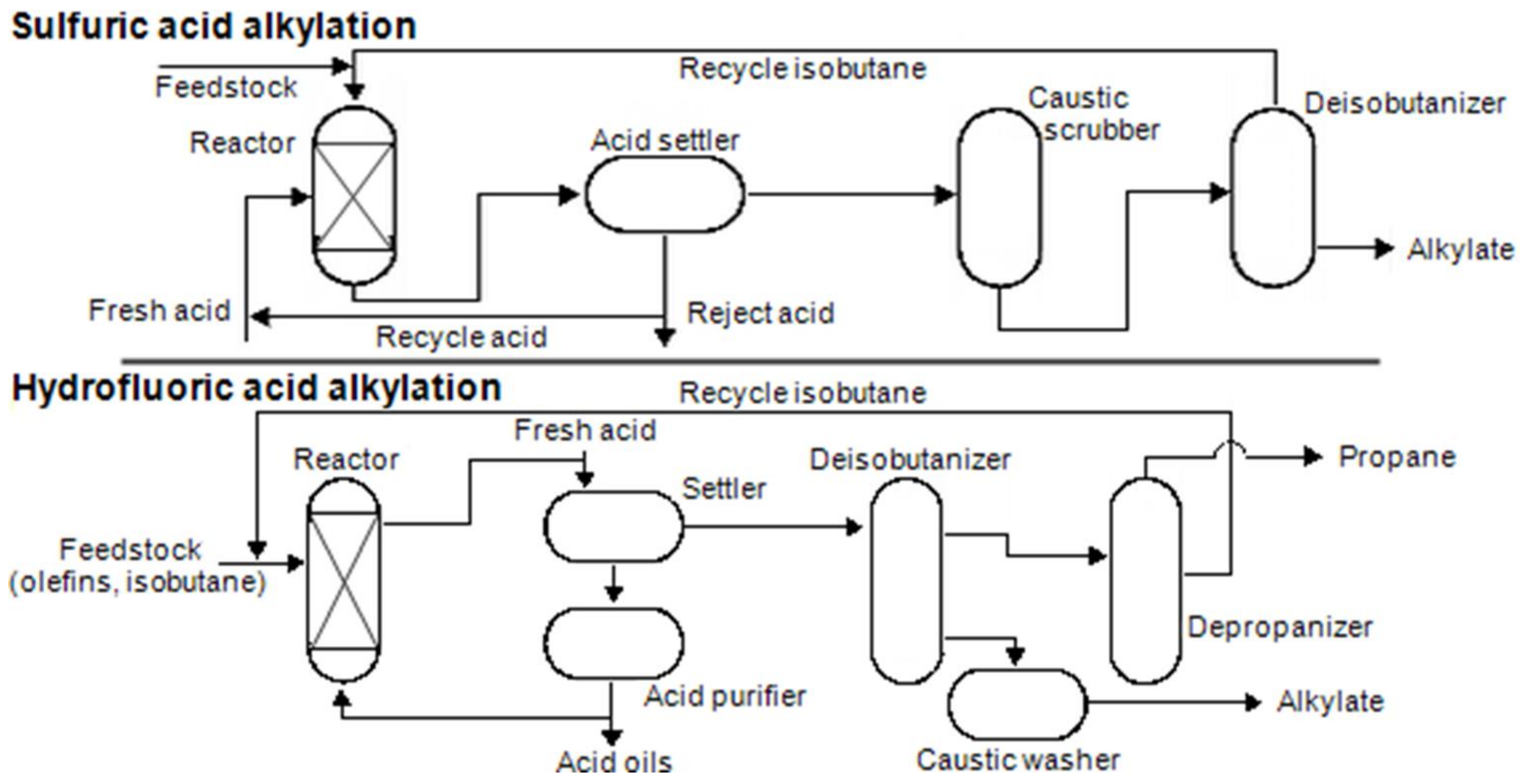
- Catalytic cracking: This is a process by which high molecular weight hydrocarbons are converted into more valuable gasoline, olefin, and other useful products in the presence of a catalyst under a suitable condition of temperature and pressure. It's a thermal decomposition of heavy petroleum hydrocarbon in the presence of a catalyst. It's an ionic process involving carbonium ions, it gives higher yield and higher-octane number.



Catalytic Reaction Processes

Example Applications

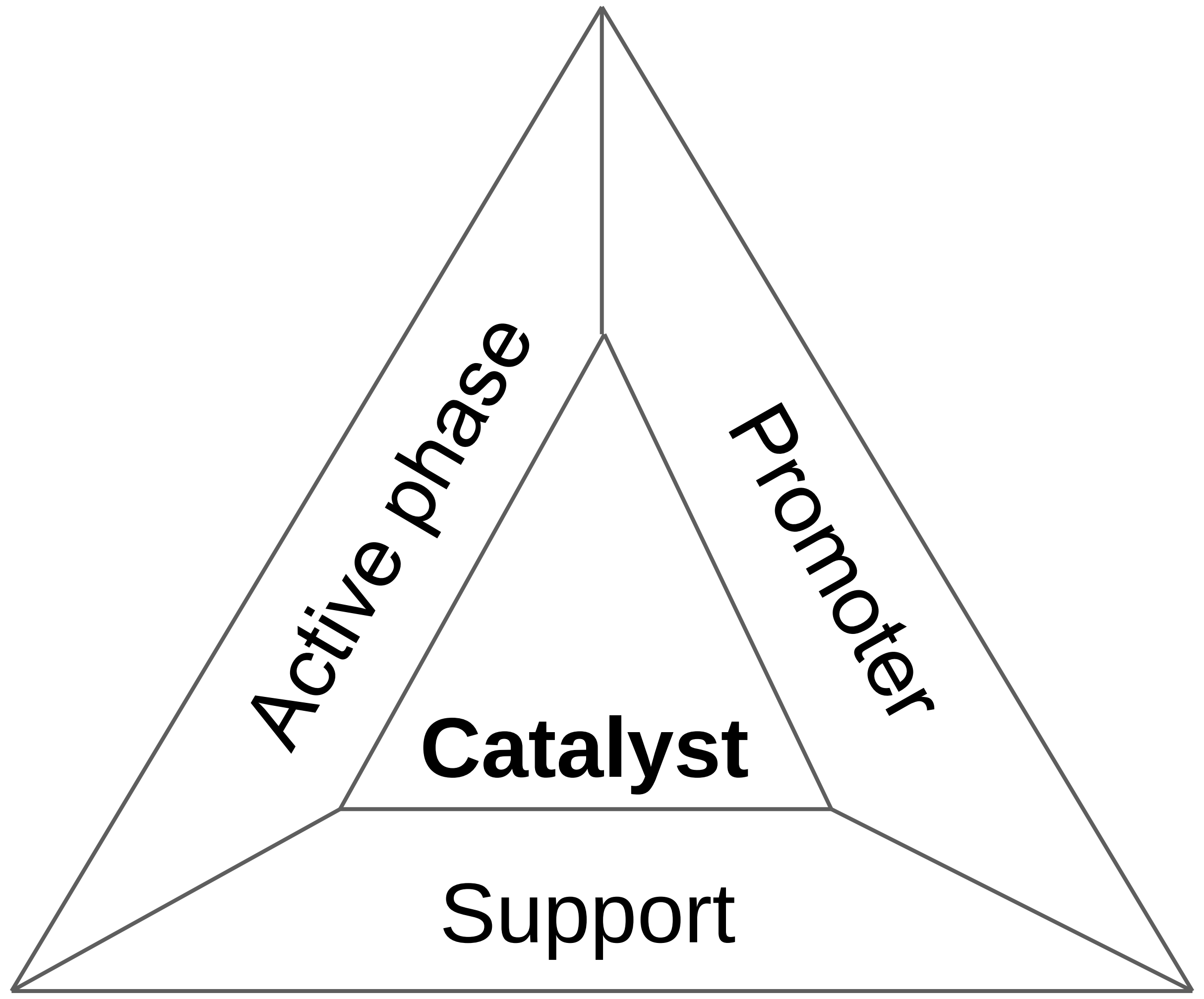
- Alkylation: This is a process whereby light hydrocarbons such as propene, butene, and isobutane are combined with the aid of a catalyst to produce high-octane petrol. It can also refer to the process of producing high-octane motor fuel components by the combination of olefins and with a tertiary carbon atom.



Solid Catalysts

Catalyst composition

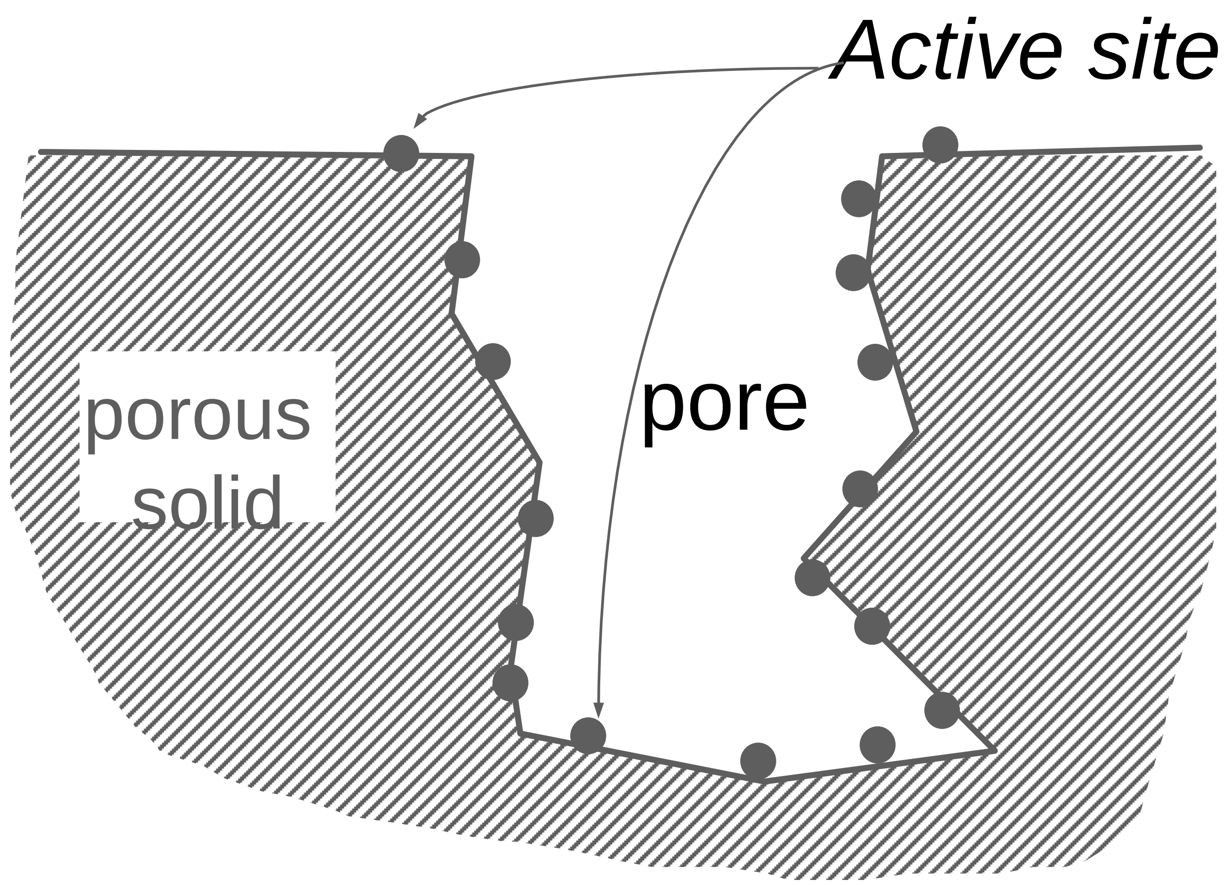
- Active phase
  - ✓ Where the reaction occurs (mostly metal/metal oxide)
- Promoter
  - ✓ Textual promoter (e.g. Al - Fe for NH_3 production)
  - ✓ Electric or Structural modifier
  - ✓ Poison resistant promoters
- Support / carrier
  - ✓ Increase mechanical strength
  - ✓ Increase surface area (98% surface area is supplied within the porous structure)
  - ✓ may or may not be catalytically active



Solid Catalysts

Common solid support / carrier materials

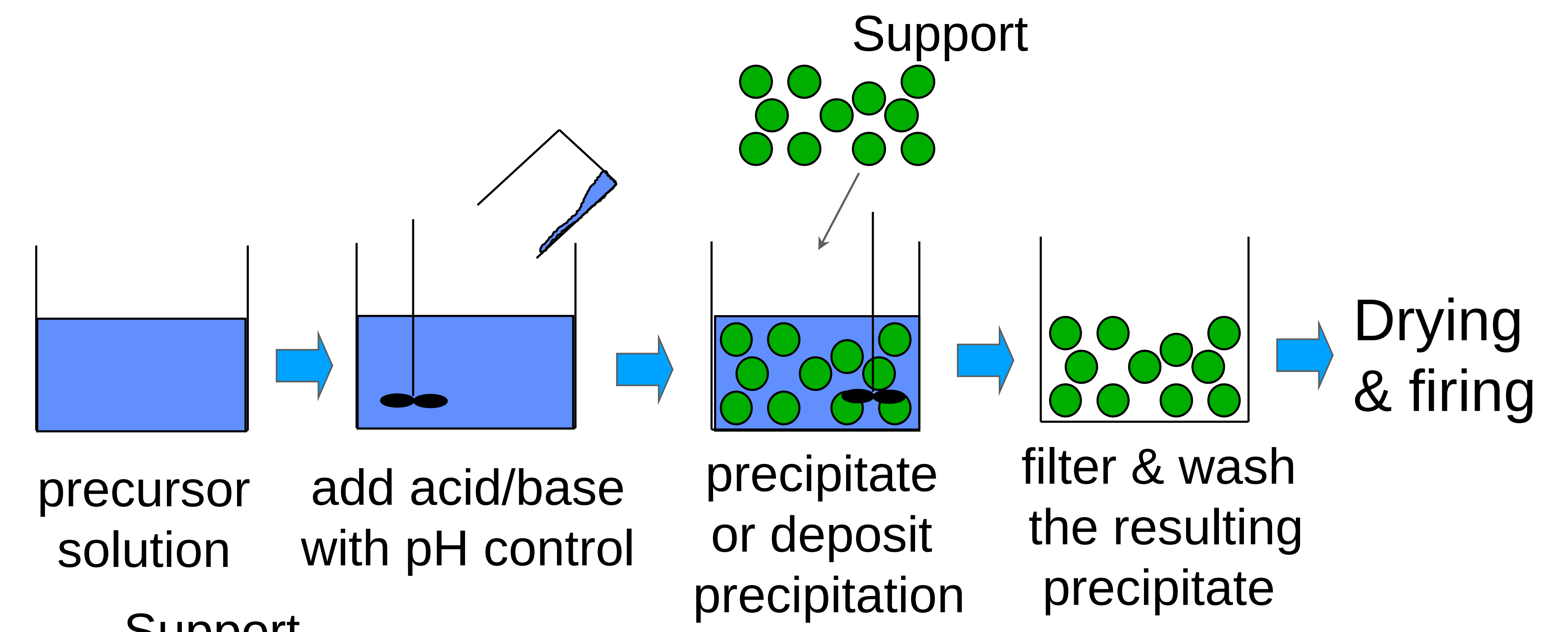
- Alumina
  - ✓ Inexpensive
  - ✓ Surface area: 1 ~ 700 m^2/g
  - ✓ Acidic
- Silica
  - ✓ Inexpensive
  - ✓ Surface area: 100 ~ 800 m^2/g
- Zeolite
  - ✓ mixture of alumina and silica,
  - ✓ often exchanged metal ion present
  - ✓ shape selective
- Other supports
  - ✓ Active carbon (S.A. up to 1000 m^2/g)
  - ✓ Titania (S.A. 10 ~ 50 m^2/g)
  - ✓ Zirconia (S.A. 10 ~ 100 m^2/g)
  - ✓ Magnesia (S.A. 10 m^2/g)
  - ✓ Lanthana (S.A. 10 m^2/g)



