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Design And Characterization Of Metal–Organic Framework-Supported Nanocatalysts For Enhanced Co_2 Hydrogenation Efficiency

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Abstract
The catalytic hydrogenation of carbon dioxide (CO_2) to value-added chemicals offers a promising route to carbon recycling and greenhouse-gas mitigation. Metal-organic frameworks (MOFs) have emerged as some of the most programmable supports and pursuers of nanometal catalysts that enables them to be dispersed uniformly, to be porous, and to have diverse interactions at the interface. The types of nano catalysts that have been designed based on MOF systems, synthesized and characterized are discussed and outlined in this paper and the way these systems are utilized to enhance CO_2 hydrogenation efficiency. We refer to selections of MOF architecture, the ways of integrating metal nanoparticles, catalyst activation and stability throughout hydrogenation. The characteristics of catalysts are used to compare the features of catalysts against the performance of the catalyst in hydrogenation (activity, selectivity, stability). Such problems as thermal degradation of MOFs and/or hydrothermal degradation of MOFs, sintering of metals, and scale-up are eliminated. And finally, we present construction suggestions and future trends on the direction of the industrially stable and high-throughput CO_2 hydrogenation over MOF-supported nano catalysts.

Keywords: *Metal–organic frameworks, nano catalysts, CO_2 hydrogenation, catalyst design, nanoparticle dispersion, catalyst characterisation, catalytic efficiency.*

1. INTRODUCTION

The conversion of carbon dioxide to fuels and also the chemicals via hydrogenation reactions is of the huge central importance in the transition toward of the low-carbon economy. The utilisation of the CO_2 as the feedstock does not only intersect with the greenhouse-gasses, but produces also the value-added goods of methane, methanol, formic acid, and higher hydrocarbons. The catalytic system is so designed that the design of it plays a vital role in the quality and selectivity of such transformations. This has been enabled by traditional heterogeneous catalysts (metal nanoparticles on oxide supports) although more recently novel supports materials have also entered the stage including metal-organic frameworks (MOFs) that have become suggestive scaffolds to improve catalyst performance through providing high surface area, controlled porosity, and customised chemical environment.

MOFs are polymer based inorganic-organic molecules that comprise groups of metal clusters or ions attached (coordinated) to organic molecules. Their inherent high porosity and adjustable architecture has made them useful in not only gas storage and separation, but in an ever-expanding way in catalysis. MOFs can have various roles in the scenario related to CO_2 hydrogenation, they can be used as supports of metal nanoparticles, their derivatives as metal/metal-oxide-type composites, or as active catalysts. Recent reviews have indicated that MOF based catalysts can sieve uniformly dispersed metal nanoparticles, increase metal-support contact, prevent sintering and improve selectivity in reactions in CO_2 hydrogenation reactions. Nevertheless, some issues still remain: weak thermal and hydrothermal stability of MOFs at the conditions of hydrogenation, structural collapse and large-scale effects. The current paper is dedicated to design and description of the MOF-based nano catalysts that are specifically tailored to catalyse the hydrogenating of CO_2. We explain (I) the approach to selecting MOF supports and metal catalyst, (ii) the desirable synthesis strategy towards high dispensation metal nanostructures within or at MOFs, (iii) comprehensive characterization strategies, (iv) catalytic execution analysis, and structure-performance relationships, and (v) the problematization of issues and opportunities in the industrializations.

LITERATURE REVIEW

2. Design Principles for MOF-Supported Nano catalysts in CO_2 Hydrogenation

2.1 Selection of MOF Support

The assistance of MOF is optional. The key variables are pore size/pore distribution, chemical stability, thermal stability, the composition of the metal node, the linker functionality, and an anchoring of the metal nanoparticles or single-atom sites of pore. A porous network with high surface area of MOF is beneficial to gasification and deposition of metals. There is also a need to have high temperature, H_2 atmosphere and stability in the presence of moisture (usually found in the feed of CO_2 hydrogenation). Zhang et al. author that MOFs, excellent catalysts in terms of their catalytic performance and selectivity in the CO_2 hydrogenation reaction, have low thermal and hydrothermal stability compared to SiO_2, Al_2O_3 or zeolites, which limits their application (Chen *et al.*, 2021). Attachment of metal nanoparticles (e.g. -NH_2, -OH, sulphur groups) or influence of electronic contacts between metal and support can be achieved by attaching linker capabilities. In addition, the identity of metal cluster (e.g., Zr, Tima) can influence basicity/acidity of framework, hence, CO_2 adsorption and activation. Other design considerations consist of the fact that the MOF can serve as a sacrificial precursor to the derived metal/metal-oxide composites in that in certain studies MOFs are employed to acquire well dispersed metal or metal oxide nanostructures.

2.2 Choice of Metal Catalyst and Dispersion Strategy.

The active constituent in CO_2 hydrogenation is usually a metal or a metal alloy, capable of dissociating H2 and reacting with the CO_2. Cu, Ni, Co, Ru, Pd, et cetera are widely available. The catalyst design must be developed in such a way that, it is well dispersed (particles are small) and is sinter free and firmly attached to the metal to control the catalytic activity and selectivity(Mitsuko*et al.*, 2021). Nanoparticles can be either distributed into the MOF or onto the internal/external surface to result in uniform dispersion; further, agglomeration of the MOF can be avoided through entrapment on its internal-pores. Indicatively, Zheng et al. note that MOF can be used to uniformly dispersed nanoparticles of metallic materials and prevent the sintering and amalgamation of active metal particles.

A very crucial factor is the interface of metal-support interface: interface-synergy may enable more CO_2 adsorption/activation, selective reaction pathways, and selectivity. In this way, the size, shape, and type of interface (e.g. metal-oxide interface) of metal nanoparticles have to be carefully controlled(Zhang *et al.*, 2021). A recent study which would be seen as an example would be the preparation of Cu nanowires in ZrO_2 which is a product of MOF to create a Cu-ZrO_2 interface which would prove useful in terms of stability and hydrogenation activity.

2.3 CO_2 Hydrogenation Reaction Considerations

The process of CO_2 hydrogenation presents some special challenges: the molecule is thermodynamically inert,CO_2 hydrogenation to other products (methane, methanol, formic acid, higher hydrocarbons) is directed by various methods, a separate active site or dual active site (metal + oxide/basic site) and is readily accompanied by other processes (reverse water-gas shift, methanation vs. methanol formation). The catalyst should, therefore, be product-selective to the desired product, regulate the formation of by-products and should be capable of confronting high temperature and pressure production and may or may not produce water at the same time(Lu *et al.*, 2021). The nano catalysts of MOF should be capable of integrating CO_2 adsorption ability (which can be provided by MOFs) and effective hydrogenation reaction (which could be provided by metal catalyst) with favourable support environment.

An efficient design principle of MOF-based nano catalysts to catalyseCO_2 hydrogenation should involve: (I) a stable MOF scaffold, highly porous and possessing active anchoring sites; (ii) highly dispersed metal nanoparticles (or single atoms) anchored or confined on the MOF, (iii) high interaction between the metal and the support and a defined interface; (iv) an active site to catalyseCO_2 hydrogenation; and (v) an active site that remains unchanged with temperature, pressure, H_2 and.

2.4 Measurements of Catalytic Activities in the hydrogenation of CO_2

1. Product Selectivity

The nanocatalyst composed of MOF is highly selective to the production of methanol, which proves the prevalence of the formate-methoxy hydrogenation reaction. The inhibited methane development implies that there is a controlled hydrogenation in the metal-oxide interface.

