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# Selection of catalysts for the regeneration step in an amine-based absorption-regeneration CO$_2$ capture process

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**Abstract**

Carbon Capture Utilization and Storage (CCUS) is a crucial technology for mitigating climate change by reducing greenhouse gas emissions. However, the energy-intensive step of regenerating amine solvents used in CO$_2$ capture remains a significant challenge. This work explores the use of solid acid catalysts (SACs) to enhance the efficiency and reduce the energy costs associated with the release of CO$_2$ during regeneration. Indeed, Brønsted and Lewis acid sites (BASs and LASs) help the carbamate breakdown reaction. Additionally, a large mesoporous surface area is necessary to allow chemical species to reach the catalytic sites. The main objective of this work is to select most promising candidates from among the catalysts already tested for the CO$_2$ desorption in literature. More than 20 catalysts were identified, divided into four families: metal oxides, zeolites, mesoporous silicas and natural clays. Four main criteria were then considered to identify the most promising ones, namely physicochemical properties, performances, cost and associated risks. Considering these four criteria, in view of performing lab and micro-pilot scales tests, the most promising candidates are metal oxides such as γ-Al$_2$O$_3$, ZrO$_2$, Cr$_2$O$_3$, Nb$_2$O$_5$, and MoO$_3$, along with the zeolites H-ZSM5, H-Mordenite, and H-Beta.

*Keywords:* Carbon Capture; Amine-based solvents regeneration; Solid acid catalysts; Selection methodology

| Nomenclature | | | |
|---|---|---|---|
| AMP | 2-amino-2-methyl-1-propanol | MEA | Monoethanolamine |
| B/L | Number of Brønsted acid sites/ Number of Lewis acid sites | MSA | Mesoporous surface area |
| BAS | Brønsted acid site | PZ | Piperazine |
| CCUS | Carbon Capture Utilization and Storage | SAC | Solid acid catalyst |
| DAC | Direct Air Capture | SSA | Specific surface area |
| LAS | Lewis acid site | TAS | Total acid sites |

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## 1. Introduction

Since the last few decades, global warming has become one of the most environmental challenges [1]. Human activities (industries, transport, etc.) require a huge amount of energy, primarily obtained through the combustion of fossil fuels, which releases $CO_2$ into the atmosphere [2]. Among greenhouse gases, carbon dioxide is the most prevalent, and its atmospheric concentration is steadily increasing, from 316 ppm in 1960 to 421 ppm in 2023 [3]. To reduce $CO_2$ emissions, around two hundred countries signed the Paris Agreement in 2015, which aims to limit the temperature increase to below 2°C [4].

Currently, the demand for industrial production is increasing, and renewable alternatives are not sufficient to meet this demand [5]. Therefore, to limit the release of $CO_2$, Carbon Capture Utilization and Storage (CCUS) is a promising solution, according to the Intergovernmental Panel on Climate Change (IPCC) [6]. Among all the $CO_2$ capture techniques (absorption, adsorption, membrane separation, cryogenics, etc.), the absorption-regeneration technology is the most mature and widespread to date [7,8]. The process employs an amine-based solvent to chemically absorb carbon dioxide from a gas stream. The solvent is then regenerated by heating the solution, producing concentrated $CO_2$ that can be converted or stored. However, the primary drawback of this process lies in the operating costs associated with the regeneration energy consumption. Consequently, various studies have focused on strategies to reduce this energy demand (innovative solvent blends, biphasic solvents, process optimization…) [9,10].

Recently, Idem et al. [11] demonstrated that adding a solid acid catalyst (SAC) in the regeneration step is an innovative strategy to reduce the energy demand (Fig. 1). The acid sites present on the catalyst facilitate the breakdown reaction of carbamate and accelerate the desorption kinetics [11,12]. As a result, a lower regeneration temperature can be applied, thereby reducing the required energy input. As well as reducing energy costs, a lower desorption temperature mitigates issues related to corrosion and solvent degradation [12,13].