Solid Catalysts

Preparation of catalysts

- Precipitation - To form non-soluble precipitate by desired reactions at certain pH and temperature

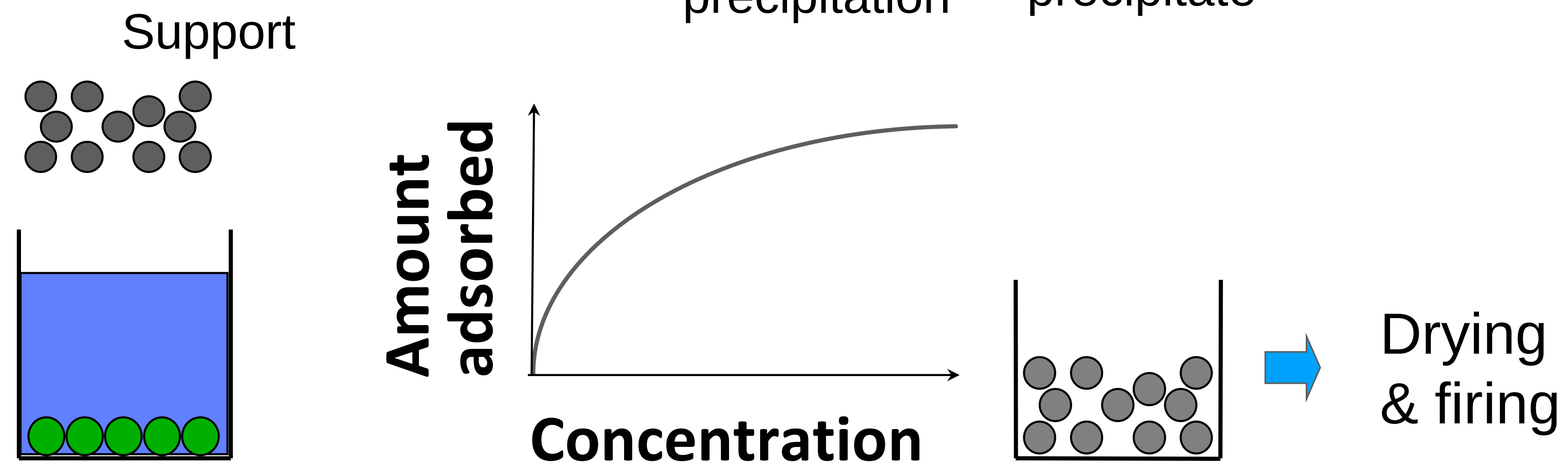


- Adsorption & ion-exchange

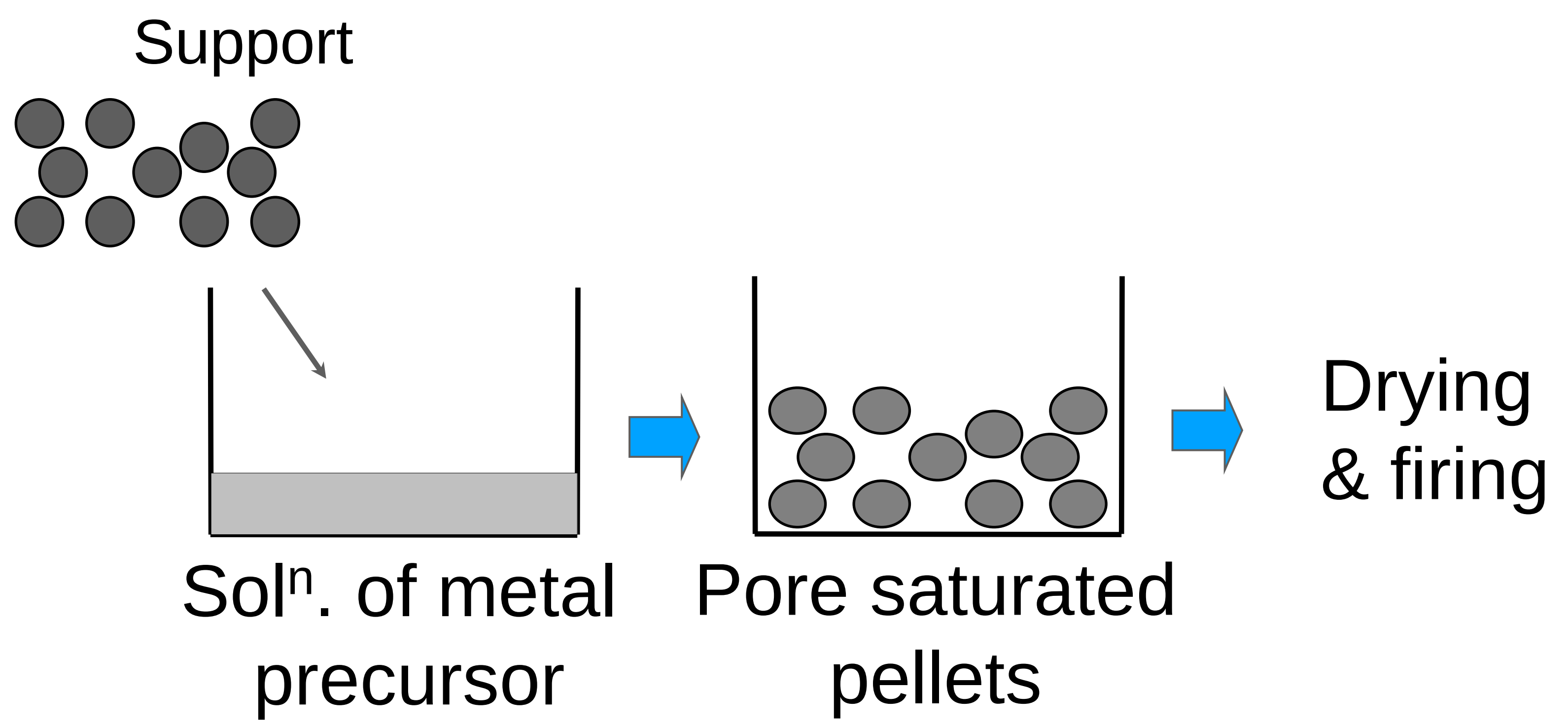
Cationic: S-OH$^+$ + C$^+$ ® SOC$^+$ + H$^+$

Anionic: S-OH$^-$ + A$^-$ ® SA$^-$ + OH$^-$

I-exch.: S-Na$^+$ + Ni $^{2+}$ D S-Ni $^{2+}$ + Na$^+$



- Impregnation - Fill the pores of support with a metal salt solution of sufficient concentration to give the correct loading.



- Dry mixing - Physically mixed, grind, and fired

Solid Catalysts

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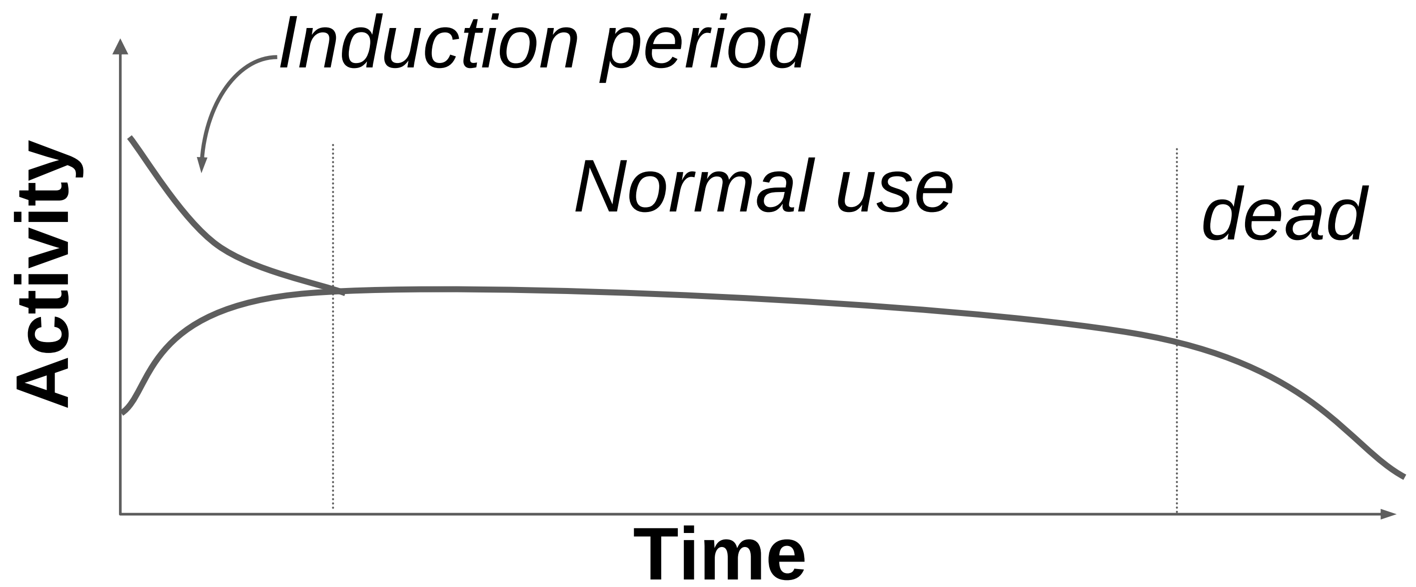
- **Preparation of catalysts**
  - Catalysts need to be calcined (fired) in order to decompose the precursor and to receive desired thermal stability.

- **Commonly used Pre-treatments**
  - Reduction
    - ✓ if elemental metal is the active phase
  - Sulphidation
    - ✓ if a metal sulphide is the active phase
  - Activation
    - ✓ Some catalysts require certain activation steps in order to receive the best performance.
    - ✓ Even when the oxide itself is the active phase it may be necessary to pre-treat the catalyst prior to the reaction

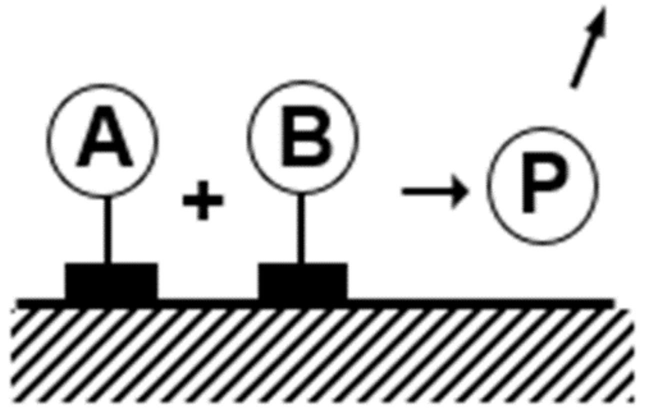
- **Typical catalyst life span**
  - Can be many years or a few mins.



Mechanism of Surface Catalysed Reaction

❑ Langmuir-Hinshelwood mechanism

- This mechanism deals with the surface-catalysed reaction in which 2 or more reactants adsorb on surface without dissociation



$$A(g) + B(g) \leftrightarrows A(ads) + B(ads) \rightarrow P$$ (the desorption of *P* is not r.d.s.)

- The rate of reaction $r_i = k[A][B] = k\theta_A\theta_B$

  From Langmuir adsorption isotherm (the case III) we know

$$\begin{cases} \theta_A = \dfrac{B_{0,A}P_A}{1 + B_{0,A}P_A + B_{0,B}P_B} \\ \theta_B = \dfrac{B_{0,B}P_B}{1 + B_{0,A}P_A + B_{0,B}P_B} \end{cases}$$

- We then have

$$r_i = k\left(\frac{B_{0,A}P_A}{1 + B_{0,A}P_A + B_{0,B}P_B}\right)\left(\frac{B_{0,B}P_B}{1 + B_{0,A}P_A + B_{0,B}P_B}\right) = \frac{kB_{0,A}B_{0,B}P_AP_B}{1 + B_{0,A}P_A + B_{0,B}P_B}$$

  - When both A and B are weakly adsorbed ($B_{0,A}P_A \ll 1$, $B_{0,B}P_B \ll 1$),

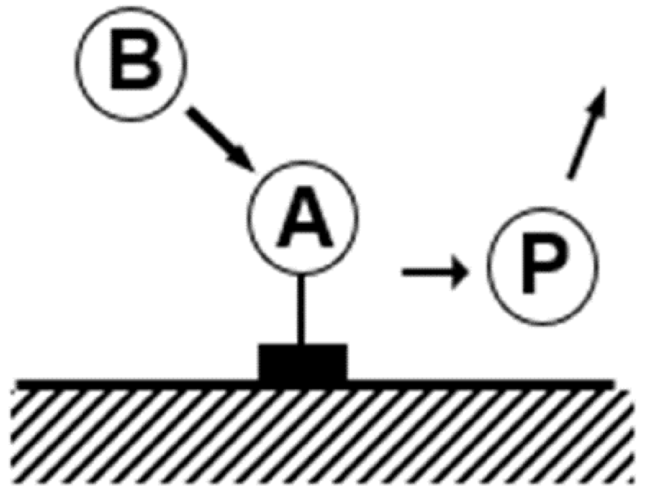
$$r_i = kB_{0,A}B_{0,B}P_AP_B = k'P_AP_B$$ 2nd order reaction

  - When A is strongly adsorbed ($B_{0,A}P_A \gg 1$) and B weakly adsorbed ($B_{0,B}P_B \ll 1 \ll B_{0,A}P_A$)

$$r_i = \frac{kB_{0,A}B_{0,B}P_AP_B}{B_{0,A}P_A} = kB_{0,B}P_B = k''P_B$$ 1st order w.r.t. B

Mechanism of Surface Catalysed Reaction

❑ Eley-Rideal mechanism



- This mechanism deals with the surface-catalysed reaction in which one reactant, A, adsorbs on a surface without dissociation and other reactant, B, approaches from the gas phase to react with A

$$\mathrm{A}(g) \leftrightarrows \mathrm{A}(ads) \xrightarrow{+\,\mathrm{B}(g)} \mathrm{P}$$ (the desorption of *P* is not r.d.s.)

- The rate of reaction $r_i = k[\mathrm{A}][\mathrm{B}] = k\theta_A P_B$

  From Langmuir adsorption isotherm (the case I) we know $\theta_A = \dfrac{B_{0,A}P_A}{1+B_{0,A}P_A}$

- We then have $r_i = k\left(\dfrac{B_{0,A}P_A}{1+B_{0,A}P_A}\right)P_B = \dfrac{kB_{0,A}P_AP_B}{1+B_{0,A}P_A}$

  - When both A is weakly adsorbed or the partial pressure of A is very low ($B_{0,A}P_A \ll 1$),

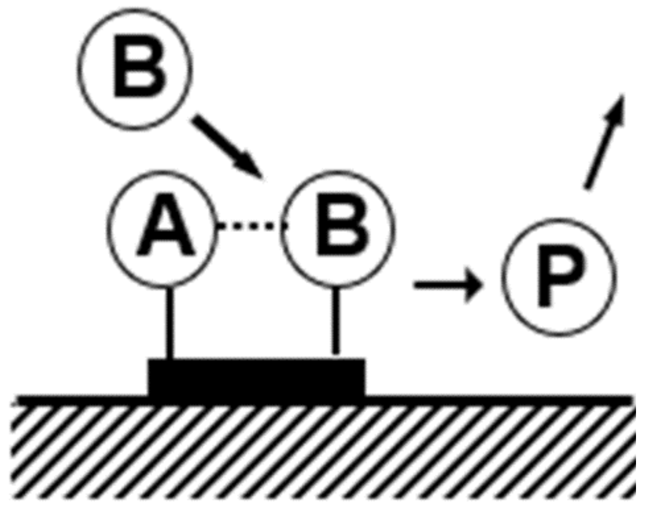
    $r_i = kB_{0,A}P_AP_B = k' P_AP_B$ 2nd order reaction

  - When A is strongly adsorbed or the partial pressure of A is very high ($B_{0,A}P_A \gg 1$)

    $r_i = \dfrac{kB_{0,A}P_AP_B}{B_{0,A}P_A} = kP_B$ 1st order w.r.t. B

Mechanism of Surface Catalysed Reaction

- **Mechanism of surface-catalysed reaction with *dissociative* adsorption**
  - The mechanism of the surface-catalysed reaction in which one reactant, AD, dissociatively adsorbs on one surface site



$$AD(g) \leftrightarrows A(ads) + D(ads) \xrightarrow{+\,B(g)} P$$

(the des. of *P* is not r.d.s.)