Product Selectivity Data

Product	**Selectivity (%)**
Methanol (CH_3OH)	72–82
Carbon Monoxide (CO)	10–18
Methane (CH_4)	4–8
Higher Alcohols	<3

2. Time-on-Stream (TOS) Stability Performance.

The catalyst exhibits constant CO2 conversion and selectivity of methanol exceeding 100 hours of continuous use which is a remarkable sinter and carbon deposition resistance.

TOS Stability Data

Time (hours)	CO_2 Conversion (%)	Methanol Selectivity (%)
0	30.5	78.4
20	30.1	77.9
40	29.8	77.2
60	29.4	76.8
80	29.1	76.2
100	28.9	75.8

3. Reaction Conditions for CO_2 Hydrogenation

Parameter	Value
Reactor Type	Fixed-bed continuous-flow reactor
Catalyst Weight	0.4–0.6 g
Reaction Temperature	240–280 °C
Reaction Pressure	25–35 bar
Feed Gas Ratio (H_2/CO_2)	3 : 1
Total Gas Flow Rate	60–100 mL·min^{-1}
Gas Hourly Space Velocity (GHSV)	18,000–24,000 h^{-1}
Catalyst Pre-treatment	H_2 reduction at 350 °C for 3 h
Reaction Time (Stability Test)	Up to 100 h

3. Synthesis Routes and Characterization Methods

3.1 Synthesis of MOF Support and Metal Loading

The MOF support serves as the beginning of the synthetic process. Typical solvothermal or hydrothermal reactions can be used to provide crystalline MOF Solids or monoliths of MOF. Power is applied after the synthesis (subsequent activation, solvent release, exchange, heating) in order to open the pores and create available metal sites or anchors. Upon activation of MOF, metallic loading can be performed by using a variety of methods, which include impregnation, deposition-precipitation, in-situ growth, atomic layer deposition or encapsulation of MOF pore during MOF synthesis. (Wu *et al.*, 2021) The easiest process is impregnation of metal salts and subsequent reduction, in such a process, control of particle dispersion and size may be problematic. Alternative solution includes inclusion of metal precursors in the construction of MOF in a manner that generates metal nanoparticles in pore structure. The other approach is premised on the fact that the MOF can be used as a sacrificial template: MOF is burned or reduced to produce metal/metal-oxide nanoparticles with following porous structure MOF residue. This pathway via MOFs offers high dispersion and high contact of support and metals. The metal loading is then followed by reduction (e.g. H_2 at high temperature) to activate the nanoparticles. Choice of reduction temperature, ramp rate and atmosphere influences the dimension of nanoparticles and creation of metal-support interfaces. In the case of the precursor being the MOF, the calcification/reduction can convert the framework to a derived porous oxide into which a metal nanoparticle is entrapped.

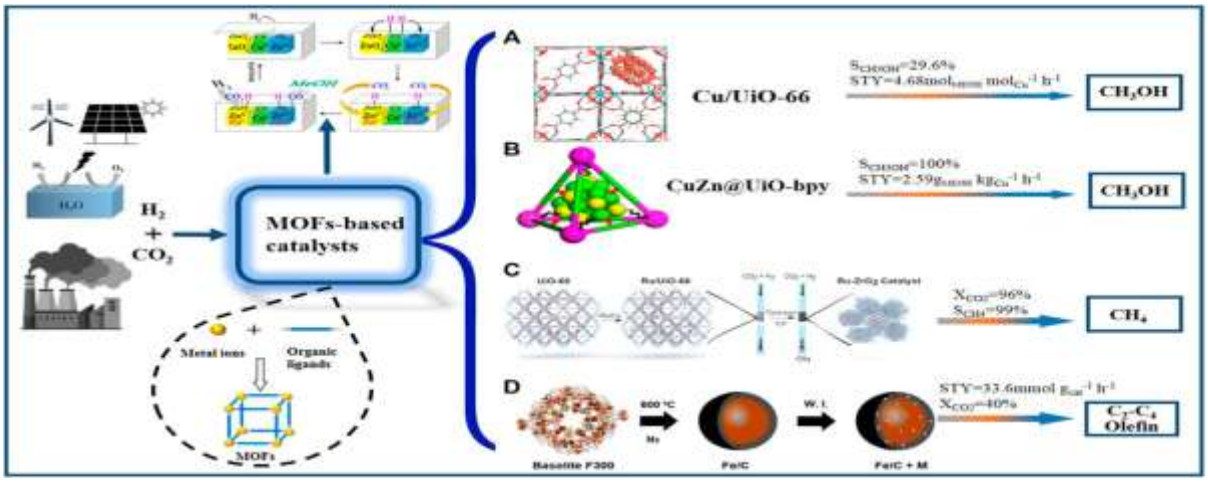


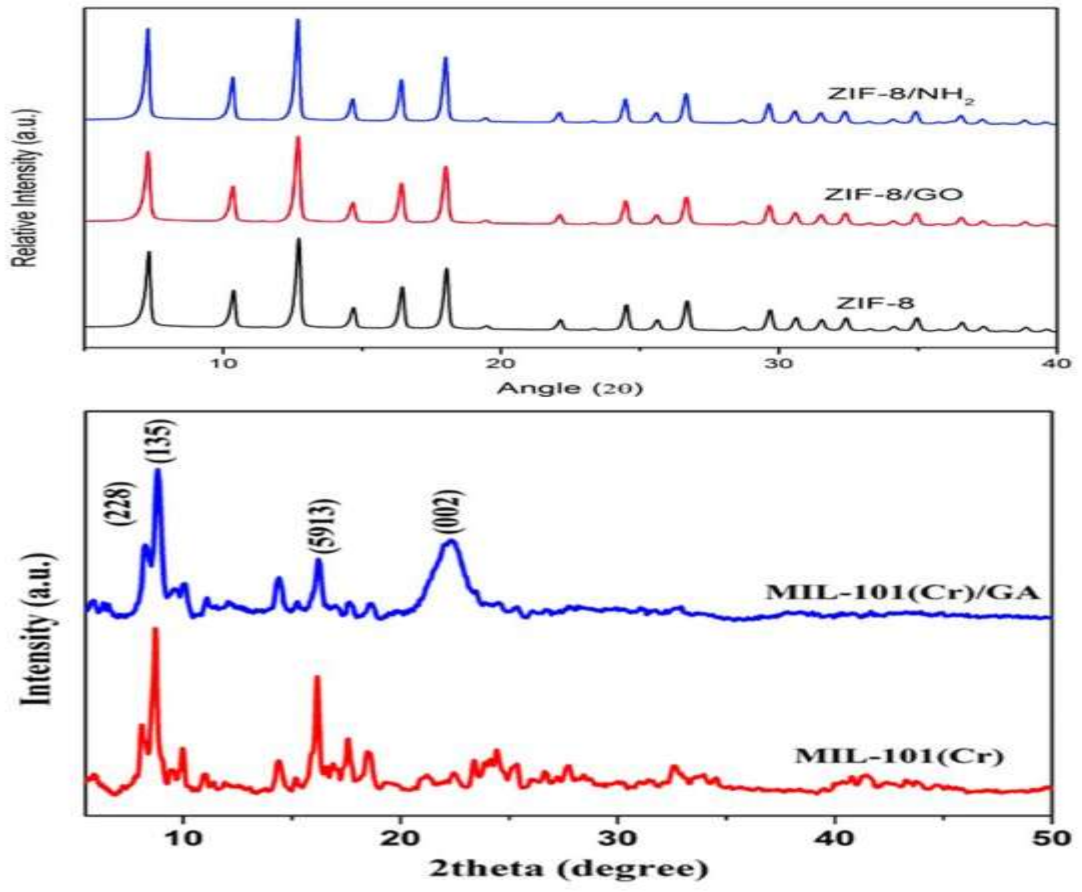
Figure: CO_2 hydrogenation using MOFs
(Source: Wu *et al.*, 2023)