Catalysts for the regeneration of amine-based solvents exist in large number in literature. The aim of this work is to select the most promising candidates from the data available in the literature. The selection focuses on catalysts readily available on the market and it is based on four criteria: the physicochemical properties of the material, the regeneration performances reported in the literature, the catalyst cost and the risks associated with the use of the material. The results of this selection will be included in a broader study aimed at determining the benefits of the catalytic absorption-regeneration process, with inlet $CO_2$ percentages ranging from 5% to 35%, or in Direct Air Capture (DAC).
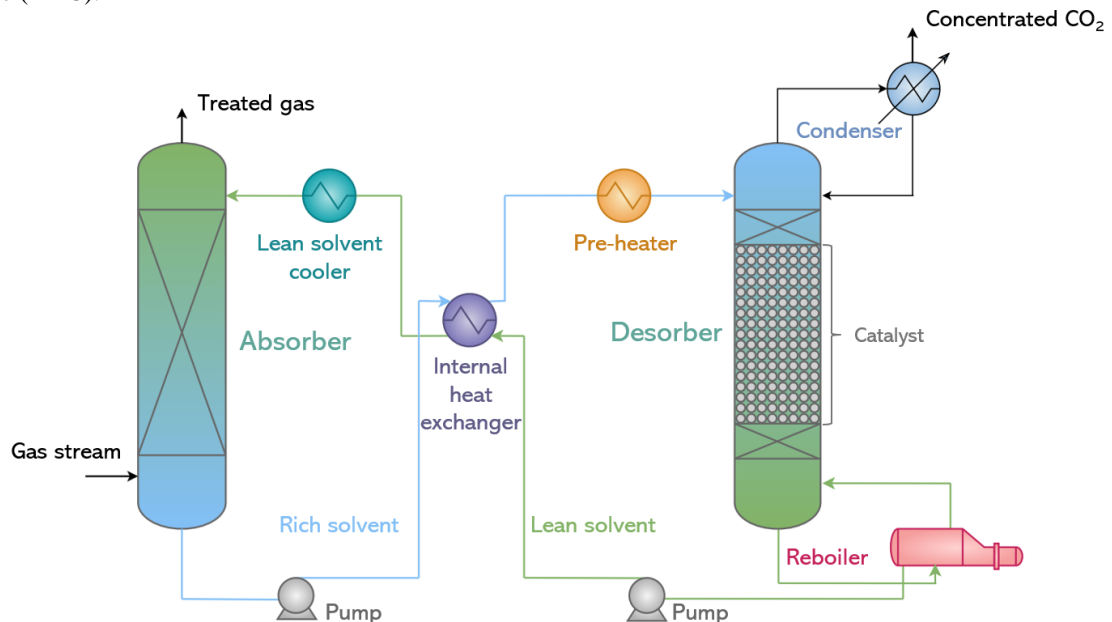


Fig. 1: Schematic representation of the absorption - catalytic regeneration process (based on [2])

## 2. Catalytic desorption of $CO_2$: mechanism

Solid acid catalysts (SACs) are particularly interesting for the regeneration of amino solvents. In fact, these catalysts possess Brønsted and Lewis acid sites which help the carbamate breakdown. Brønsted sites (from hydroxyl groups on the surface of the material) are proton donors and provide free $H^+$ to convert AmineCOO$^-$ into AmineCOOH. In the absence of catalysts, protons come from deprotonation of the protonated amine [2,7,8]. However, this reaction has a high energy barrier attributable to the high alkalinity of monoethanolamine (MEA) (73.4 kJ/mol) [2,14]. Lewis sites (unsaturated metal atoms on the surface of the material) are able to accept a lone pair of electrons [2,7,8]. These sites help desorption by interacting with the nitrogen and oxygen atoms as explained hereafter. At present, the most accepted catalytic mechanism with a primary amine solvent especially MEA (often used as an R&D reference) is described as follows (Fig. 2 (a)) [11]:

1. **Carbamate formation.** Reaction between carbon dioxide and amine leads to carbamate formation (equation 1).