  - The rate of reaction $r_i = k[A][B] = k\theta_{AD}P_B$

From Langmuir adsorption isotherm (the case I) we know $\theta_{AD} = \dfrac{(B_{0,AD}P_{AD})^{1/2}}{1+(B_{0,AD}P_{AD})^{1/2}}$

  - We then have $r_i = k\dfrac{(B_{0,AD}P_{AD})^{1/2}}{1+(B_{0,AD}P_{AD})^{1/2}}P_B = \dfrac{k(B_{0,AD}P_{AD})^{1/2}P_B}{1+(B_{0,AD}P_{AD})^{1/2}}$
    - When both AD is weakly adsorbed or the partial pressure of AD is very low ($B_{0,AD}P_{AD} \ll 1$),

$r_i = k(B_{0,AD}P_{AD})^{1/2}P_B = k'\,P_{AD}^{1/2}P_B$ The reaction orders, 0.5 w.r.t. AD and 1 w.r.t. B

    - When A is strongly adsorbed or the partial pressure of A is very high ($B_{0,A}P_A \gg 1$)

$r_i = \dfrac{k(B_{0,AD}P_{AD})^{1/2}P_B}{(B_{0,AD}P_{AD})^{1/2}} = kP_B$ 1st order w.r.t. B

Catalysts In Chemical Industry

Catalysts in Chemical Industry

- ~$2 billion annual sale of catalysts
- ~$200 billion annual sale of the chemicals that are related products
- ~90% of chemical industry has catalysis-related processes
- Catalysts contributes ~2% of total investment in a chemical process

Benefits of catalysts in the Industry

- Reduce production time
- Help in total and complete refining
- Save energy
- Help increase capacity
- Reduce waste
- Improve desired results
- Reduce the risks
- Suppress explosive reactions

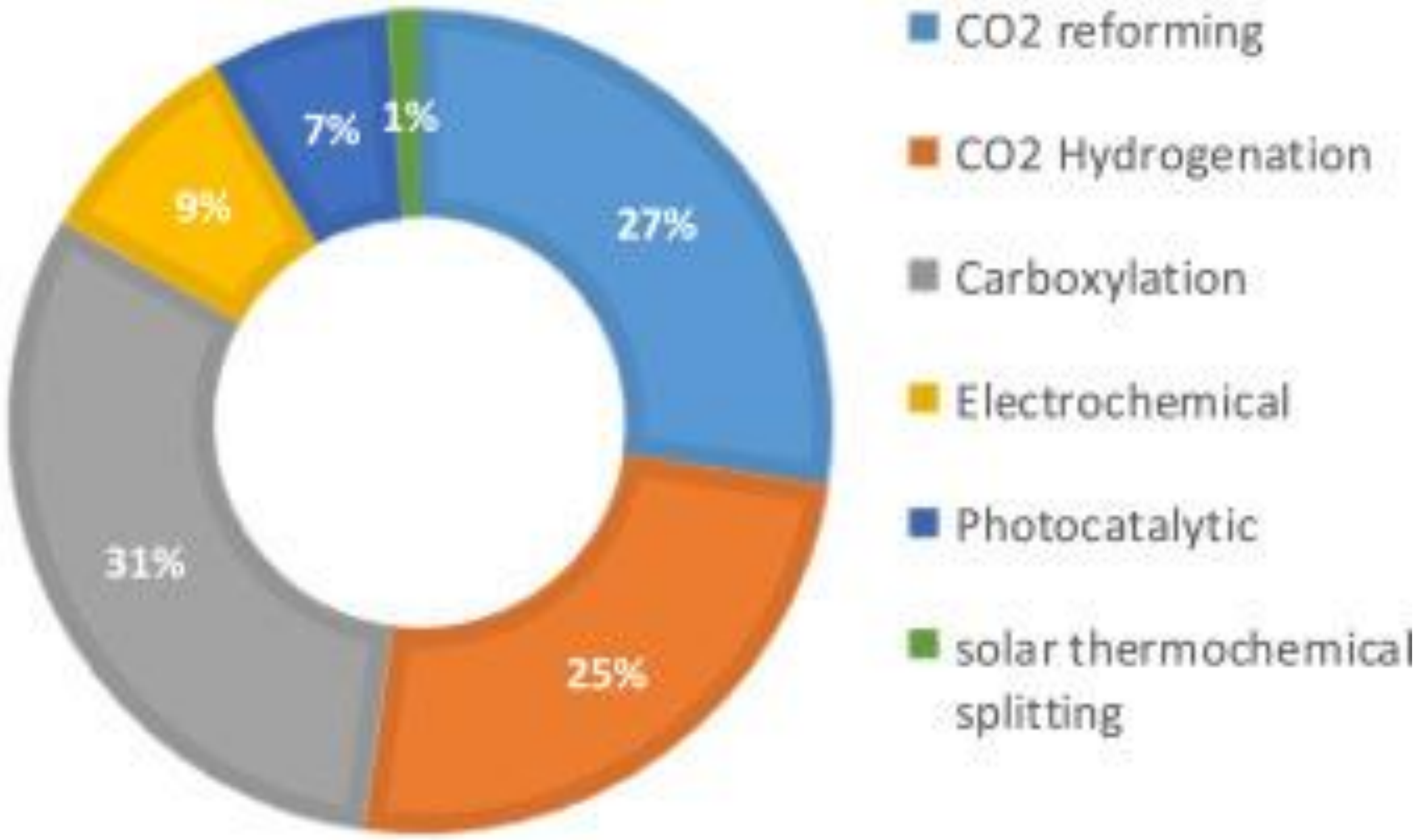
Benefits of catalysts to environment

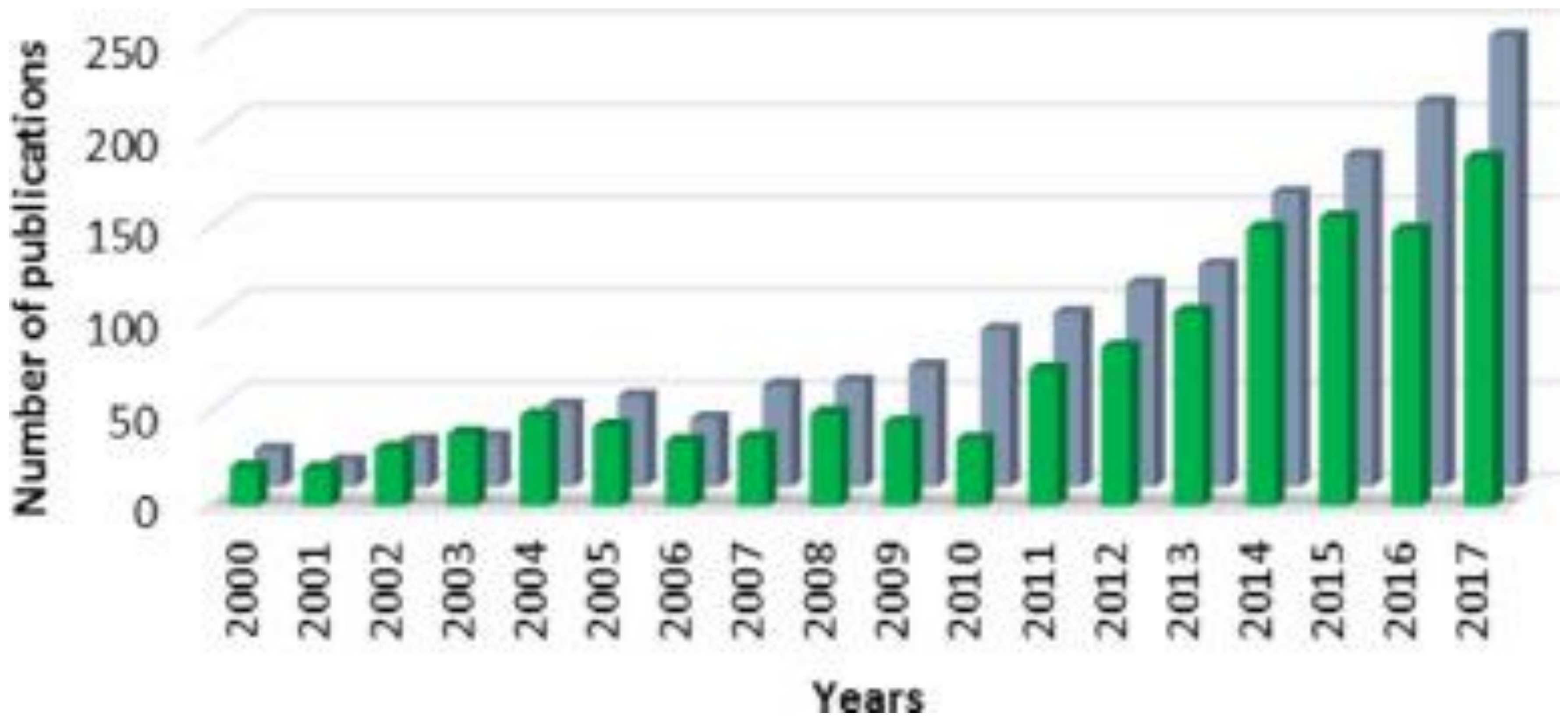
- Save energy and produce more with less work
- Can be reused multiple times till they become spent
- Help facilitate the production of a better product
- Reduce the temperature at which reactions occur

PART 2
ROLE OF CATALYST DEVELOPMENTS ON THE SUSTAINABLE CHEMICAL PROCESSES

Case Study 1: Catalytic CO_2 Conversion

- CO_2 has become focal points of interest because of its position as the primary greenhouse gas, thus, utilization of CO_2 is becoming an important subject for both academic and industrial perspectives
- Numerous methods have been employed for catalytic CO_2 conversion through homogeneous and heterogeneous catalytic reaction such as CO_2 reforming, CO_2 hydrogenation, carboxylation, electrochemical conversion, photocatalytic reaction and solar thermochemical CO_2 splitting
- CO_2 reforming of CH_4 has attracted considerable attention, where CO_2 is utilized in catalytic reforming of hydrocarbons to produce syngas (hydrogen and carbon monoxide) which is vital in generating other useful output or chemical (i.e. electrical, methanol, olefin and ammonia).
- Although there is no progress for commercialization, several attempts have been made on a pilot scale of dry reforming process.



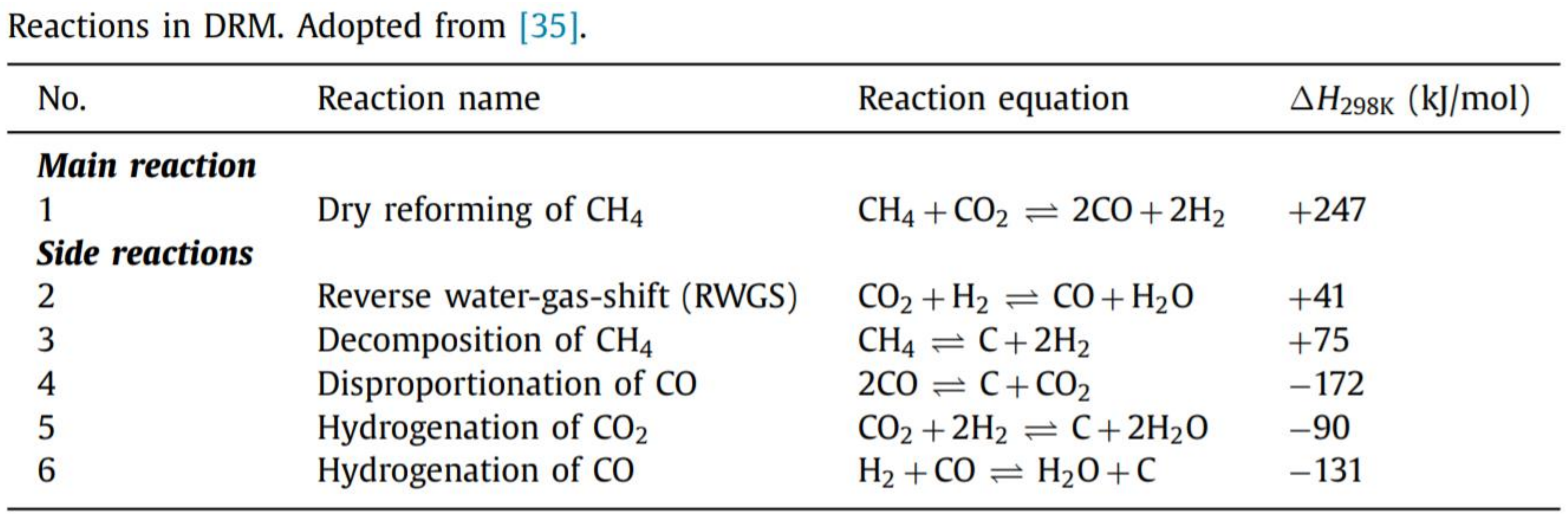


Reference:
Aziz, M. A. A., Setiabudi, H. D., Teh, L. P., Annuar, N. H. R., & Jalil, A. A. (2019). A review of heterogeneous catalysts for syngas production via dry reforming. Journal of the Taiwan Institute of Chemical Engineers, 101, 139-158.