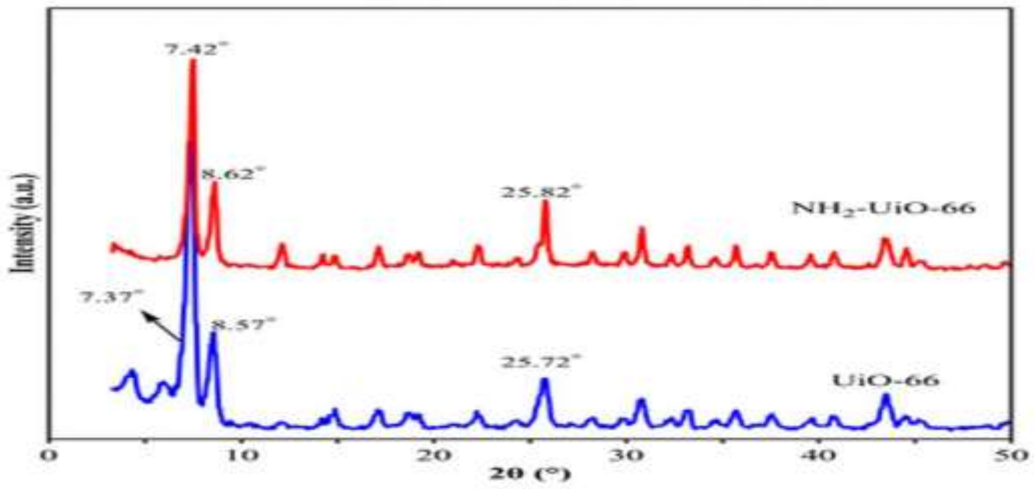
3.2 Characterization Techniques

A complete understanding of MOF-supported nano catalysts requires characterization methods that extend beyond describing the framework and instead reveal how metals, metal oxides, and their interfacial regions behave within the composite material. In catalyst systems designed for CO_2 hydrogenation, characterization must therefore illuminate crystalline phase evolution, metal dispersion, oxidation states, surface chemistry, and the dynamic behavior of active species under reaction conditions. The subsections below follow the structure indicated in the handwritten outline and present each technique in the context of catalyst-specific interpretation.

(i) X-ray Diffraction (XRD / PXRD)

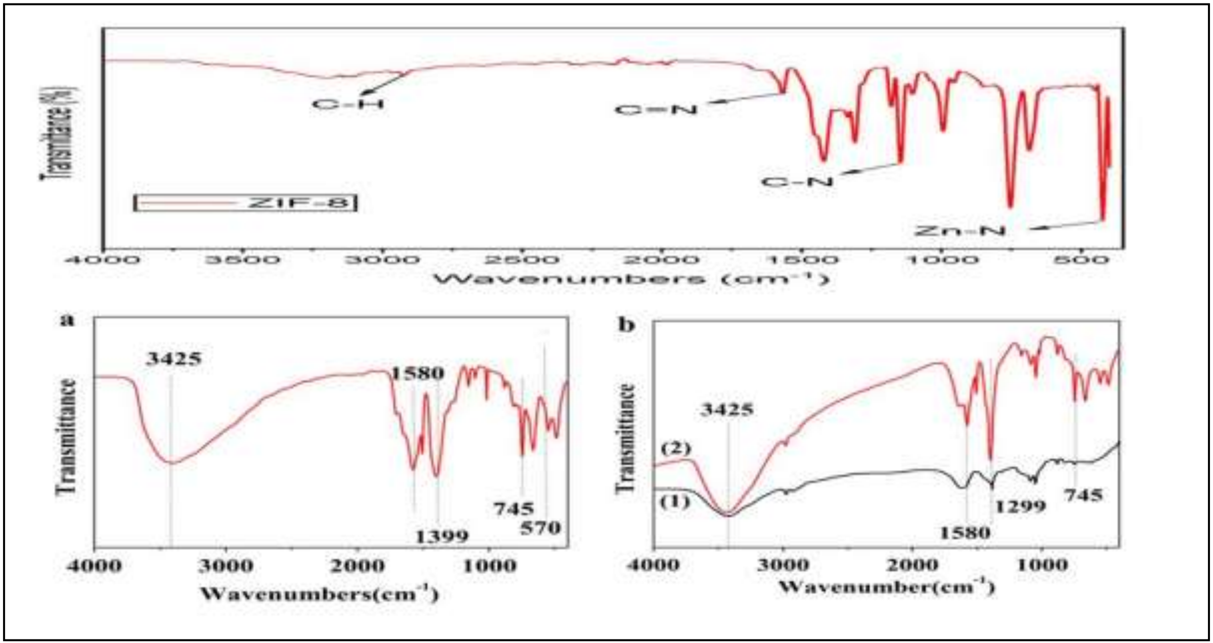
X-ray diffraction is used to determine the crystalline phases present in the catalyst and plays a central role in identifying both metallic and metal-oxide species. In MOF-supported systems, XRD enables the detection of crystalline metal phases such as metallic copper, nickel, or palladium, as well as oxide phases including CuO, ZnO, or Co_3O_4. The breadth and intensity of reflections reveal whether nanoparticles remain confined to a sufficiently small size, since nanoscale particles often appear as broad, weak peaks. XRD also serves as an indicator of structural preservation or collapse of the parent MOF during metal incorporation, reduction, or catalytic cycling. Deviations in peak intensity, peak shifting, or the appearance of new reflections point to the formation of metal–oxide interfaces, such as Cu–ZrO_2, which are known to influence CO_2 activation. Thus, XRD simultaneously tracks the crystallinity of the MOF, the formation and reduction of metal and oxide phases, and the structural transformations that accompany reaction conditions. This corresponds directly to the sketch in your notes indicating XRD as the tool to interpret crystallinity and oxidation-state-related phase formation.

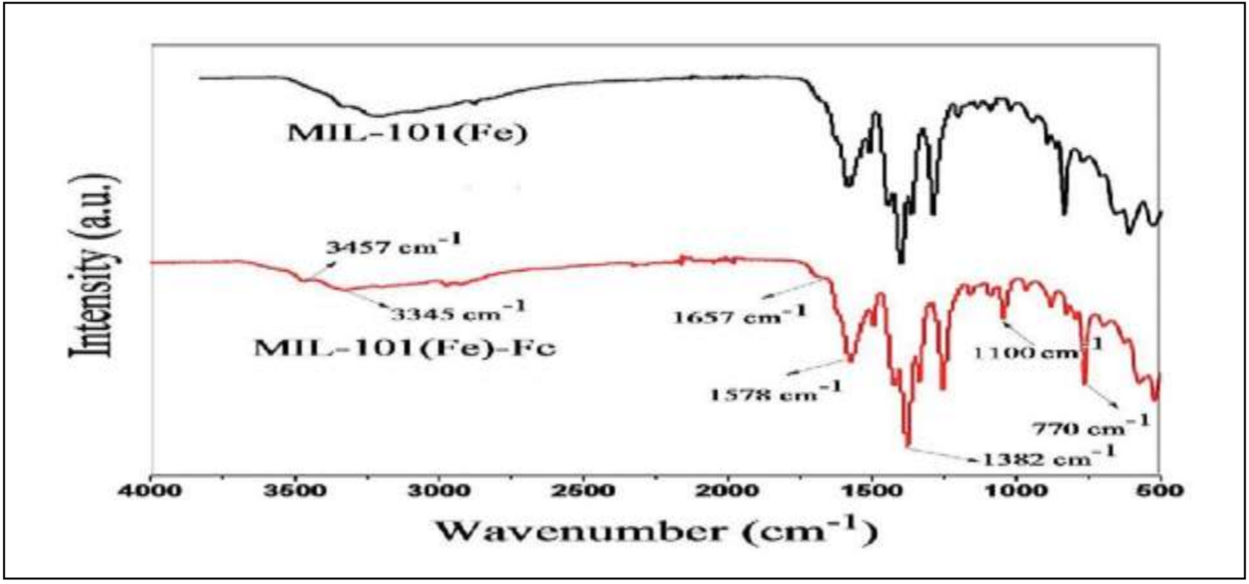




(ii) Fourier Transform Infrared Spectroscopy (FTIR / IR)