$$CO_2 + 2\ Amine \rightleftharpoons AmineCOO^- (carbamate) + AmineH^+ \tag{1}$$

2. **Proton acceptance.** A proton from a Brønsted acid site (or from the amine deprotonation reaction) attacks the carbamate.
3. **Chemisorption.** A Lewis site binds with the oxygen atom and the AmineCOOH molecule adsorbs on the surface of the catalyst.
4. **Proton transfer.** The hydrogen bonded to the oxygen atom moves to the nitrogen atom.
5. **N-C bond stretch.** The hydrogen atom destroys the conjugation between the N-C-O atoms. As a result, the nitrogen is hybridized sp$^3$ and the bond between the N-C bond begins to stretch.
6. **N-C bond breakage.** A second Lewis acid site attacks the lone pair of electrons of the N$^+$ atom and further stretches the N-C bond. In the absence of a catalyst, this stage is carried out solely by the action of heat. The catalyst therefore adds extra strength to the elongation of the N-C bond.
7. **Separation.** The N-C bond breaks and the zwitterion splits into amine and carbon dioxide molecules. The Brønsted site can be regenerated by accepting a proton from protonated amine (Fig. 2 (b)).
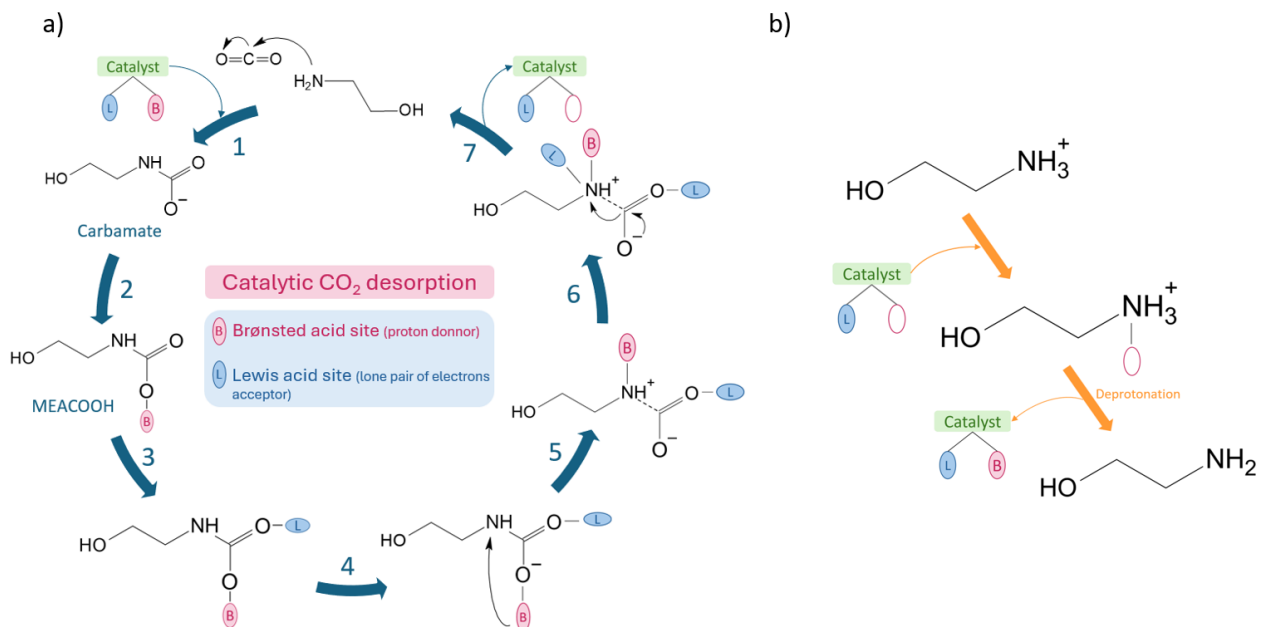


*Fig. 2: (a) Catalytic desorption mechanism with a solid acid catalyst (based on [15]); (b) Brønsted acid site regeneration [15].*

## 3. Selection of catalysts

Solid acid catalysts suitable for amine-based solvent regeneration are numerous and are divided into four main groups:

- Metal oxides are commonly used as catalysts in the industrial sector due to their easy production. The unsaturated metal on the surface of the catalyst consists of an electron acceptor (Lewis acid) and is able to accelerate carbamate breakdown [2]. In presence of water, a few Brønsted acid sites on the surface can be created by dissociation of water (equation 2) and the hydroxyl groups can facilely give protons. However, not all metal oxides produce acidic Brønsted sites in aqueous media [16].

$$MO + H_2O \rightleftharpoons MO.H_2O \rightleftharpoons MOH.OH \tag{2}$$

- Zeolites are aluminosilicate materials with a crystalline three-dimensional structure and are mainly composed of silicon, aluminum and oxygen atoms [2,17]. In the field of catalysis, and more specifically in catalytic $CO_2$ desorption, zeolites are interesting candidates thanks to their properties such as high specific surface area and large pore size [18]. In addition, aluminum and silicon atoms can act as Lewis sites, while hydroxyl groups on the surface act as Bronsted sites.
- Mesoporous silicas constitute solid materials characterized by a regular honeycomb structure, featuring large mesoporous specific surface area (MSA) [2]. This mesoporous structure is an asset for the accessibility of species to the active sites. However, the disadvantage of these materials is their low acidity.
- Natural clays are phyllosilicate minerals which possess a structure composed of two silicate or aluminosilicate layers within are located metal ions. Clays exhibit both Brønsted acid sites (-OH groups on the surface in the presence of water) and Lewis sites (unsaturated metal ions on the surface) [17].

Moreover, scientific teams specialising in the field of catalysis are currently investigating the modification of the composition of the material (incorporation of elements…) or the structure with a view to enhancing the physical and chemical properties [19–23]. As a result, a large number of different catalysts can be found in the scientific literature, making it difficult to choose promising candidates.

A selection based on four criteria: the physical and chemical properties, performance based on data available in the literature, cost of the material and the risks to people and the environment associated with their use is established. For reasons of ease of supply and technical simplicity of preparation, the selection focuses on catalysts that are directly available on the market i.e. catalysts that have not undergone any special treatment. This narrows the list to 23 candidates (Fig. 3).
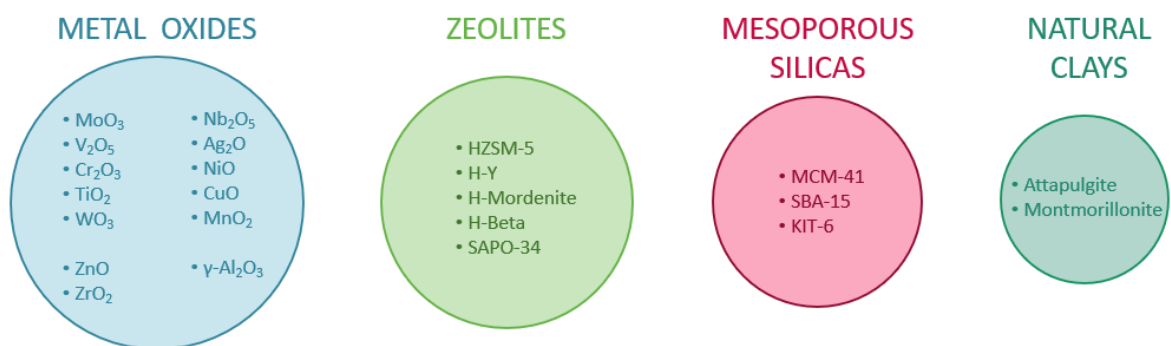


*Fig. 3: Catalyst candidates considered for selection*

## *3.1. Physical and chemical properties*

The positive effect of the catalyst is directly linked to its physical and chemical properties. On the one hand, a large specific surface area (SSA) enables the deployment of numerous active sites within a small amount of catalyst and particularly the mesoporous surface area (MSA) which allows chemical species to access catalytic sites [8,23,24]. On the other hand, Brønsted acid sites (BASs) and Lewis acid sites (LASs) help the carbamate breakdown, their concentration is a significant parameter. Consequently, the catalyst must have the largest possible mesoporous surface area with the greatest number of available acid sites. Indeed, according to several experimental studies [12,25,26], the product MSA*B/L (or sometimes MSA*TSA, MSA*BAS) is correlated to the performance of the catalysts. Besides, based on the product MSA*B/L, it is preferable for the catalysts to be of the Brønsted type rather than the Lewis type. The physical and chemical properties of the materials considered can be found in Tables 1 to 4.