Recent Catalyst Development

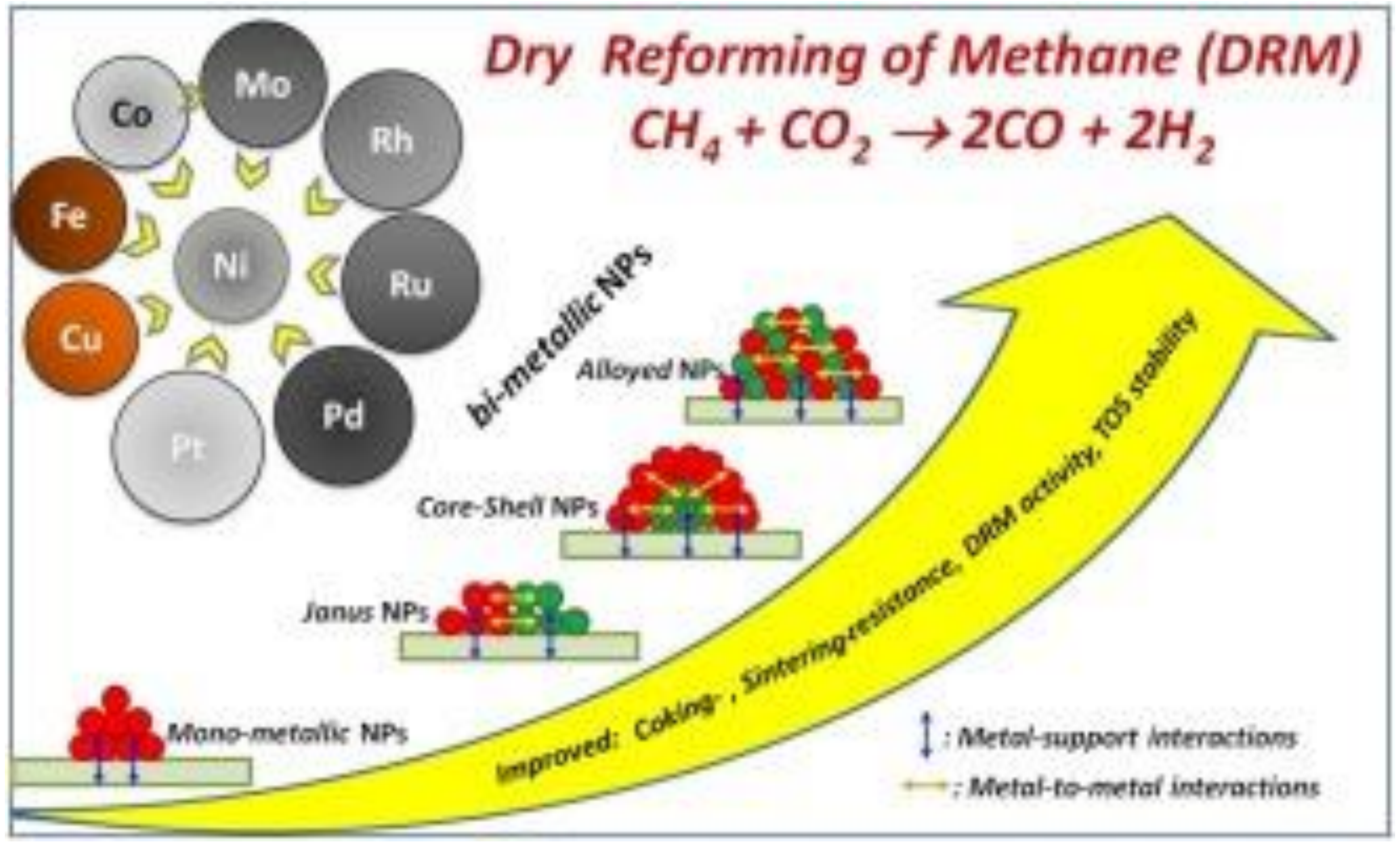
- At lower reaction temperature (<400°C), Boudouard reaction and reverse carbon gasification is favored. While, in the higher reaction temperature (>600°C), methane decomposition is preferred. These reactions led to the carbon deposition and must be avoided.

- Due to the carbon formation which cannot be avoided thermodynamically at high temperature, a kinetic control such as developing a catalyst that does not favor carbon formation could be the only a promising way to improve the stability of the catalyst. Therefore, the development study of this reaction has been centered on finding a better catalyst with aiming at higher activity and stability with better resistance toward coke formation, metal sinterization, metal oxidation and inactive chemical species formation.

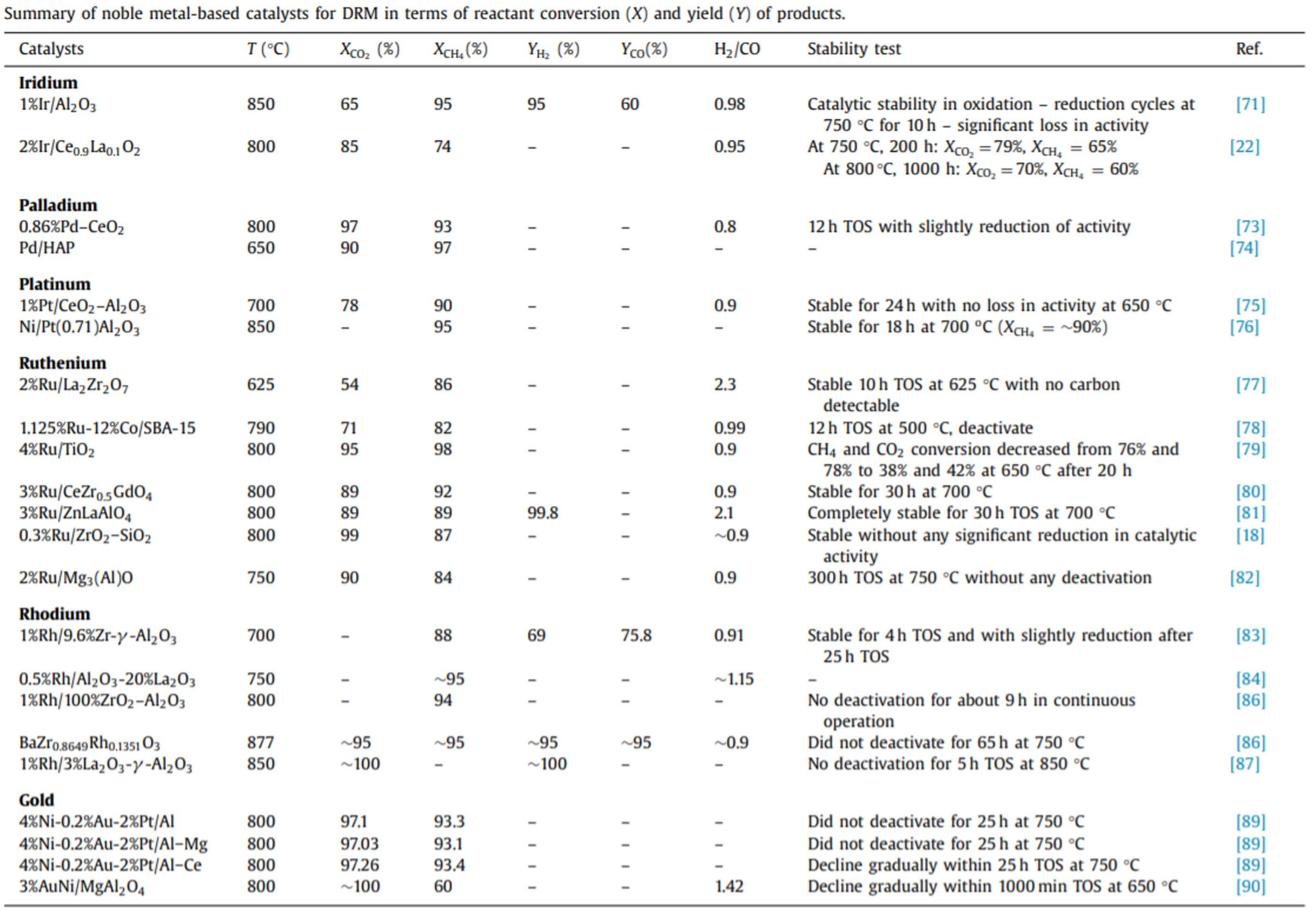


Reactions in DRM. Adopted from [35].

No.	Reaction name	Reaction equation	ΔH_{298K} (kJ/mol)
Main reaction			
1	Dry reforming of CH_4	$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	+247
Side reactions			
2	Reverse water-gas-shift (RWGS)	$CO_2 + H_2 \rightleftharpoons CO + H_2O$	+41
3	Decomposition of CH_4	$CH_4 \rightleftharpoons C + 2H_2$	+75
4	Disproportionation of CO	$2CO \rightleftharpoons C + CO_2$	−172
5	Hydrogenation of CO_2	$CO_2 + 2H_2 \rightleftharpoons C + 2H_2O$	−90
6	Hydrogenation of CO	$H_2 + CO \rightleftharpoons H_2O + C$	−131



Recent Catalyst Development

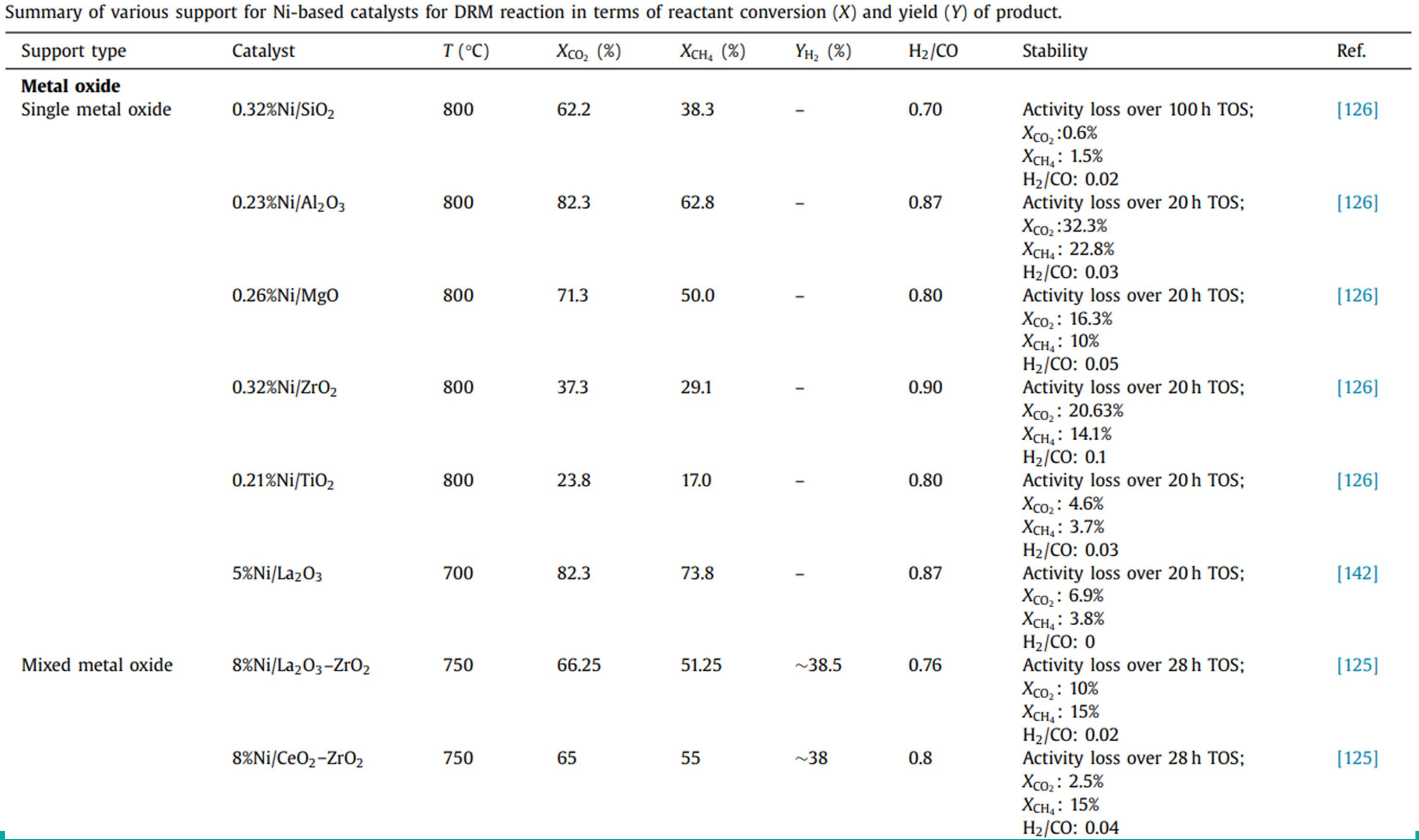


Summary of noble metal-based catalysts for DRM in terms of reactant conversion (*X*) and yield (*Y*) of products.

Catalysts	*T* (°C)	X_{CO_2} (%)	X_{CH_4}(%)	Y_{H_2} (%)	Y_{CO}(%)	H_2/CO	Stability test	Ref.
Iridium								
1%Ir/Al_2O_3	850	65	95	95	60	0.98	Catalytic stability in oxidation – reduction cycles at 750 °C for 10 h – significant loss in activity	[71]
2%Ir/$Ce_{0.9}La_{0.1}O_2$	800	85	74	–	–	0.95	At 750 °C, 200 h: X_{CO_2} = 79%, X_{CH_4} = 65% At 800 °C, 1000 h: X_{CO_2} = 70%, X_{CH_4} = 60%	[22]
Palladium								
0.86%Pd–CeO_2	800	97	93	–	–	0.8	12 h TOS with slightly reduction of activity	[73]
Pd/HAP	650	90	97	–	–	–	–	[74]
Platinum								
1%Pt/CeO_2–Al_2O_3	700	78	90	–	–	0.9	Stable for 24 h with no loss in activity at 650 °C	[75]
Ni/Pt(0.71)Al_2O_3	850	–	95	–	–	–	Stable for 18 h at 700 °C (X_{CH_4} = ~90%)	[76]
Ruthenium								
2%Ru/$La_2Zr_2O_7$	625	54	86	–	–	2.3	Stable 10 h TOS at 625 °C with no carbon detectable	[77]
1.125%Ru-12%Co/SBA-15	790	71	82	–	–	0.99	12 h TOS at 500 °C, deactivate	[78]
4%Ru/TiO_2	800	95	98	–	–	0.9	CH_4 and CO_2 conversion decreased from 76% and 78% to 38% and 42% at 650 °C after 20 h	[79]
3%Ru/$CeZr_{0.5}GdO_4$	800	89	92	–	–	0.9	Stable for 30 h at 700 °C	[80]
3%Ru/$ZnLaAlO_4$	800	89	89	99.8	–	2.1	Completely stable for 30 h TOS at 700 °C	[81]
0.3%Ru/ZrO_2–SiO_2	800	99	87	–	–	~0.9	Stable without any significant reduction in catalytic activity	[18]
2%Ru/Mg_3(Al)O	750	90	84	–	–	0.9	300 h TOS at 750 °C without any deactivation	[82]
Rhodium								
1%Rh/9.6%Zr-γ-Al_2O_3	700	–	88	69	75.8	0.91	Stable for 4 h TOS and with slightly reduction after 25 h TOS	[83]
0.5%Rh/Al_2O_3-20%La_2O_3	750	–	~95	–	–	~1.15	–	[84]
1%Rh/100%ZrO_2–Al_2O_3	800	–	94	–	–	–	No deactivation for about 9 h in continuous operation	[86]
$BaZr_{0.8649}Rh_{0.1351}O_3$	877	~95	~95	~95	~95	~0.9	Did not deactivate for 65 h at 750 °C	[86]
1%Rh/3%La_2O_3-γ-Al_2O_3	850	~100	–	~100	–	–	No deactivation for 5 h TOS at 850 °C	[87]
Gold								
4%Ni-0.2%Au-2%Pt/Al	800	97.1	93.3	–	–	–	Did not deactivate for 25 h at 750 °C	[89]
4%Ni-0.2%Au-2%Pt/Al–Mg	800	97.03	93.1	–	–	–	Did not deactivate for 25 h at 750 °C	[89]
4%Ni-0.2%Au-2%Pt/Al–Ce	800	97.26	93.4	–	–	–	Decline gradually within 25 h TOS at 750 °C	[89]
3%AuNi/$MgAl_2O_4$	800	~100	60	–	–	1.42	Decline gradually within 1000 min TOS at 650 °C	[90]

- Noble metals have been reported as active metals for dry reforming catalysts.
- Among these metals, noble metals such as Ru and Rh have shown to be the most active catalysts and high resistant from carbon deposition.
- However, upscale towards industrial level of noble metal catalysts are not feasible due to their high cost and restricted availability.