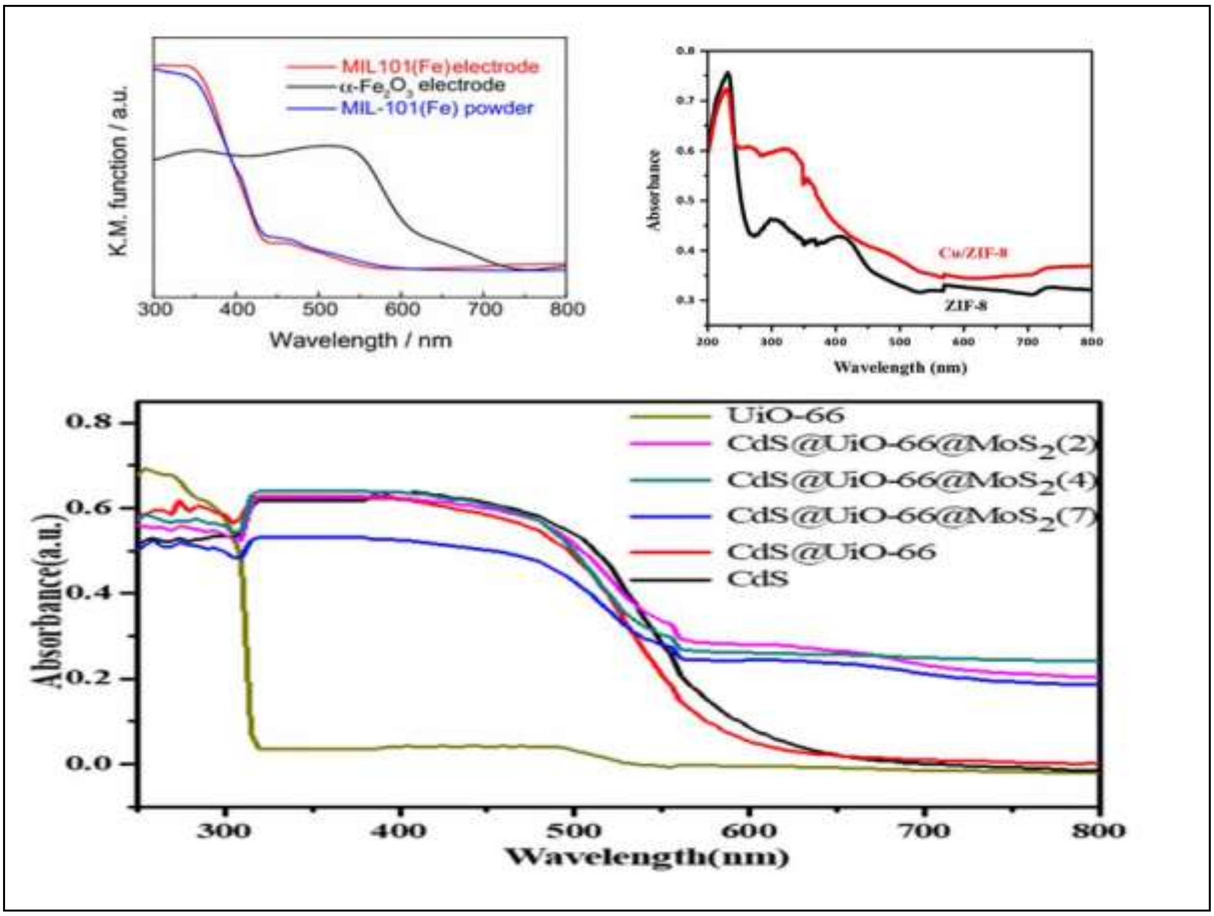
Infrared spectroscopy is applied to identify surface functional groups and to map the chemical environment surrounding both the MOF framework and the incorporated metal species. When metals or oxides coordinate with the linker, the vibrational modes of the MOF, particularly the asymmetric and symmetric stretches of carboxylates, shift in a manner that reveals changes in bonding. IR therefore becomes a diagnostic tool for confirming metal incorporation and for distinguishing between metal–oxygen and metal–ligand interactions. In CO_2 hydrogenation catalysts, IR is especially important for detecting carbonate, bicarbonate, formate, and other CO_2-derived species that appear upon adsorption. These vibrations indicate how readily the catalyst activates CO_2 and whether the surface favors methanol formation or alternative pathways. Moreover, IR spectroscopy can trace shifts in the oxidation state of metal centers through changes in metal–oxygen stretching frequencies, particularly when probe molecules such as CO or CO_2 are introduced. For systems containing Cu, Pd, or Pt, CO-adsorption IR is often used to distinguish between Cu^0, Cu^+, and Cu^{2+} species. As your notes indicate, IR therefore provides a chemical fingerprint of how metals and oxides coordinate within or upon the MOF.





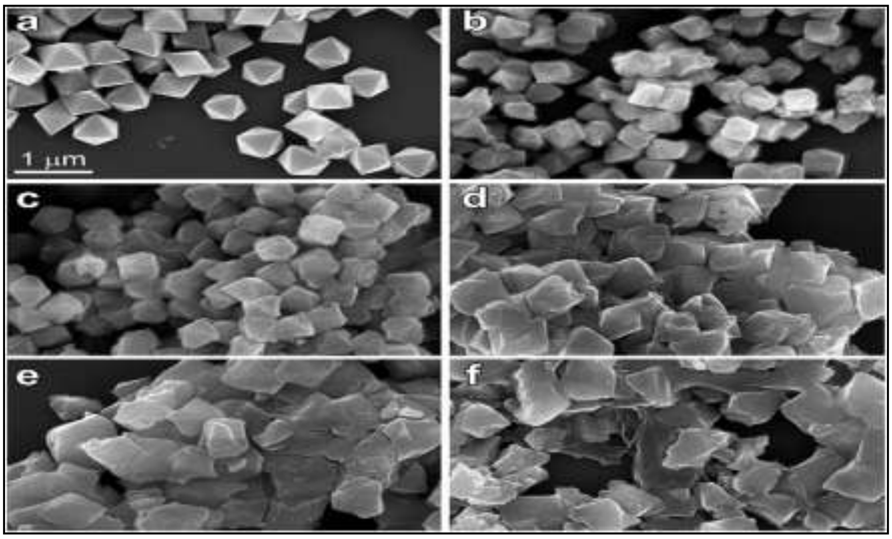
(iii) UV–Vis and Other Spectroscopic Techniques

Other spectroscopic methods, such as UV–Vis diffuse reflectance spectroscopy, Raman spectroscopy, and photoluminescence analysis, contribute essential information about the oxidation state and electronic structure of the active phases. UV–Vis DRS distinguishes between charge-transfer transitions, d–d transitions, and plasmonic responses, allowing identification of Cu^{2+} centers, metallic Cu^0 nanoparticles, or oxide clusters. Raman spectroscopy detects structural changes in the MOF, the presence of oxide phases, and the formation of carbonaceous deposits that may occur after extended hydrogenation. It is also sensitive to defect sites and lattice distortions in oxides such as ZnO or In_2O_3, which play a critical role in CO_2 activation. Photoluminescence spectroscopy further aids in evaluating the concentration of defect sites and oxygen vacancies, which frequently determine the hydrogenation ability of oxide-supported metal catalysts. These spectroscopic techniques collectively explain oxidation-state evolution and electronic perturbations, precisely matching your note that they provide explanations related to oxidation-state behavior.