$\gamma$-$Al_2O_3$ is the metal oxide the most commonly found in literature as a catalyst for $CO_2$ desorption. Nevertheless, this material can have different properties depending on the synthesis method, as shown in Table 1. Compared to $\gamma$-$Al_2O_3$, other metal oxides considered present a low specific surface area (total and mesoporous) below 5.5 m²/g. Regarding acidity, the number of total acid sites (TAS) is moderate. Especially, only $MoO_3$, $V_2O_5$, $Nb_2O_5$, $Ag_2O$ and $ZrO_2$ produce Brønsted sites. Unfortunately, the quantities are not communicated in the associated paper. For this group of materials (except for $\gamma$-$Al_2O_3$), the low MSA has the effect of lowering the value of MSA*B/L. However, these candidates are still of interest, as they could potentially improve the properties of other materials with a wider MSA.

Table 1: Physical and chemical properties of metal oxides.

| Catalyst | MSA (m²/g) | SSA (m²/g) | BAS (mmol/g) | LAS (mmol/g) | TAS (mmol/g) | B/L (-) | MSA*B/L | Reference |
|---|---|---|---|---|---|---|---|---|
| $MoO_3$ | 0.0008 | 0.31 | Presence | Presence | 0.82 | 0.320 | 0.0003 | Bhatti et al. (2017) [16] |
| $V_2O_5$ | 2.40 | 2.72 | Presence | Presence | 0.70 | 0.490 | 1.176 | Bhatti et al. (2017) [16] |
| $Cr_2O_3$ | 2.30 | 3.10 | Absence | Presence | 0.62 | 0.013 | 0.030 | Bhatti et al. (2017) [16] |
| $TiO_2$ | 8.23 | 10.13 | Absence | Presence | 0.49 | 0.031 | 0.255 | Bhatti et al. (2017) [16] |
| $WO_3$ | 0.09 | 0.18 | Absence | Presence | 0.42 | 0.024 | 0.002 | Bhatti et al. (2017) [16] |
| $Nb_2O_5$ | 2.17 | 2.73 | Presence | Presence | - | - | - | Bhatti et al. (2018) [27] |
| $Ag_2O$ | 0.15 | 0.24 | Presence | Presence | - | - | - | Bhatti et al. (2018) [27] |
| NiO | 0.33 | 0.38 | Absence | Presence | - | - | - | Bhatti et al. (2018) [27] |
| CuO | 0.14 | 0.15 | Absence | Presence | - | - | - | Bhatti et al. (2018) [27] |
| $MnO_2$ | 0.01 | 0.03 | Absence | Presence | - | - | - | Bhatti et al. (2018) [27] |
| ZnO | 4.47 | 5.49 | Absence | Presence | 0.12 | - | - | Bhatti et al. (2018) [28] |
| $ZrO_2$ | 3.48 | 4.42 | Presence | Presence | 0.13 | - | - | Bhatti et al. (2018) [28] |
| $\gamma$-$Al_2O_3$ | 234.60 | 234.60 | 0.098 | 0.287 | 0.385 | 0.340 | 80.107 | Zhang et al. (2019) [13] |
| $\gamma$-$Al_2O_3$ | 163.06 | 180.19 | 0.044 | 0.838 | 0.882 | 0.050 | 8.153 | Zhang et al. (2018) [22] |
| $\gamma$-$Al_2O_3$ | 173.50 | 173.50 | - | - | 3.570 | 0.670 | 116.200 | Zhang et al (2018) [29] |