Recent Catalyst Development

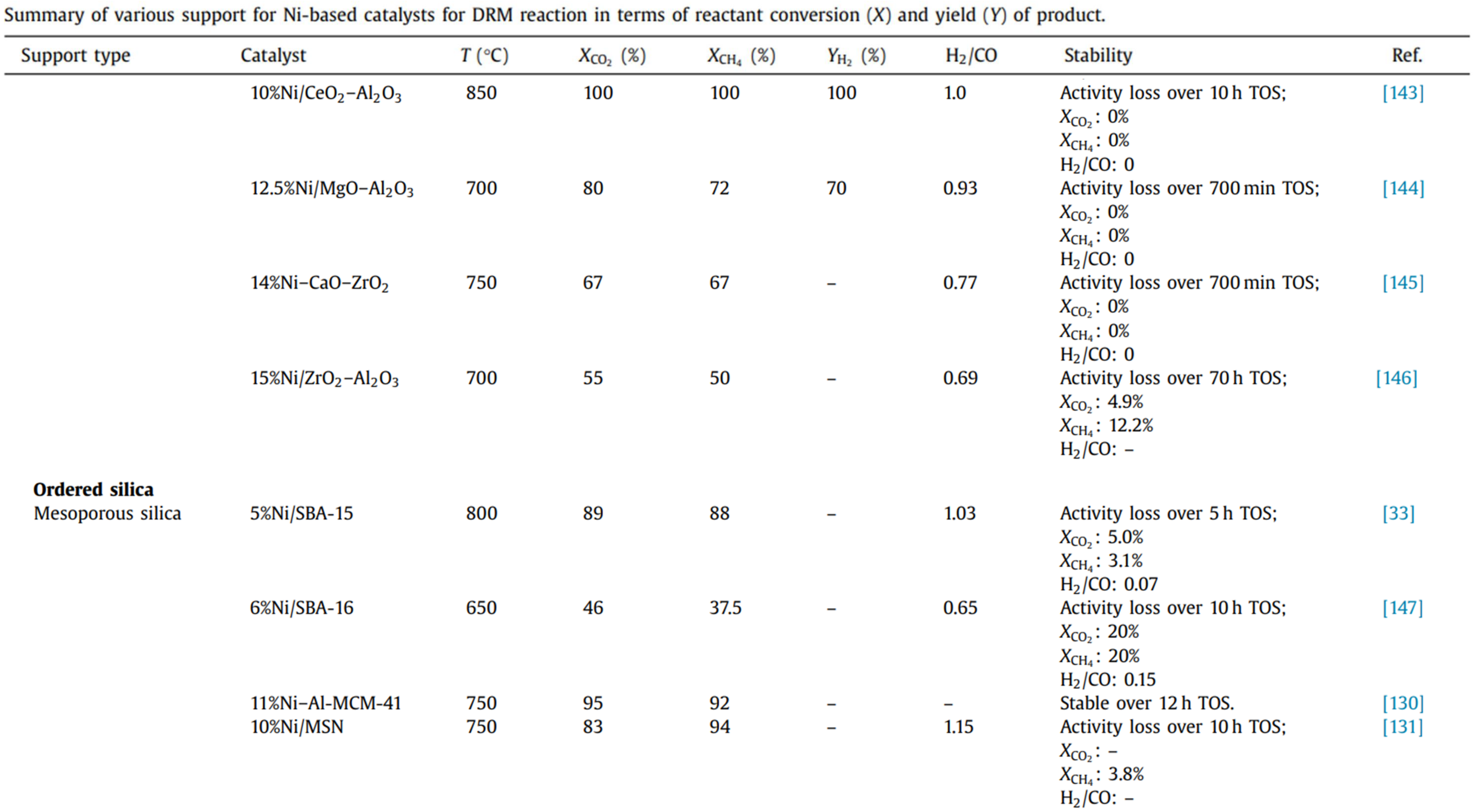


Summary of various support for Ni-based catalysts for DRM reaction in terms of reactant conversion (*X*) and yield (*Y*) of product.

Support type	Catalyst	T (°C)	X_{CO_2} (%)	X_{CH_4} (%)	Y_{H_2} (%)	H_2/CO	Stability	Ref.
Metal oxide								
Single metal oxide	0.32%Ni/SiO_2	800	62.2	38.3	–	0.70	Activity loss over 100 h TOS; X_{CO_2} :0.6% X_{CH_4}: 1.5% H_2/CO: 0.02	[126]
	0.23%Ni/Al_2O_3	800	82.3	62.8	–	0.87	Activity loss over 20 h TOS; X_{CO_2} :32.3% X_{CH_4}: 22.8% H_2/CO: 0.03	[126]
	0.26%Ni/MgO	800	71.3	50.0	–	0.80	Activity loss over 20 h TOS; X_{CO_2}: 16.3% X_{CH_4}: 10% H_2/CO: 0.05	[126]
	0.32%Ni/ZrO_2	800	37.3	29.1	–	0.90	Activity loss over 20 h TOS; X_{CO_2}: 20.63% X_{CH_4}: 14.1% H_2/CO: 0.1	[126]
	0.21%Ni/TiO_2	800	23.8	17.0	–	0.80	Activity loss over 20 h TOS; X_{CO_2}: 4.6% X_{CH_4}: 3.7% H_2/CO: 0.03	[126]
	5%Ni/La_2O_3	700	82.3	73.8	–	0.87	Activity loss over 20 h TOS; X_{CO_2}: 6.9% X_{CH_4}: 3.8% H_2/CO: 0	[142]
Mixed metal oxide	8%Ni/La_2O_3–ZrO_2	750	66.25	51.25	~38.5	0.76	Activity loss over 28 h TOS; X_{CO_2}: 10% X_{CH_4}: 15% H_2/CO: 0.02	[125]
	8%Ni/CeO_2–ZrO_2	750	65	55	~38	0.8	Activity loss over 28 h TOS; X_{CO_2}: 2.5% X_{CH_4}: 15% H_2/CO: 0.04	[125]

- Ni catalyst is much preferred because of its low cost and inherent availability.
- However, this catalyst suffers from deactivation due to carbon formation which cover the active sites of the catalyst's surface, and metal particles sintering which occurs by migration of atomic or molecular over the catalyst surface.
- Thus, a new opportunity for the catalysis development on dry reforming of hydrocarbon needs to be developed.

Recent Catalyst Development



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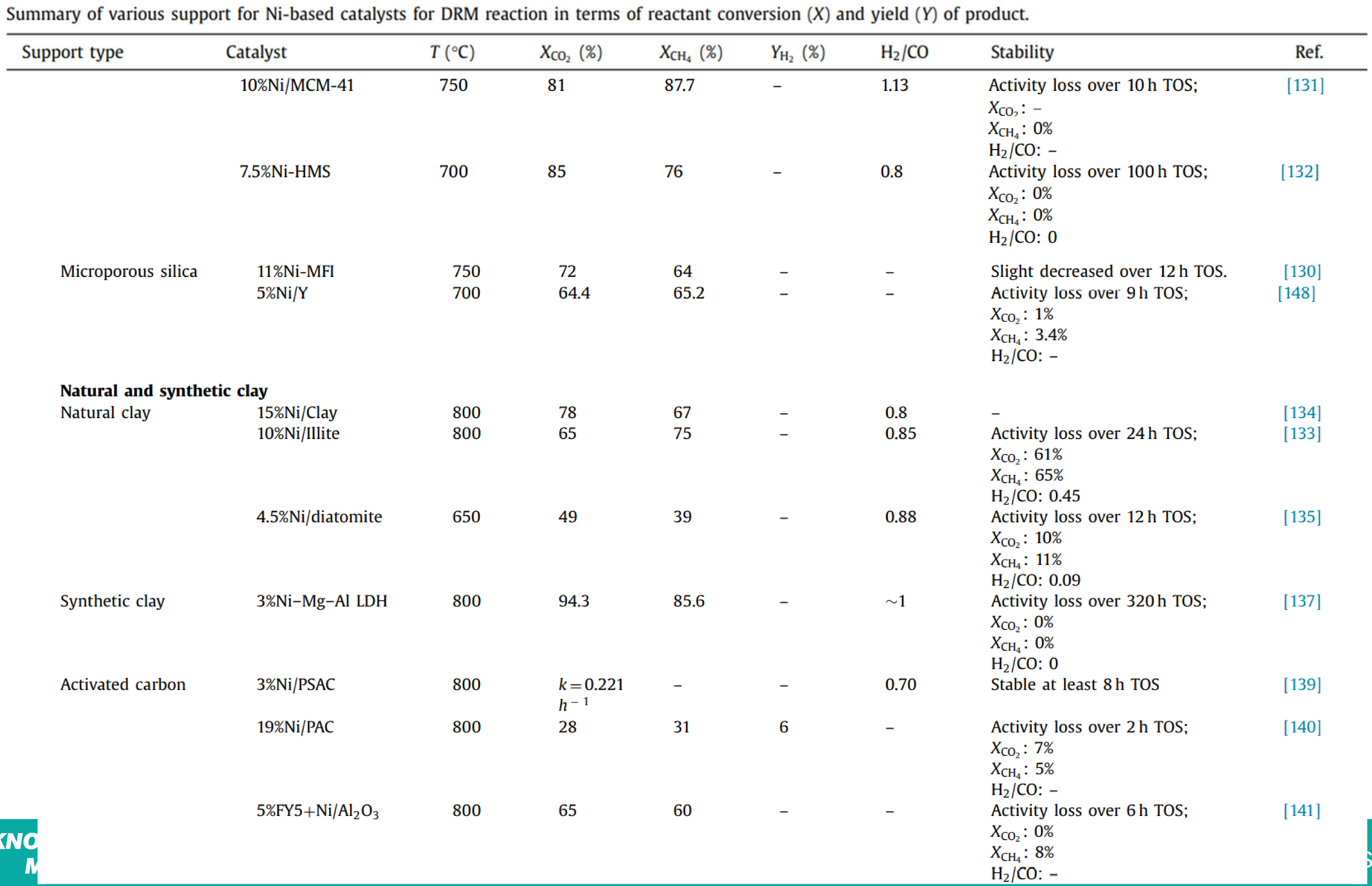
Support type	Catalyst	T (°C)	X_{CO_2} (%)	X_{CH_4} (%)	Y_{H_2} (%)	H_2/CO	Stability	Ref.
	10%Ni/CeO_2–Al_2O_3	850	100	100	100	1.0	Activity loss over 10 h TOS; X_{CO_2}: 0% X_{CH_4}: 0% H_2/CO: 0	[143]
	12.5%Ni/MgO–Al_2O_3	700	80	72	70	0.93	Activity loss over 700 min TOS; X_{CO_2}: 0% X_{CH_4}: 0% H_2/CO: 0	[144]
	14%Ni–CaO–ZrO_2	750	67	67	–	0.77	Activity loss over 700 min TOS; X_{CO_2}: 0% X_{CH_4}: 0% H_2/CO: 0	[145]
	15%Ni/ZrO_2–Al_2O_3	700	55	50	–	0.69	Activity loss over 70 h TOS; X_{CO_2}: 4.9% X_{CH_4}: 12.2% H_2/CO: –	[146]
Ordered silica								
Mesoporous silica	5%Ni/SBA-15	800	89	88	–	1.03	Activity loss over 5 h TOS; X_{CO_2}: 5.0% X_{CH_4}: 3.1% H_2/CO: 0.07	[33]
	6%Ni/SBA-16	650	46	37.5	–	0.65	Activity loss over 10 h TOS; X_{CO_2}: 20% X_{CH_4}: 20% H_2/CO: 0.15	[147]
	11%Ni–Al-MCM-41	750	95	92	–	–	Stable over 12 h TOS.	[130]
	10%Ni/MSN	750	83	94	–	1.15	Activity loss over 10 h TOS; X_{CO_2}: – X_{CH_4}: 3.8% H_2/CO: –	[131]

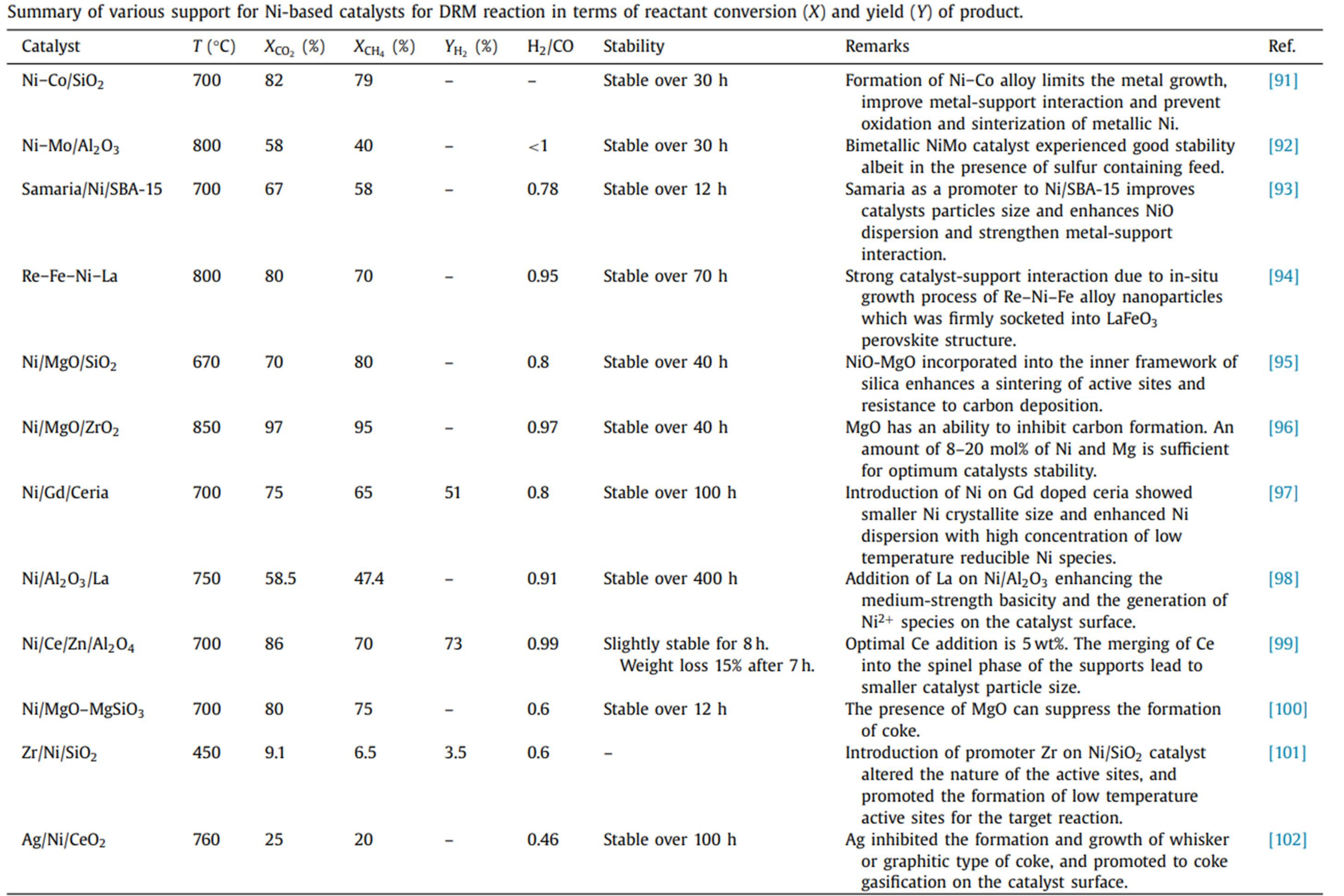
Recent Catalyst Development



Summary of various support for Ni-based catalysts for DRM reaction in terms of reactant conversion (*X*) and yield (*Y*) of product.