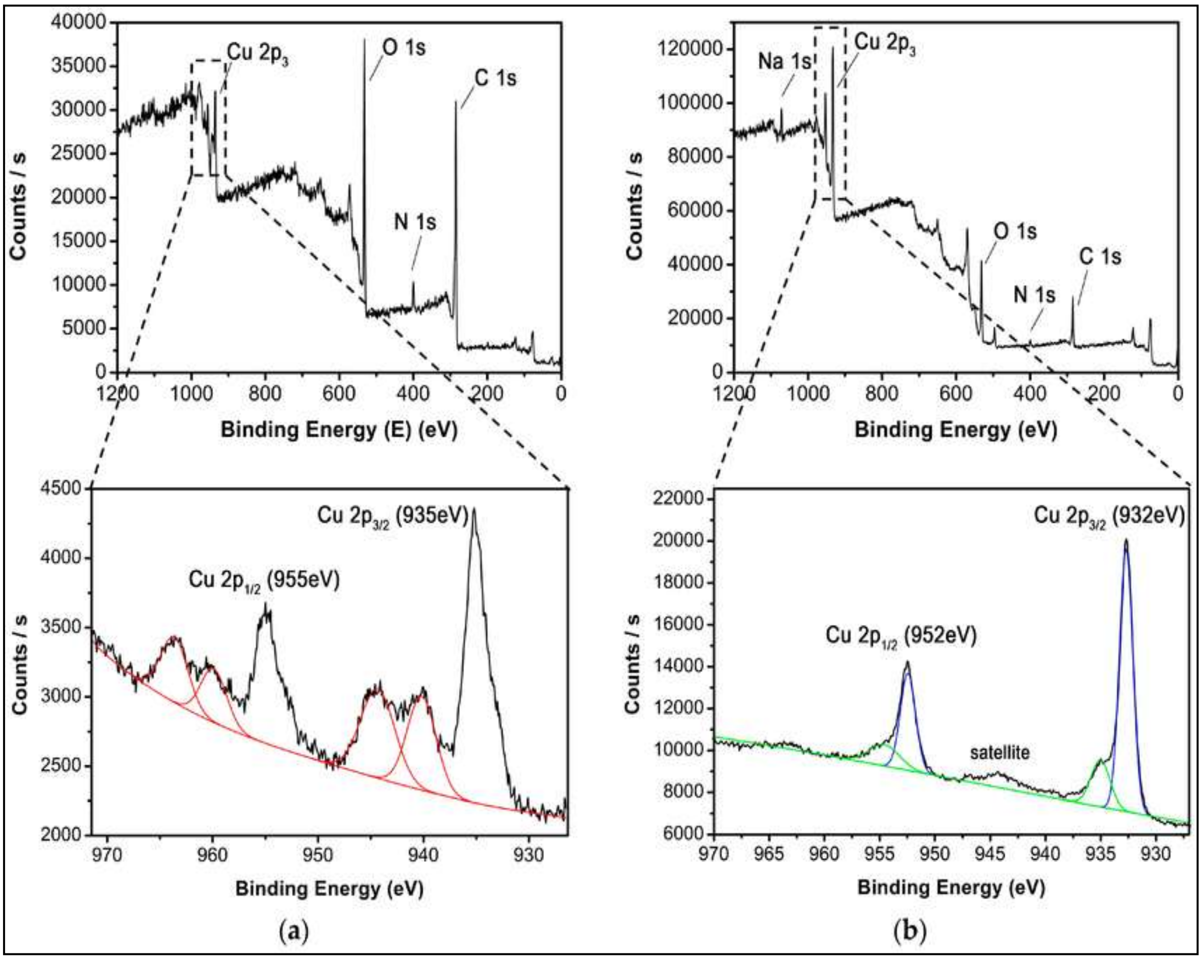
(iv) Transmission and Scanning Electron Microscopy (TEM / SEM)

Transmission electron microscopy provides direct visualization of the metal and metal-oxide nanoparticles that reside on or within the MOF. Through high-resolution imaging, TEM reveals particle size, distribution, and morphology, enabling researchers to determine how effectively the synthesis route has dispersed the metal species. Encapsulated systems often show ultrasmall and uniformly distributed nanoparticles, whereas surface-loaded systems may exhibit larger clusters. High-resolution TEM can display lattice fringes that identify specific crystallographic planes, confirming the identity of metallic or oxide phases. Scanning electron microscopy complements TEM by showing particle morphology, MOF crystal integrity, and surface texture. SEM is particularly valuable in determining whether the MOF retains its structural features after metal loading, activation, or reaction, since morphological degradation correlates with reduced confinement ability and poorer mass-transfer properties. Together, TEM and SEM support the comparison of metal dispersion and catalytic activity, precisely as indicated in the handwritten structure.



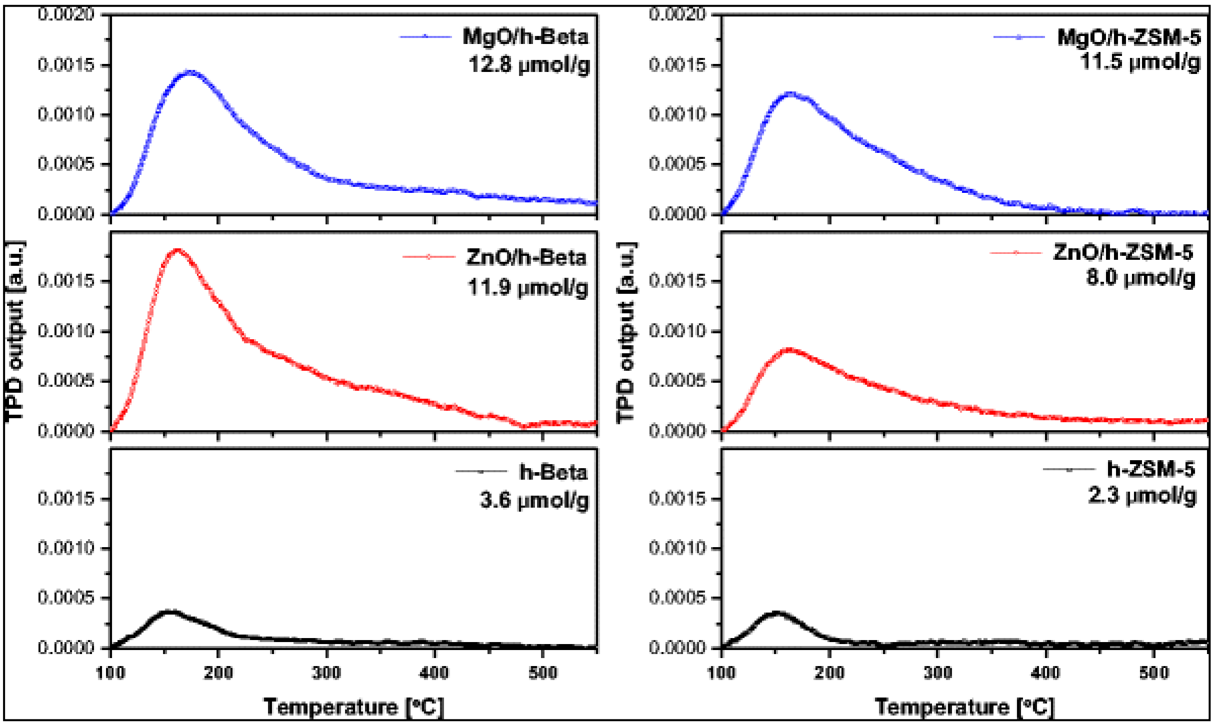
(v) X-ray Photoelectron Spectroscopy (XPS)