Zeolites possess large SSA and MSA greater than 100 m²/g (except for H-Y and H-Mordenite). Particularly, H-Mordenite and H-Beta have an extensive amount of BAS resulting in a total acid sites concentration of 10.403 and 16.359 mmol/g, respectively (Table 2). In this category, the protonated version of Zeolite Socony Mobil-5 (H-ZSM5) is the most commonly encountered in the literature relative to the catalytic solvent regeneration. Once again, the origin and the composition (notably the $SiO_2$/$Al_2O_3$ ratio) of the catalyst has a significant impact on the properties. This class of materials looks promising in view of the high MSA*B/L product, which exceeds several hundreds

Table 2: Physical and chemical properties of zeolites.

| Catalyst | MSA (m²/g) | SSA (m²/g) | BAS (mmol/g) | LAS (mmol/g) | TAS (mmol/g) | B/L (-) | MSA*B/L | Reference |
|----------|------------|------------|--------------|--------------|--------------|---------|---------|-----------|
| H-ZSM5 | 175.50 | 337.70 | 0.125 | 0.029 | 0.154 | 4.310 | 756.466 | Zhang et al. (2018) [30] |
|  |  |  |  |  |  |  |  | Zhang et al. (2019) [13] |
| H-ZSM5 | 151.56 | 279.97 | 0.210 | 0.139 | 0.349 | 1.512 | 229.140 | Liu et al. (2017) [25] |
| H-ZSM5 | 120.90 | 291.6 | - | - | - | 1.587 | 191.868 | Liang et al. (2016)[12] |
| H-ZSM5 | 151.60 | 279.9 | - | - | 9.502 | 1.510 | 228.916 | Zhang et al (2018) [29] |
| H-ZSM5 | 47.6 | 376.3 | 0.268 | 0.198 | 0.466 | 1.350 | 64.260 | Bhatti et al. (2020) [31] |
| H-Y | 24.3 | 474.1 | Presence | Presence | - | 2.300 | 55.890 | Liang et al. (2016) [12] |
| H-Mordenite | 14.5 | 396.4 | 10.165 | 0.238 | 10.403 | 42.690 | 619.296 | Zhang et al. (2019) [13] |
| H-Beta | 129.4 | 534.5 | 12.496 | 3.890 | 16.359 | 3.200 | 414.779 | Zhang et al. (2019) [13] |
| SAPO-34 | 146.5 | 407.21 | 1.082 | 0.741 | 1.823 | 1.461 | 214.036 | Zhang et al. (2017) [26] |
| SAPO-34 | 146.5 | 553.74 | - | - | 2.102 | 1.460 | 213.890 | Zhang et al. (2018) [29] |

Mesoporous silicas have an exceptional specific surface area, but they are not as acidic as H-Mordenite and H-Beta previously mentioned. Indeed, TAS values are under 1 mmol/g (except for KIT-6) which is ten times less than some zeolites (Table 3). The product MSA*B/L reaches very high values mainly due to the very large MSA. These materials seem interesting, but the lack of acidity may be a disadvantage. The other criteria will determine whether this category is really promising.

Table 3: Physical and chemical properties of mesoporous silicas.

| Catalyst | MSA (m²/g) | SSA (m²/g) | BAS (mmol/g) | LAS (mmol/g) | TAS (mmol/g) | B/L (-) | MSA*B/L | Reference |
|----------|------------|------------|--------------|--------------|--------------|---------|---------|-----------|
| MCM-41 | 963.19 | 963.19 | 0.008 | 0.011 | 0.019 | 0.751 | 726.771 | Liu et al. (2017) [25] |
| MCM-41 | 171.5 | 963.19 | - | - | 0.001 | 0.750 | 128.625 | Hu et al. (2019) [32] |
| SBA-15 | 476.1 | - | 0.490 | 0.090 | 0.580 | 5.400 | 2570.940 | Gao et al. (2020) [33] |
| KIT-6 | 723.6 | 829.8 | 1.480 | 1.010 | 2.490 | 1.470 | 1060.291 | Zhang et al. (2022) [21] |

According to the values given in Table *4*, natural clays do not have particularly interesting physical and chemical properties. In fact, the mesoporous specific surface area is not high, and the acidity is low, leading to a small MSA*B/L factor.