Support type	Catalyst	*T* (°C)	X_{CO_2} (%)	X_{CH_4} (%)	Y_{H_2} (%)	H_2/CO	Stability	Ref.
	10%Ni/MCM-41	750	81	87.7	–	1.13	Activity loss over 10 h TOS; X_{CO_2}: – X_{CH_4}: 0% H_2/CO: –	[131]
	7.5%Ni-HMS	700	85	76	–	0.8	Activity loss over 100 h TOS; X_{CO_2}: 0% X_{CH_4}: 0% H_2/CO: 0	[132]
Microporous silica	11%Ni-MFI	750	72	64	–	–	Slight decreased over 12 h TOS.	[130]
	5%Ni/Y	700	64.4	65.2	–	–	Activity loss over 9 h TOS; X_{CO_2}: 1% X_{CH_4}: 3.4% H_2/CO: –	[148]
Natural and synthetic clay								
Natural clay	15%Ni/Clay	800	78	67	–	0.8	–	[134]
	10%Ni/Illite	800	65	75	–	0.85	Activity loss over 24 h TOS; X_{CO_2}: 61% X_{CH_4}: 65% H_2/CO: 0.45	[133]
	4.5%Ni/diatomite	650	49	39	–	0.88	Activity loss over 12 h TOS; X_{CO_2}: 10% X_{CH_4}: 11% H_2/CO: 0.09	[135]
Synthetic clay	3%Ni–Mg–Al LDH	800	94.3	85.6	–	~1	Activity loss over 320 h TOS; X_{CO_2}: 0% X_{CH_4}: 0% H_2/CO: 0	[137]
Activated carbon	3%Ni/PSAC	800	$k = 0.221\ h^{-1}$	–	–	0.70	Stable at least 8 h TOS	[139]
	19%Ni/PAC	800	28	31	6	–	Activity loss over 2 h TOS; X_{CO_2}: 7% X_{CH_4}: 5% H_2/CO: –	[140]
	5%FY5+Ni/Al_2O_3	800	65	60	–	–	Activity loss over 6 h TOS; X_{CO_2}: 0% X_{CH_4}: 8% H_2/CO: –	[141]

Recent Catalyst Development



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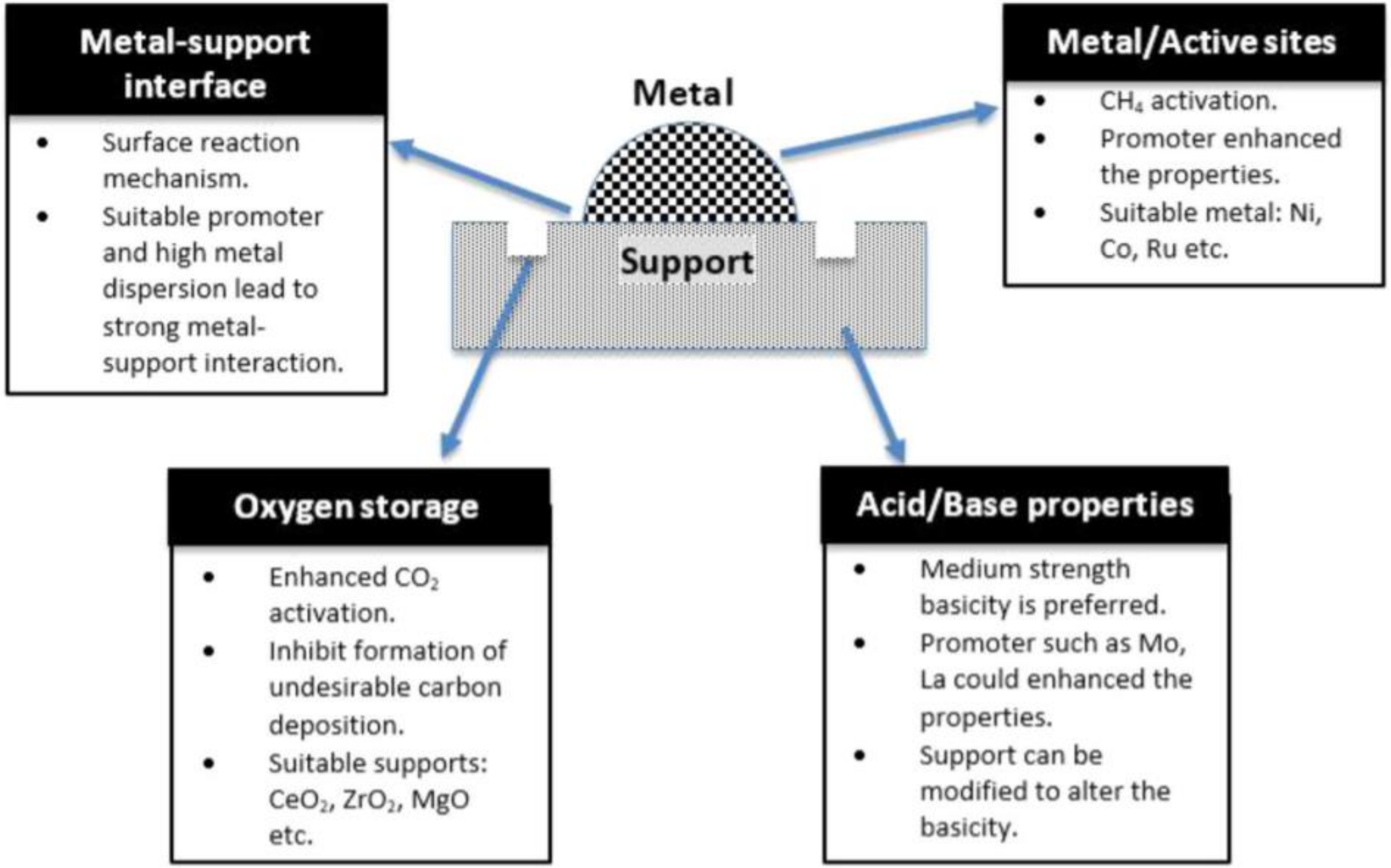
Catalyst	*T* (°C)	X_{CO_2} (%)	X_{CH_4} (%)	Y_{H_2} (%)	H_2/CO	Stability	Remarks	Ref.
Ni–Co/SiO_2	700	82	79	–	–	Stable over 30 h	Formation of Ni–Co alloy limits the metal growth, improve metal-support interaction and prevent oxidation and sinterization of metallic Ni.	[91]
Ni–Mo/Al_2O_3	800	58	40	–	<1	Stable over 30 h	Bimetallic NiMo catalyst experienced good stability albeit in the presence of sulfur containing feed.	[92]
Samaria/Ni/SBA-15	700	67	58	–	0.78	Stable over 12 h	Samaria as a promoter to Ni/SBA-15 improves catalysts particles size and enhances NiO dispersion and strengthen metal-support interaction.	[93]
Re–Fe–Ni–La	800	80	70	–	0.95	Stable over 70 h	Strong catalyst-support interaction due to in-situ growth process of Re–Ni–Fe alloy nanoparticles which was firmly socketed into $LaFeO_3$ perovskite structure.	[94]
Ni/MgO/SiO_2	670	70	80	–	0.8	Stable over 40 h	NiO-MgO incorporated into the inner framework of silica enhances a sintering of active sites and resistance to carbon deposition.	[95]
Ni/MgO/ZrO_2	850	97	95	–	0.97	Stable over 40 h	MgO has an ability to inhibit carbon formation. An amount of 8–20 mol% of Ni and Mg is sufficient for optimum catalysts stability.	[96]
Ni/Gd/Ceria	700	75	65	51	0.8	Stable over 100 h	Introduction of Ni on Gd doped ceria showed smaller Ni crystallite size and enhanced Ni dispersion with high concentration of low temperature reducible Ni species.	[97]
Ni/Al_2O_3/La	750	58.5	47.4	–	0.91	Stable over 400 h	Addition of La on Ni/Al_2O_3 enhancing the medium-strength basicity and the generation of Ni^{2+} species on the catalyst surface.	[98]
Ni/Ce/Zn/Al_2O_4	700	86	70	73	0.99	Slightly stable for 8 h. Weight loss 15% after 7 h.	Optimal Ce addition is 5 wt%. The merging of Ce into the spinel phase of the supports lead to smaller catalyst particle size.	[99]
Ni/MgO–$MgSiO_3$	700	80	75	–	0.6	Stable over 12 h	The presence of MgO can suppress the formation of coke.	[100]
Zr/Ni/SiO_2	450	9.1	6.5	3.5	0.6	–	Introduction of promoter Zr on Ni/SiO_2 catalyst altered the nature of the active sites, and promoted the formation of low temperature active sites for the target reaction.	[101]
Ag/Ni/CeO_2	760	25	20	–	0.46	Stable over 100 h	Ag inhibited the formation and growth of whisker or graphitic type of coke, and promoted to coke gasification on the catalyst surface.	[102]

General Role of Catalyst



Metal-support interface

- Surface reaction mechanism.
- Suitable promoter and high metal dispersion lead to strong metal-support interaction.

Metal/Active sites

- CH_4 activation.
- Promoter enhanced the properties.
- Suitable metal: Ni, Co, Ru etc.

Oxygen storage

- Enhanced CO_2 activation.
- Inhibit formation of undesirable carbon deposition.
- Suitable supports: CeO_2, ZrO_2, MgO etc.

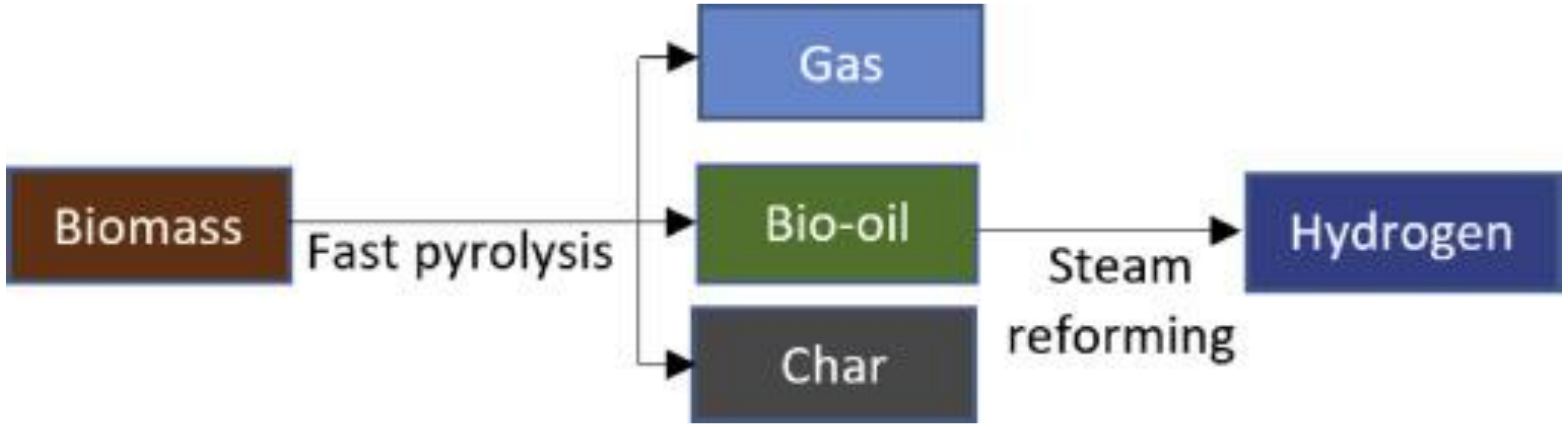
Acid/Base properties

- Medium strength basicity is preferred.
- Promoter such as Mo, La could enhanced the properties.
- Support can be modified to alter the basicity.

- The activity of a catalyst is strongly related to its surface composition and morphology of the catalysts.
- The surface composition is related to the metal-support interaction and its physicochemical properties.
- The factors affecting reaction not only depends on the nature of the active metals and supports, but also on the operation conditions such as reaction temperature, feed compositions, pretreatment temperature and flow rates of the reactants.

Case Study 2: Catalytic Steam Reforming of Biomass Pyrolysis Oil Or Bio-Oil Derivatives

- Hydrogen energy plays a key role in future energy demand especially as an energy medium for fuel cells and other devices. It is projected that renewable energy sources will make up approximately 30% of the total energy consumption in the year 2025 and this estimation is expected to climb up to 75% by the year 2050.
- Hydrogen fuel is primarily produced through steam ethane reforming of fossil fuel. However, continuous utilization of fossil fuel resources is not sustainable since it is nonrenewable and contributes significantly to global warming.
- Steam reforming of biomass pyrolysis oil or bio-oil derivatives is one of the attractive approaches for hydrogen production.
- Coke deposition is a crucial issue in bio-oil steam reforming. In addition, the complex mixture of bio-oil has restrained the application of steam reforming at an industrial scale.



Reference:
Setiabudi, H. D., Aziz, M. A. A., Abdullah, S., Teh, L. P., & Jusoh, R. (2020). Hydrogen production from catalytic steam reforming of biomass pyrolysis oil or bio-oil derivatives: A review. International Journal of Hydrogen Energy, 45(36), 18376-18397.

Recent Catalyst Development

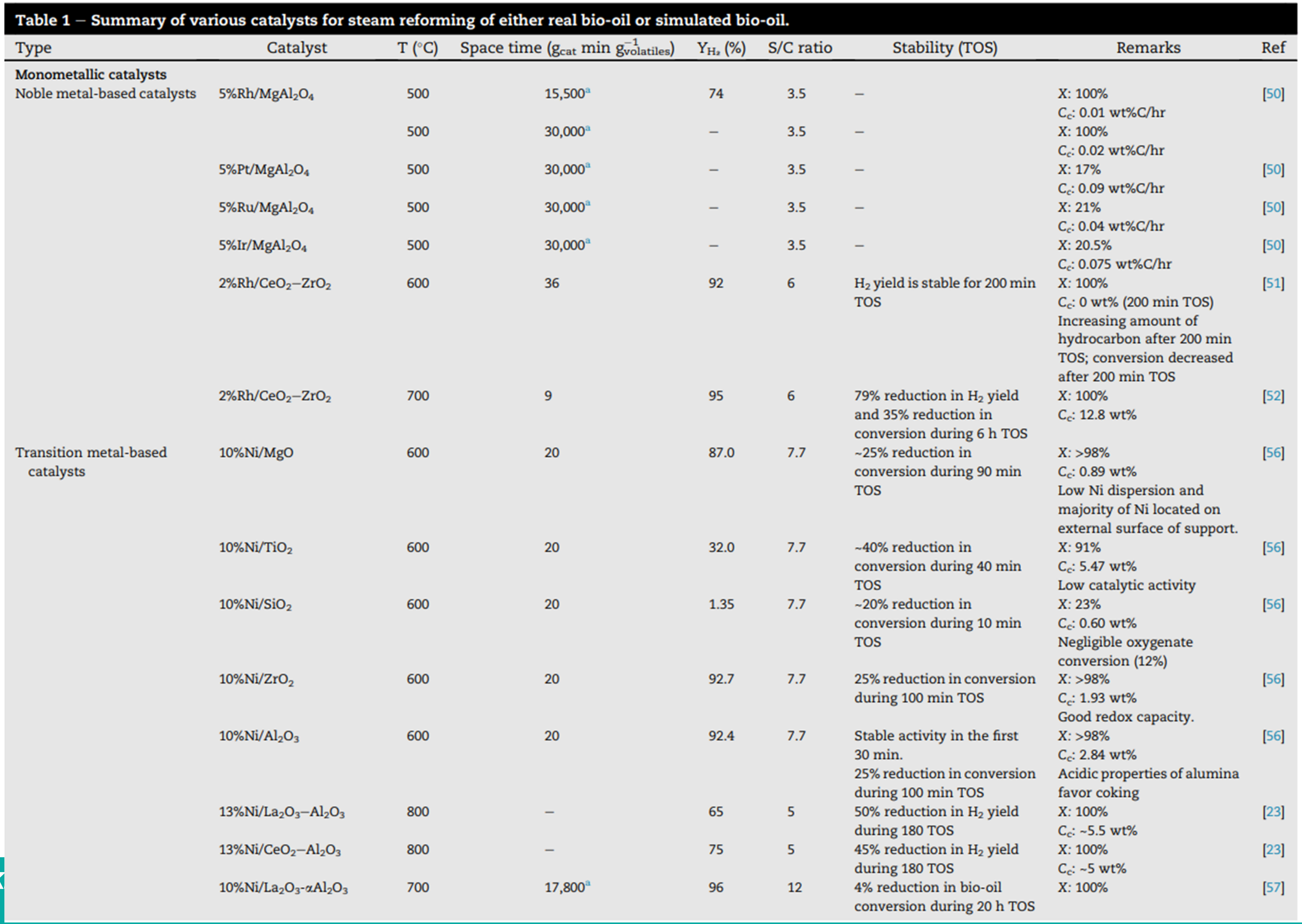
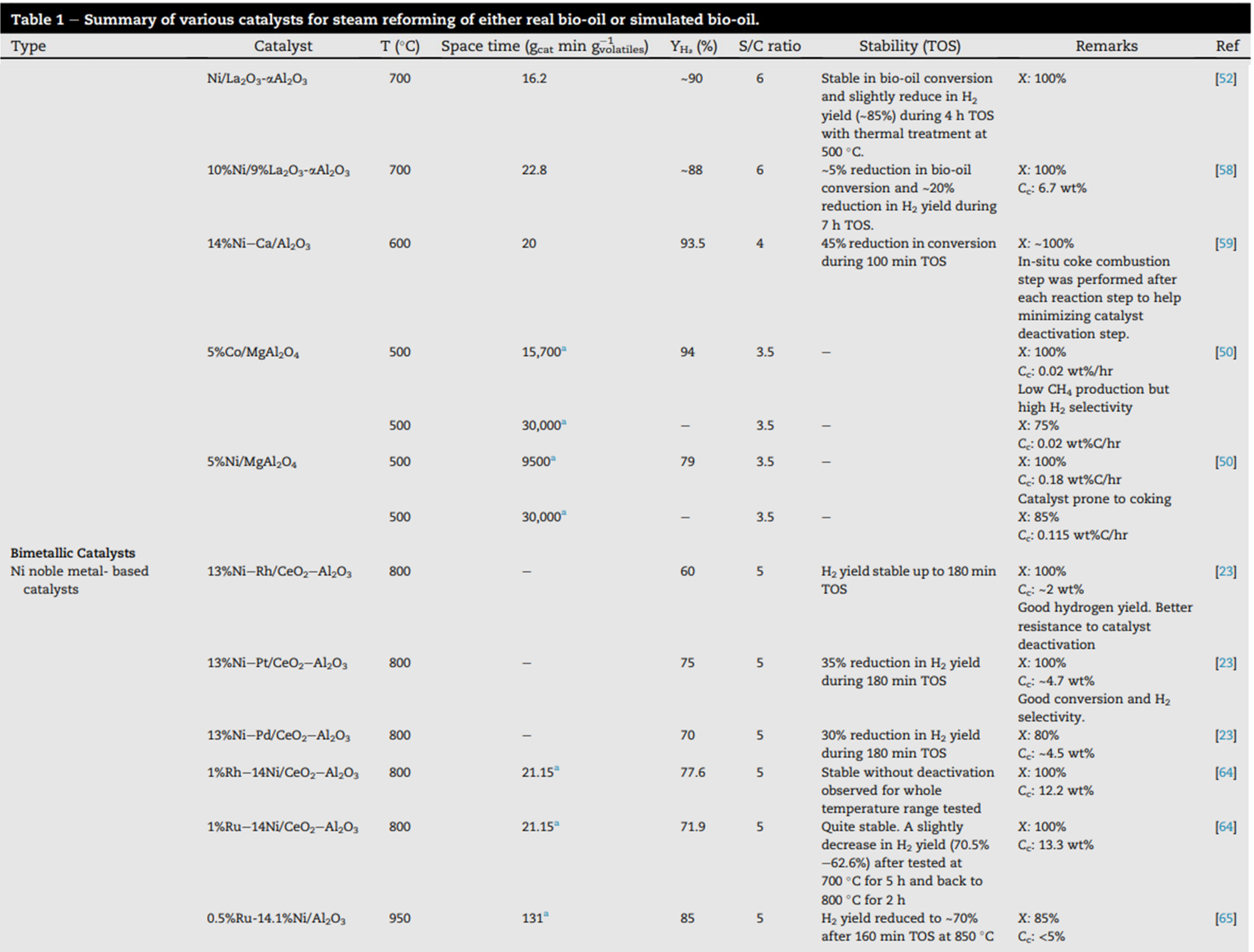