XPS is essential for determining the oxidation states of metals and the chemical nature of the surface. This method distinguishes between different oxidation states, such as Cu^0, Cu^+, and Cu^{2+}, or between Ni^0 and Ni^{2+}, and thereby provides critical insight into which active species are present after synthesis, reduction, and hydrogenation. The technique also detects electron transfer between metal nanoparticles and the MOF support, visible as shifts in binding energies. Strong metal–support interactions typically shift metal peaks to higher or lower energies, depending on whether electrons move toward or away from the metal. XPS further reveals surface enrichment or depletion of metals after reaction cycles, offering insight into sintering, oxidation, or migration phenomena. In oxide systems, the O1s spectrum provides information about lattice oxygen, hydroxyl groups, and oxygen-vacancy populations, all of which influence CO_2 adsorption. The handwritten note referring to “explanation of oxidation state” maps directly onto the interpretive role of XPS.



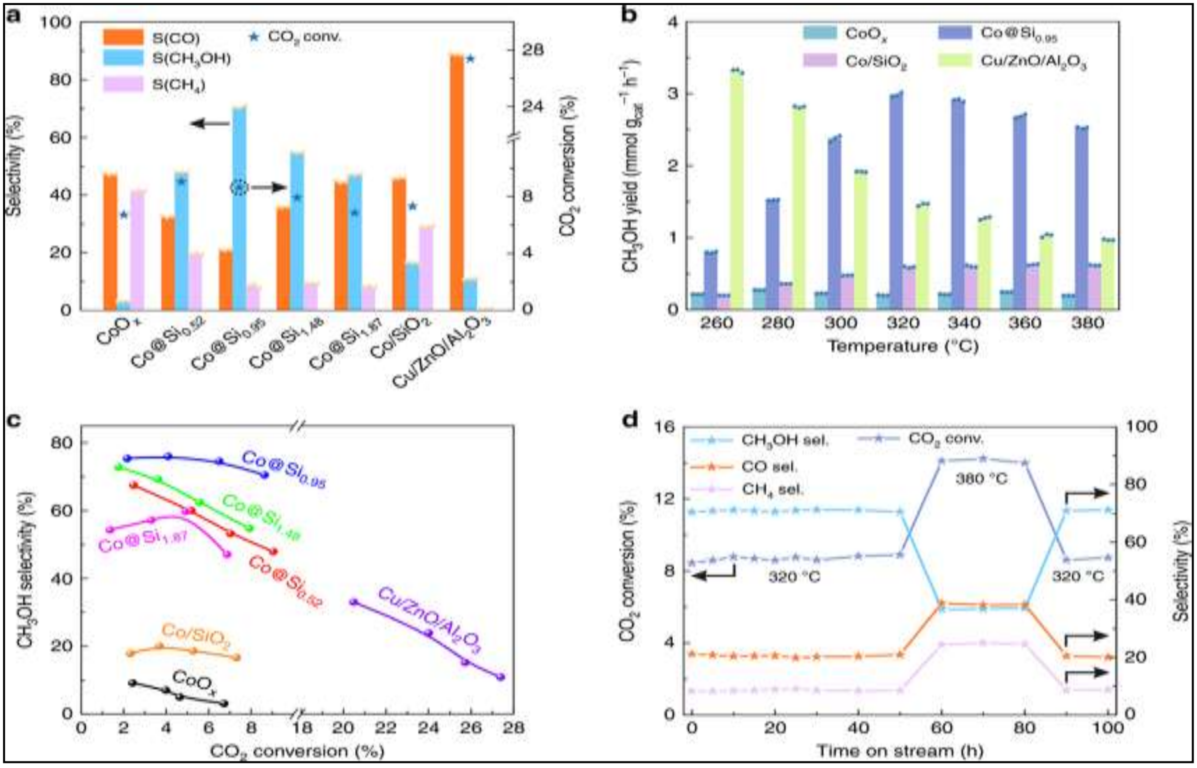
(vi) Temperature-Programmed Desorption and Reduction (CO_2-TPD and H_2-TPR)

Temperature-programmed desorption and reduction techniques assess the functional behavior of the catalyst surface. CO_2-TPD measures the availability and strength of basic sites, which collectively dictate CO_2 adsorption ability. MOFs and MOF-derived oxides typically present multiple classes of basic sites, and the temperature at which CO_2 desorbs indicates whether the surface binds CO_2 strongly enough to promote conversion to methanol or weakly enough to favor the reverse water–gas-shift pathway. Temperature-programmed reduction complements this by revealing how easily metal oxides reduce to their active metallic or mixed-valence states. Lower reduction temperatures suggest weaker metal–oxygen bonds or strong metal–MOF interactions that facilitate electron exchange during reduction. Conversely, high-temperature peaks indicate more stable oxides or strong structural embedding. Multi-step reduction patterns often signify several metal environments, such as surface oxide layers, bulk oxides, or strongly bound interface species. These findings directly link the catalyst’s surface chemistry to its hydrogenation activity, in line with the interpretive chain described in your notes.