Table 1 — Summary of various catalysts for steam reforming of either real bio-oil or simulated bio-oil.

Type	Catalyst	T (°C)	Space time (g_{cat} min $g_{volatiles}^{-1}$)	Y_{H_2} (%)	S/C ratio	Stability (TOS)	Remarks	Ref
Monometallic catalysts								
Noble metal-based catalysts	5%Rh/$MgAl_2O_4$	500	15,500[a]	74	3.5	–	X: 100% C_c: 0.01 wt%C/hr	[50]
		500	30,000[a]	–	3.5	–	X: 100% C_c: 0.02 wt%C/hr	
	5%Pt/$MgAl_2O_4$	500	30,000[a]	–	3.5	–	X: 17% C_c: 0.09 wt%C/hr	[50]
	5%Ru/$MgAl_2O_4$	500	30,000[a]	–	3.5	–	X: 21% C_c: 0.04 wt%C/hr	[50]
	5%Ir/$MgAl_2O_4$	500	30,000[a]	–	3.5	–	X: 20.5% C_c: 0.075 wt%C/hr	[50]
	2%Rh/CeO_2–ZrO_2	600	36	92	6	H_2 yield is stable for 200 min TOS	X: 100% C_c: 0 wt% (200 min TOS) Increasing amount of hydrocarbon after 200 min TOS; conversion decreased after 200 min TOS	[51]
	2%Rh/CeO_2–ZrO_2	700	9	95	6	79% reduction in H_2 yield and 35% reduction in conversion during 6 h TOS	X: 100% C_c: 12.8 wt%	[52]
Transition metal-based catalysts	10%Ni/MgO	600	20	87.0	7.7	~25% reduction in conversion during 90 min TOS	X: >98% C_c: 0.89 wt% Low Ni dispersion and majority of Ni located on external surface of support.	[56]
	10%Ni/TiO_2	600	20	32.0	7.7	~40% reduction in conversion during 40 min TOS	X: 91% C_c: 5.47 wt% Low catalytic activity	[56]
	10%Ni/SiO_2	600	20	1.35	7.7	~20% reduction in conversion during 10 min TOS	X: 23% C_c: 0.60 wt% Negligible oxygenate conversion (12%)	[56]
	10%Ni/ZrO_2	600	20	92.7	7.7	25% reduction in conversion during 100 min TOS	X: >98% C_c: 1.93 wt% Good redox capacity.	[56]
	10%Ni/Al_2O_3	600	20	92.4	7.7	Stable activity in the first 30 min. 25% reduction in conversion during 100 min TOS	X: >98% C_c: 2.84 wt% Acidic properties of alumina favor coking	[56]
	13%Ni/La_2O_3–Al_2O_3	800	–	65	5	50% reduction in H_2 yield during 180 TOS	X: 100% C_c: ~5.5 wt%	[23]
	13%Ni/CeO_2–Al_2O_3	800	–	75	5	45% reduction in H_2 yield during 180 TOS	X: 100% C_c: ~5 wt%	[23]
	10%Ni/La_2O_3-αAl_2O_3	700	17,800[a]	96	12	4% reduction in bio-oil conversion during 20 h TOS	X: 100%	[57]

Recent Catalyst Development



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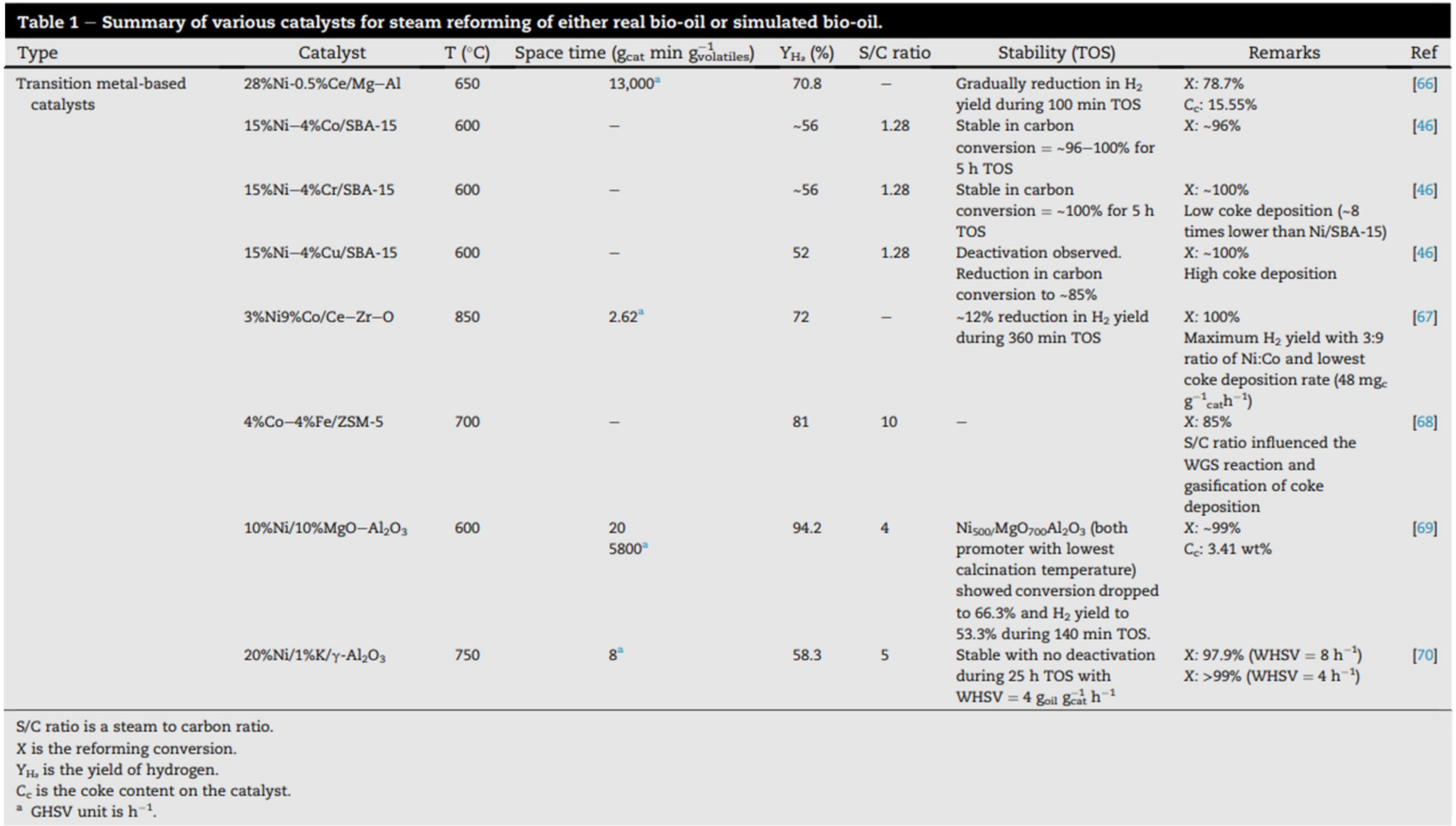
	Ni/La_2O_3-αAl_2O_3	700	16.2	~90	6	Stable in bio-oil conversion and slightly reduce in H_2 yield (~85%) during 4 h TOS with thermal treatment at 500 °C.	X: 100%	[52]
	10%Ni/9%La_2O_3-αAl_2O_3	700	22.8	~88	6	~5% reduction in bio-oil conversion and ~20% reduction in H_2 yield during 7 h TOS.	X: 100% C_c: 6.7 wt%	[58]
	14%Ni–Ca/Al_2O_3	600	20	93.5	4	45% reduction in conversion during 100 min TOS	X: ~100% In-situ coke combustion step was performed after each reaction step to help minimizing catalyst deactivation step.	[59]
	5%Co/$MgAl_2O_4$	500	15,700[a]	94	3.5	–	X: 100% C_c: 0.02 wt%/hr Low CH_4 production but high H_2 selectivity	[50]
		500	30,000[a]	–	3.5	–	X: 75% C_c: 0.02 wt%C/hr	
	5%Ni/$MgAl_2O_4$	500	9500[a]	79	3.5	–	X: 100% C_c: 0.18 wt%C/hr Catalyst prone to coking	[50]
		500	30,000[a]	–	3.5	–	X: 85% C_c: 0.115 wt%C/hr	
Bimetallic Catalysts								
Ni noble metal- based catalysts	13%Ni–Rh/CeO_2–Al_2O_3	800	–	60	5	H_2 yield stable up to 180 min TOS	X: 100% C_c: ~2 wt% Good hydrogen yield. Better resistance to catalyst deactivation	[23]
	13%Ni–Pt/CeO_2–Al_2O_3	800	–	75	5	35% reduction in H_2 yield during 180 min TOS	X: 100% C_c: ~4.7 wt% Good conversion and H_2 selectivity.	[23]
	13%Ni–Pd/CeO_2–Al_2O_3	800	–	70	5	30% reduction in H_2 yield during 180 min TOS	X: 80% C_c: ~4.5 wt%	[23]
	1%Rh–14Ni/CeO_2–Al_2O_3	800	21.15[a]	77.6	5	Stable without deactivation observed for whole temperature range tested	X: 100% C_c: 12.2 wt%	[64]
	1%Ru–14Ni/CeO_2–Al_2O_3	800	21.15[a]	71.9	5	Quite stable. A slightly decrease in H_2 yield (70.5% –62.6%) after tested at 700 °C for 5 h and back to 800 °C for 2 h	X: 100% C_c: 13.3 wt%	[64]
	0.5%Ru-14.1%Ni/Al_2O_3	950	131[a]	85	5	H_2 yield reduced to ~70% after 160 min TOS at 850 °C	X: 85% C_c: <5%	[65]

Recent Catalyst Development



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Transition metal-based catalysts	28%Ni-0.5%Ce/Mg–Al	650	13,000[a]	70.8	–	Gradually reduction in H_2 yield during 100 min TOS	X: 78.7% C_c: 15.55%	[66]
	15%Ni–4%Co/SBA-15	600	–	~56	1.28	Stable in carbon conversion = ~96–100% for 5 h TOS	X: ~96%	[46]
	15%Ni–4%Cr/SBA-15	600	–	~56	1.28	Stable in carbon conversion = ~100% for 5 h TOS	X: ~100% Low coke deposition (~8 times lower than Ni/SBA-15)	[46]
	15%Ni–4%Cu/SBA-15	600	–	52	1.28	Deactivation observed. Reduction in carbon conversion to ~85%	X: ~100% High coke deposition	[46]
	3%Ni9%Co/Ce–Zr–O	850	2.62[a]	72	–	~12% reduction in H_2 yield during 360 min TOS	X: 100% Maximum H_2 yield with 3:9 ratio of Ni:Co and lowest coke deposition rate (48 mg_c $g^{-1}{}_{cat}h^{-1}$)	[67]
	4%Co–4%Fe/ZSM-5	700	–	81	10	–	X: 85% S/C ratio influenced the WGS reaction and gasification of coke deposition	[68]
	10%Ni/10%MgO–Al_2O_3	600	20 5800[a]	94.2	4	$Ni_{500}/MgO_{700}Al_2O_3$ (both promoter with lowest calcination temperature) showed conversion dropped to 66.3% and H_2 yield to 53.3% during 140 min TOS.	X: ~99% C_c: 3.41 wt%	[69]
	20%Ni/1%K/γ-Al_2O_3	750	8[a]	58.3	5	Stable with no deactivation during 25 h TOS with WHSV = 4 g_{oil} g_{cat}^{-1} h^{-1}	X: 97.9% (WHSV = 8 h^{-1}) X: >99% (WHSV = 4 h^{-1})	[70]

S/C ratio is a steam to carbon ratio.
X is the reforming conversion.
Y_{H_2} is the yield of hydrogen.
C_c is the coke content on the catalyst.
[a] GHSV unit is h^{-1}.