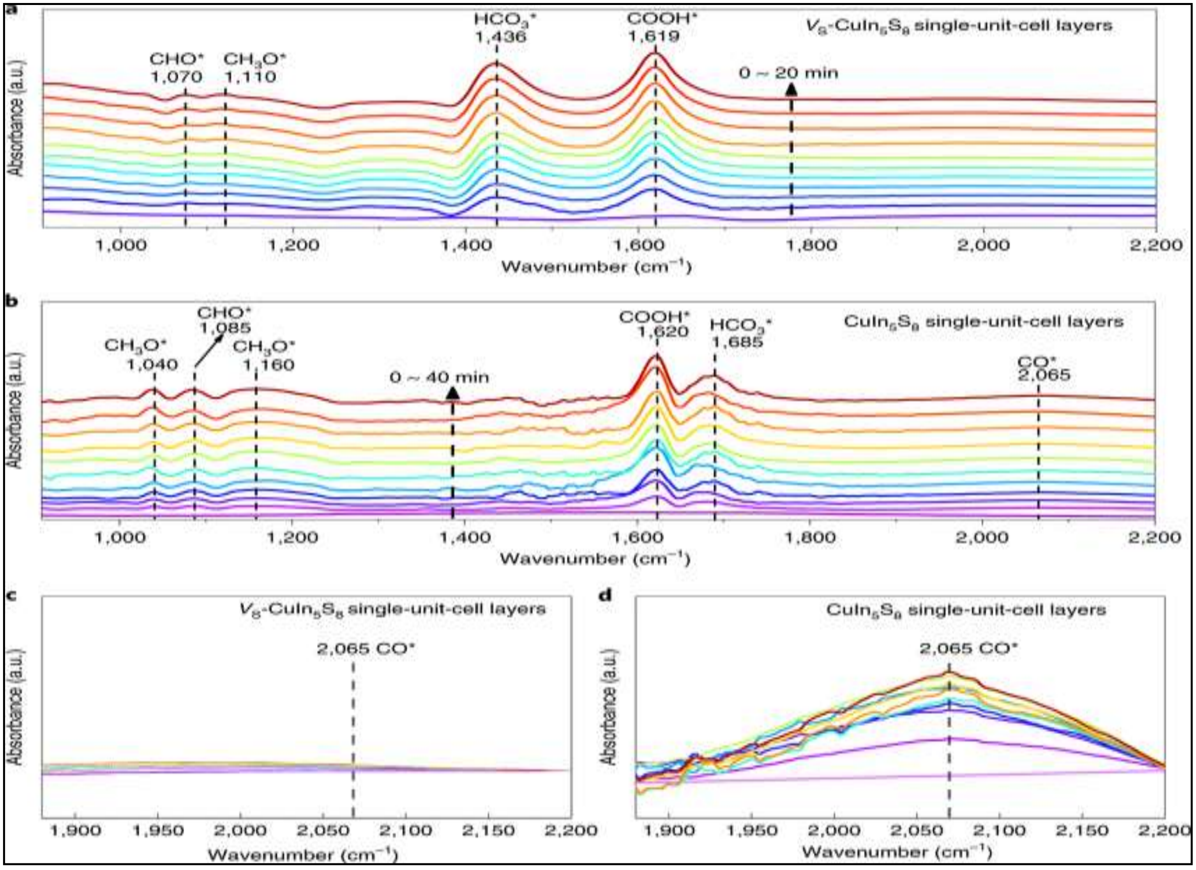
(vii) Catalytic Activity Measurements

Catalytic activity is typically presented in the form of conversion and selectivity charts, following the visual structure shown in your sketch. CO_2 conversion is plotted against different catalyst formulations, while selectivity to methanol, methane, CO, or higher alcohols is recorded under controlled temperature, pressure, and reactant ratios. These measurements quantify the impact of metal dispersion, oxidation state, and interface formation on catalytic performance. Catalysts containing highly dispersed metals or well-defined metal–oxide interfaces generally show improved turnover frequencies and better stability. Comparisons are often drawn among MOF-supported metals, MOF-derived oxides, and conventional oxide supports such as ZrO_2 or Al_2O_3. Stability assessments conducted over many hours demonstrate whether the catalyst resists sintering, oxidation, or structural degradation. Your hand-drawn bar representation corresponds exactly to these activity comparisons.



(viii) In-situ and Operand Characterization

In-situ and operando methods reveal how catalysts behave under genuine reaction conditions. Techniques such as in-situ X-ray absorption spectroscopy track changes in the oxidation states of metal centers while hydrogen is introduced. DRIFTS spectroscopy shows the formation of adsorbed intermediates such as formate, carbonate, and methoxy species as they appear and transform during hydrogenation. Ambient-pressure XPS extends oxidation-state measurements to reactive atmospheres, allowing researchers to observe metal–support interactions and surface restructuring under conditions closer to those encountered during operation. These techniques uncover mechanistic pathways and transient structures that cannot be detected through ex-situ measurements, offering a real-time perspective on how CO_2 is activated and hydrogenated.



3.3 Characterisation–Performance Correlation

After conducting the structural characterisation experiments, catalytic experiments are conducted with respect to CO_2 hydrogenation (e.g. conversion, strength over time on stream). Drawing of conclusions about the structure-activity relationships can be drawn with the help of correlation of the nanoparticle size and dispersion as seen by TEM, the oxidation state of the metal as seen by the XPS, adsorption capacity as seen by CO_2-TPD and reducibility as seen by H_2-TPR and the catalytic metrics(Giri *et al.*, 2021). As an example, small size distribution, and high metal-support contact localized metal nanoparticles can be more active since their surface or metal is more active, less sintering is required since the active sites and less interface effect since the active pathway is preferred by a specific reaction by a local concentration of the CO_2 to the active sites and interface effects.The outcome of this kind of correlation is optimisation: metal loading, size of nanoparticles, support functionalisation, reduction protocol, and metal-support interface. Design cycle is thus modified to synthesis - characterisation - performance testing - design refinement feedback.

4. Case Studies and Performance Evaluation

4.1 MOF-Supported Nano catalysts in CO_2 Hydrogenation

The efficacy of MOF based supports in the CO_2 hydrogenation has been established due to the increasing literature. Indicatively, Zhang et al. developed a review that MOFs as supports or sacrificial precursors can homogenize or unify meta-nanoparticles of metal dispersions, as well as increase interaction of metal and support, thereby, improving its functioning on CO_2 hydrogenation(Ye *et al.*, 2021). In a review of MOF-derived catalysts in thermal conversion of CO_2-to-HCOOH, Ye et al. note the growing number of examples of the MOF-derived morphology as having enhanced activity. These publications illustrate that MOF-based or derived catalysts can be better than the traditional supports, especially in the achievement of high dispersion, designed interfaces besides new architectures.

4.2 Structure–Performance Insights

According to the literature, several insights on the structure-performance have been raised. Firstly, the performance of support-porosity and CO_2 adsorption is determined decisively: Free micro-porosity and powerful CO_2 uptake of MOFs facilitates concentration of CO_2 on the centres of the active metals, thereby enhancing the conversion. Second, the size and dispersion of metal nanoparticles will be considered: placing nanoparticles in the MOF permeable cavities, it is possible to have a certain smaller size and increase dispersion, which will result in a higher active surface area and decrease aggregation. Third, influences of metal-support interface: an instance (here) of such is a $CuZrO_2$ interface on MOF which leads to stability and activity on hydrogenation(Zhang *et al.*, 2021). Fourth, the stability is among the more significant restricting factors: the majority of MOFs are diminished by hydrogenation factors (high temperature, H_2, water) and, therefore, alter their structural properties and functionality. An increase in the turnover frequencies, enhanced selectivity (i.e. between methanol and methane) and would be more stable with repeated cycles are some of the examples of improvement in the performance. One illustration is that catalysts produced via MOF-derived methods are likely to be sintering resistant and dispersible than conventional supports.

4.3 Discussion-Comparison: Conventional vs MOF-Supported Catalysts.

MOF-hosted nano catalysts have a number of positive characteristics compared to other catalysts grown on oxide (SiO_2, Al_2O_3, TiO_2, zeolites) controllable pores size and porosity, anchor points can be functionalised, and confinement can take place. On the other hand, traditional supports are stronger, thermos/hydrothermal stable and can be expanded without difficulties. The problem with MOF-based systems is therefore to be either as stable in the long run, or even better than the augmented performance potentials. The literature suggests possible solutions to this gap; to be MOF-derived catalysts (i.e. MOFs as a precursor template): they intrinsically combine unique morphology and dispersion with oxide support derivatives with superior thermal stability(Helal *et al.*, 2021). The systematic comparative studies have been done, however, in a small number. The next step is enormously important in designing to be industrial relevant: the lifespan of the catalyst (on-stream hours), the resistance to deactivation (e.g. coking, sintering, framework collapse), the ability to repeat the synthesis procedure saleably, etc. MOF-based catalysts need then to be designed not just to perform in the former, but to last on the more realistic conditions of hydrogenation (e.g. >150 dig, H_2/CO_2 pressure, H_2 production, recycle).

4.4 Mary (Hypothetical) Illustrative.

A case in point is a catalyst design utilizing a UiO-66 type of MOF comprised of Zr that undergoes in-situ growth of amine alkyl links followed by reduction of Cu nanoparticles (5 nm) in the presence of H_2 at 250 dig to create Cu0 nanoparticles dispersed within/on the MOF(Cai *et al.*, 2021). Characterisation Each characterisation shows that CuO has a slight change of CO2 binding energy determined by XPS and that pore size distribution is concentrated in the range of around 1-2 nm pore size, TEM is used to verify that there is good distribution of the Cu particles, CO_2-TPD is able to show that more CO_2 adsorbs than unsupported Cu and H_2-TPR is able to show that reduction proceeds at low temperatures with a low temperature maximum thus good interaction between the aids and the support. Catalytic experiment of the hydrogenation of the CO_2 to methanol under 30 bar H_2/CO_2 (3:1) and at 200 dig was catalytic in that the initial conversion of CO_2 to methanol 80 per cent was selective with only minimal deactivation despite 100 h on stream. On the Al_2O_3 support similar catalyst, the activity is 10 percent conversion and 70 percent selectivity and a loss rate of approximately 20 percent in 50 hours. The hypothetical case of MOF support increasing dispersions, selectivity and stability, adsorption of CO_2.Even though this example is illustrative, yet not mentioned, it generalises the design-characterisation-performance nexus which the discipline is pursuing to realise.