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Recent Catalyst Development

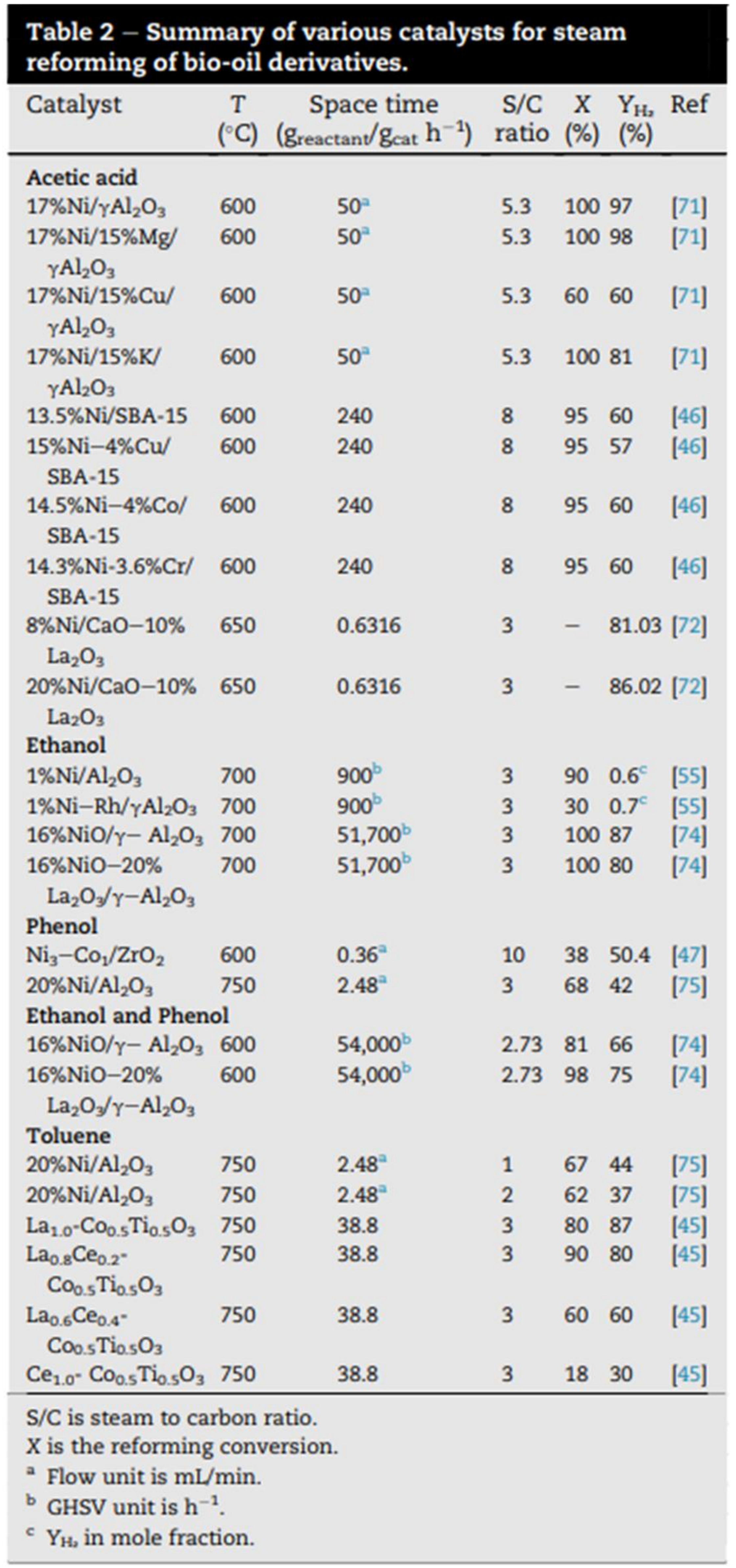

Table 2 – Summary of various catalysts for steam reforming of bio-oil derivatives.

Catalyst	T (°C)	Space time ($g_{reactant}/g_{cat}$ h^{-1})	S/C ratio	X (%)	Y_{H_2} (%)	Ref
Acetic acid						
17%Ni/γAl_2O_3	600	50^a	5.3	100	97	[71]
17%Ni/15%Mg/ γAl_2O_3	600	50^a	5.3	100	98	[71]
17%Ni/15%Cu/ γAl_2O_3	600	50^a	5.3	60	60	[71]
17%Ni/15%K/ γAl_2O_3	600	50^a	5.3	100	81	[71]
13.5%Ni/SBA-15	600	240	8	95	60	[46]
15%Ni–4%Cu/ SBA-15	600	240	8	95	57	[46]
14.5%Ni–4%Co/ SBA-15	600	240	8	95	60	[46]
14.3%Ni-3.6%Cr/ SBA-15	600	240	8	95	60	[46]
8%Ni/CaO–10% La_2O_3	650	0.6316	3	–	81.03	[72]
20%Ni/CaO–10% La_2O_3	650	0.6316	3	–	86.02	[72]
Ethanol						
1%Ni/Al_2O_3	700	900^b	3	90	0.6^c	[55]
1%Ni–Rh/γAl_2O_3	700	900^b	3	30	0.7^c	[55]
16%NiO/γ– Al_2O_3	700	$51{,}700^b$	3	100	87	[74]
16%NiO–20% $La_2O_3/\gamma-Al_2O_3$	700	$51{,}700^b$	3	100	80	[74]
Phenol						
Ni_3-Co_1/ZrO_2	600	0.36^a	10	38	50.4	[47]
20%Ni/Al_2O_3	750	2.48^a	3	68	42	[75]
Ethanol and Phenol						
16%NiO/γ– Al_2O_3	600	$54{,}000^b$	2.73	81	66	[74]
16%NiO–20% $La_2O_3/\gamma-Al_2O_3$	600	$54{,}000^b$	2.73	98	75	[74]
Toluene						
20%Ni/Al_2O_3	750	2.48^a	1	67	44	[75]
20%Ni/Al_2O_3	750	2.48^a	2	62	37	[75]
$La_{1.0}$-$Co_{0.5}Ti_{0.5}O_3$	750	38.8	3	80	87	[45]
$La_{0.8}Ce_{0.2}$-$Co_{0.5}Ti_{0.5}O_3$	750	38.8	3	90	80	[45]
$La_{0.6}Ce_{0.4}$-$Co_{0.5}Ti_{0.5}O_3$	750	38.8	3	60	60	[45]
$Ce_{1.0}$- $Co_{0.5}Ti_{0.5}O_3$	750	38.8	3	18	30	[45]

S/C is steam to carbon ratio.
X is the reforming conversion.
[a] Flow unit is mL/min.
[b] GHSV unit is h^{-1}.
[c] Y_{H_2} in mole fraction.

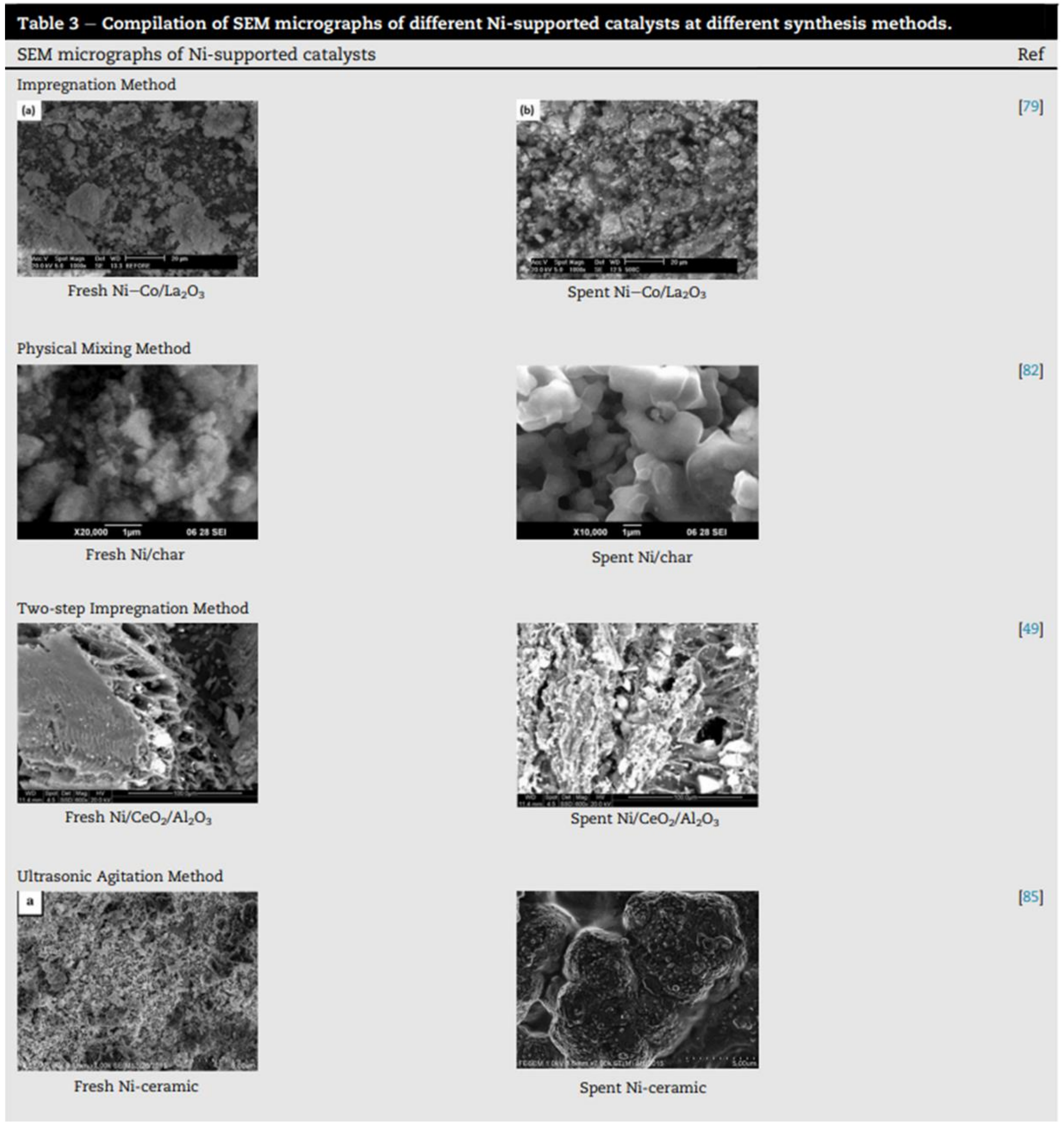

Table 3 – Compilation of SEM micrographs of different Ni-supported catalysts at different synthesis methods.

SEM micrographs of Ni-supported catalysts		Ref
Impregnation Method		
(a) Fresh Ni–Co/La_2O_3	(b) Spent Ni–Co/La_2O_3	[79]
Physical Mixing Method		
Fresh Ni/char	Spent Ni/char	[82]
Two-step Impregnation Method		
Fresh Ni/CeO_2/Al_2O_3	Spent Ni/CeO_2/Al_2O_3	[49]
Ultrasonic Agitation Method		
a Fresh Ni-ceramic	Spent Ni-ceramic	[85]

General Role of Catalyst

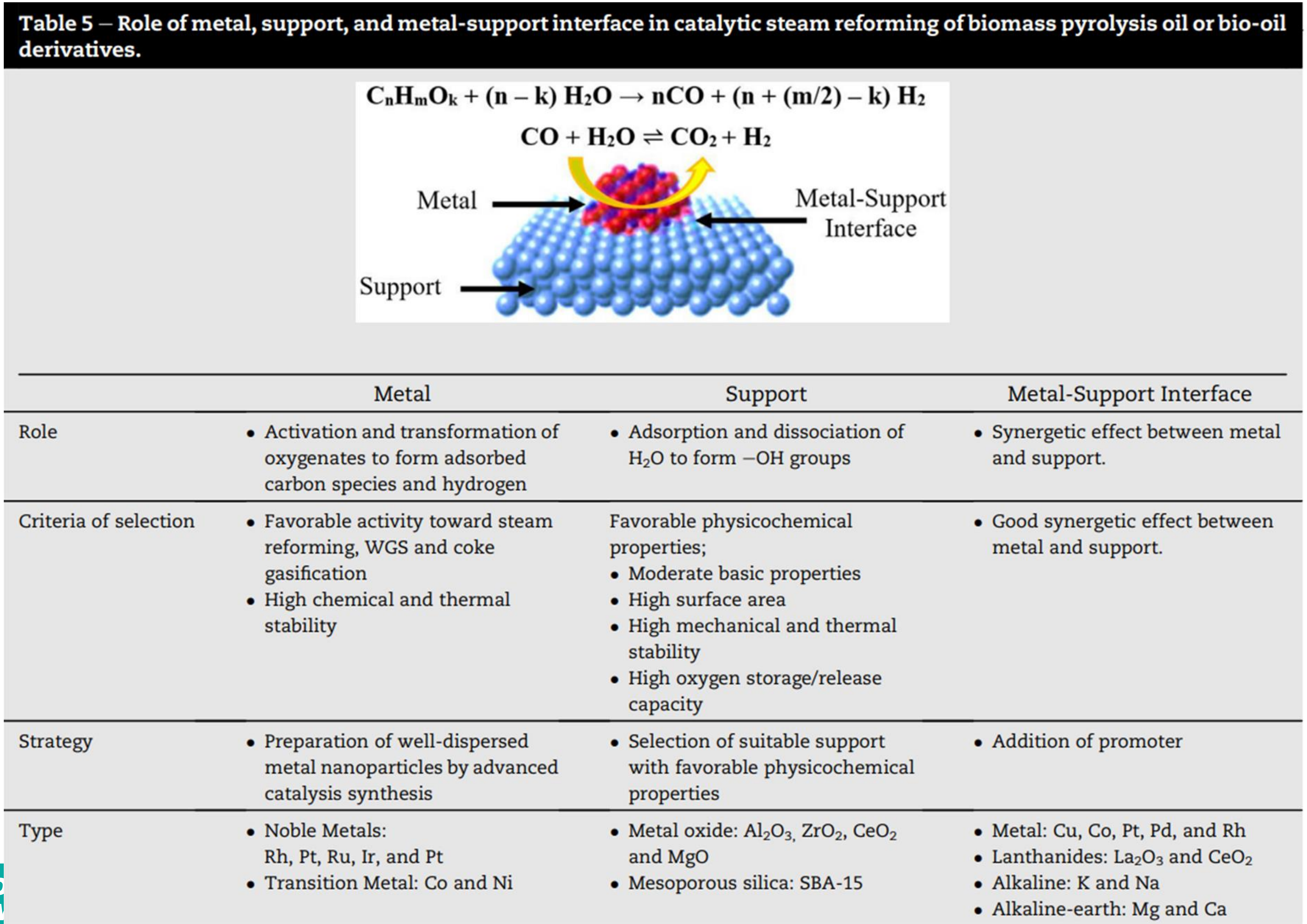

Table 5 – Role of metal, support, and metal-support interface in catalytic steam reforming of biomass pyrolysis oil or bio-oil derivatives.

$$C_nH_mO_k + (n-k)\,H_2O \rightarrow nCO + (n + (m/2) - k)\,H_2$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

	Metal	Support	Metal-Support Interface
Role	• Activation and transformation of oxygenates to form adsorbed carbon species and hydrogen	• Adsorption and dissociation of H_2O to form –OH groups	• Synergetic effect between metal and support.
Criteria of selection	• Favorable activity toward steam reforming, WGS and coke gasification • High chemical and thermal stability	Favorable physicochemical properties; • Moderate basic properties • High surface area • High mechanical and thermal stability • High oxygen storage/release capacity	• Good synergetic effect between metal and support.
Strategy	• Preparation of well-dispersed metal nanoparticles by advanced catalysis synthesis	• Selection of suitable support with favorable physicochemical properties	• Addition of promoter
Type	• Noble Metals: Rh, Pt, Ru, Ir, and Pt • Transition Metal: Co and Ni	• Metal oxide: Al_2O_3, ZrO_2, CeO_2 and MgO • Mesoporous silica: SBA-15	• Metal: Cu, Co, Pt, Pd, and Rh • Lanthanides: La_2O_3 and CeO_2 • Alkaline: K and Na • Alkaline-earth: Mg and Ca

THANK YOU!

thank you!