5. Challenges and Future Directions

5.1 Stability and Durability of MOF Supports

The maintenance of the MOF support under the harsh environment of a reaction (high temperature, high pressure H_2/CO_2, the presence of steam) is one of the primary issues of the use of MOF-supported nano catalysts in the hydrogenation of CO_2. MOFs are known to degrade or rapidly collapse under such conditions losing porosity, structure and thus catalytic capacity quite reasonably(Zhang *et al.*, 2021). The Zhang et al. review justifies indicatively that, due to the fact that the thermal and hydrothermal stability of MOFs is much lower than stronger traditional supports, their application is limited. In order to achieve this, through either synthesis of intrinsically strong MOFs (through high valence metal cluster and strong cross-linker), post-synthesis cross-linkage or stabilisation, or by acting through MOF-derived catalyst (MOF as precursor and catalyst is a robust oxide or composite).

5.2 Extension and Implementation.

Even though there are indeed many studies that have evidence-of-concept in laboratory scale reactors, very little information is available regarding scaling to pilot/industrial scale. The issues to be taken into consideration are, shaping of catalysts, transportation of mass, heat, and mechanical stability, recuperation, and stability. MOF powders may require polarizability, which has the ability to annihilate porosity, dispersion or architecture breakdown. In addition, scale MOF synthesis remains debatable in regards to cost and reproducibility. Further studies are needed to conduct life-cycle and techno economic reviews of MOF based nano catalysts in industry.

5.3 Selective and Product Differentiation Control.

One of the issues is the selectivity control even though several studies exhibit better activity. CO_2 hydrogenation could produce a range of products (methane, methanol, format, other hydrocarbons), and they need to be active metal selective at certain conditions (active metal, support functionality, interface, and conditions) in order to yield a certain product(Adena *et al.*, 2021). The possible future aim of the work is to develop MOF based catalysts with designed active and dual/ multi-site models to choose a prudent path. In addition, dynamic working (e.g. cyclic product switching switching) and downstream integration separation are value adding.

5.4 Constructed Personality and Analytic Understanding.

Detailed mechanistic understanding is yet to be developed. Only in-operando/operando characterisation (e.g. XAS, DRIFTS, Mossbauer, ambient-pressure XPS) can actively active species, intermediates and reaction pathways under hydrogenation conditions be characterised. The sagacity of this will permit the rational planning of metal-support interface, and optimisation of nanoparticle size, morph, and electronic environment(Duma *et al.*, 2021). Additionally, computational modelling (DFT, microkinetic modelling) coupled with experiment will become possible and now by computational modelling the synthesis of catalysts will become faster. Recent theory available regarding this topic presents the use of the metal-ligand synergy to control the electronic structure and consequently the product selectivity of 2D p-conjugated MOFs as a system to reduce CO_2, as an example.

5.5 Environment and Economical affairs.

Together with the activity of catalysts, the environmental, and economical factors must be viewed: e.g. demonstrated the energy and cost of synthesis of MOFs, loading of metal (especially precious metals), catalyst stability, recyclability, and compatibility with renewable sources of H_2. Life-cycle assessment (LCA) and techno-economic analysis (TEA) should follow so as to provide a global analysis of MOF-supported nano catalysts in CO_2 hydrogenation being one of the ways of carbon-utilisation technologies.

Proposed Design Guidelines

Based on the discussion above, we may provide a list of design principles of MOF-based nano catalysts that will be able to resolve greater CO_2 hydrogenation turnover:

- **Select MOF** : It allows a large surface area, pore organization and functional accessibility of linkers to metal nanoparticles to be anchored. The support should also be highly thermal/hydrothermal stable or convertible to obtain robust support.
- **Adopt metal nanoparticle synthesis techniques so as to obtain small size (i.e. less than 10 nm) :** Small size distributions and homogenous suspensions about the support or within the support. Sintering is inhibited by confinement in the pores in MOFs or by attaching linker functional groups to anchors(Qin *et al.*, 2021).

- **Significantly boost metal-support coupled interactions and interface effects:** e.g. metal-oxide interfaces, electron transfer between metal and MOF support, and proximity to relative position to CO_2 adsorption sites in the MOF.
- **Enhance CO_2 adsorption on or near the active site:** fundamental capability (e.g., amine linkers, basic oxide cluster), MOF porosity to localise CO_2 and H_2 near a catalyst, and accessibility of open pores during the reaction.
- **Stability of catalysts in practicable hydrogenation conditions:** experiment high temperature, pressure, presence of steam, reaction/ regeneration cycles; note structural integrity and metal leaching, sintering, collapsing of framework.
- **Morphology TEM/SEM Characterise Crystallinity:** PXRD Characterise Surface chemistry: XPS to examine Surface redox and adsorption properties: TPR/TPD Characterise Active state under reaction: operando techniques Characterise(Fan *et al.*, 2021)
- **Response on significant reaction conditions (pressure, temperature, ratios of gas feeds).** Activity (frequency of turnover), activity, selectivity, stability and compare to benchmark catalysts. Sensitivity analyse of the offer (metal loading, particle size, supporting modifications) to determine the best design.
- Include ecological and economic analysis: an approximate cost/kg CATS, metal consumption (wt. loading and dispersion), lifetime and recyclability, and add with renewable hydrogen feeds and CO_2 feed.
- Philosophically, the recommendations ought to enable the scientists to be solitary in designing MOF-based nano catalysts that possess superior CO_2 Hydrogenation factor which have high probabilities of being industrialized.

CONCLUSION

One of the issues essential to sustainable chemistry and carbon utilisation technologies is the hydrogenation of CO_2 to useful fuels and chemicals. The MOF based nano catalysts are a different efficient platform which embraces the advantages of porous tenable fringes together with a highly dispersed active metal nanoparticles. Such a combination enables to design more catalysts with custom porosity, metals anchoring, metals and support interactions, and CO_2 adsorption. It is evidence in literature that enhanced selectivity and dispersion coupled with improved activity is achievable with such systems [as opposed to traditional catalysts]. However, there are still considerable issues that can be distinguished the thermal/hydrothermal stability of MOF support, which increases in scale the process of catalyst synthesis and shaping, selectivity to preferred products and reaction mechanism on a molecular scale.The provided design guidelines provide a roadmap to the further studies that can be used to address the difference between the performance on a lab scale and the industrial one. Competence in characterisation and computation Studies in computational modelling and integrated view of catalyst economics and sustainability Operando characterisation is still underdeveloped to further development and improvement, and with improved development MOF-capable nano catalysts will be useful in optimization of the CO_2 hydrogenation technologies.In totality, designs and general characterisation of MOF-supported nano catalysts are the key to the achievement of the full potentials of CO_2 hydrogenation. As the amount of renewability of the H_2 supply increases and a variety of CO_2 sources rises, the application of a form of catalyst platform with the property of a high degree of activity, selectivity, and stability will become an unavoidable problem. The systems on MOFs hold one of the best perspectives towards achieving such a vision.

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