Table 4: Physical and chemical properties of natural clays.

| Catalyst | MSA (m²/g) | SSA (m²/g) | BAS (mmol/g) | LAS (mmol/g) | TAS (mmol/g) | B/L (-) | MSA*B/L | Reference |
|----------|------------|------------|--------------|--------------|--------------|---------|---------|-----------|
| Attapulgite | 56.8 | 88.8 | 0.002 | 0.019 | 0.021 | 0.110 | 5.981 | Tan et al. (2023) [34] |
| Montmorillonite | 17.8 | 24.4 | 0.002 | 0.157 | 0.159 | 0.013 | 0.226 | Bhatti et al. (202) [35] |

### 3.2. $CO_2$ desorption performances

The main objective of adding a catalyst in the regeneration step is to increase the kinetics of carbon dioxide desorption, maintaining the same chemical equilibrium obviously. If the desorption time (in a batch system) is not too long, the increase of kinetics results in a greater amount of $CO_2$ released, used in this study as a criterion for highlighting the improvement of carbon dioxide desorption. This is of course linked to the objective of reducing the regeneration energy, since for the same amount of energy (the temperature is identical and the catalyst does not seem to influence the temperature rise), a larger quantity of $CO_2$ is released. As the catalytic effect is often associated to physico-chemical properties, the data in Tables 1 to 4 will often be correlated with the results. To identify the best candidates, it would be logical that catalyst performance should be compared between studies. However, the

experimental conditions used are not identical from one study to another, which hinders the comparison. Hereinbelow are listed the experimental conditions that can differ between studies:

- Desorption temperature. The higher the temperature, the easier carbon dioxide desorbs. This makes difficult to compare catalysts operated at different temperatures.
- Desorption time. The catalyst does not change the thermodynamic equilibrium, but rather the reaction kinetics. After a long time (near equilibrium), the catalyst will no longer be useful. This is why the time at which the data are recorded is important.
- Catalyst concentration. The relationship is not necessarily linear, but up to a certain quantity, the more catalyst is added the better performance is expected.
- The solvent and its concentration. The catalyst acts in a reaction where $CO_2$ and solvent interact. Therefore, a catalyst can have different effects depending on the solvent.

Considering the arguments mentioned above and the data available in the literature, a comparison between studies can only be made for the group of metal oxides. Indeed, desorption tests were conducted by the same research department under the same experimental conditions. Their works are divided into three studies where different metal oxides were tested, namely:

- $MoO_3$, $V_2O_5$, $Cr_2O_3$, $TiO_2$ and $WO_3$ in Bhatti et al. (2017) [16].
- $Nb_2O_5$, $Ag_2O$, $CuO$, $NiO$ and $MnO_2$ in Bhatti et al. (2018) [27].
- $ZnO$ and $ZrO_2$ in Bhatti et al. (2018) [28].

To compare the catalytic effect of these metal oxides, the increase in the amount of $CO_2$ desorbed compared to a baseline (a blank of 5M monoethanolamine) was plotted against the amount of catalyst added (at a desorption temperature of 85°C during a 140-minute test) (Fig. 4). Before discussing individual performances, results highlight that the increase in the amount of $CO_2$ released evolves almost linearly with the catalyst concentration (with the concentration range from 20 to 100 g/L). According to Fig. 4 , several catalysts stand out: $MoO_3$ allows an increase in desorbed $CO_2$ by 94.44%, $V_2O_5$ by 83.33%, $Ag_2O$ and $Nb_2O_5$ by 68.75% (at a concentration of 100 g/L), $ZrO_2$ by 51.25% and $ZnO$ by 56.25% (at 80 g/L). Apart from $ZnO$, all these catalysts have Brønsted acid sites. Moreover, the very low value of $MoO_3$'s MSA is intriguing. It seems very small compared to other oxides although molybdenum trioxide seems to give the best performance. As it will be discussed hereafter, H-ZSM5 is a popular acid catalyst in an amine-based absorption-regeneration $CO_2$ capture process. Fig. 4 shows that several metal oxides outperform this zeolite, which is encouraging (although no data relating to the physicochemical properties of H-ZSM5 is provided).
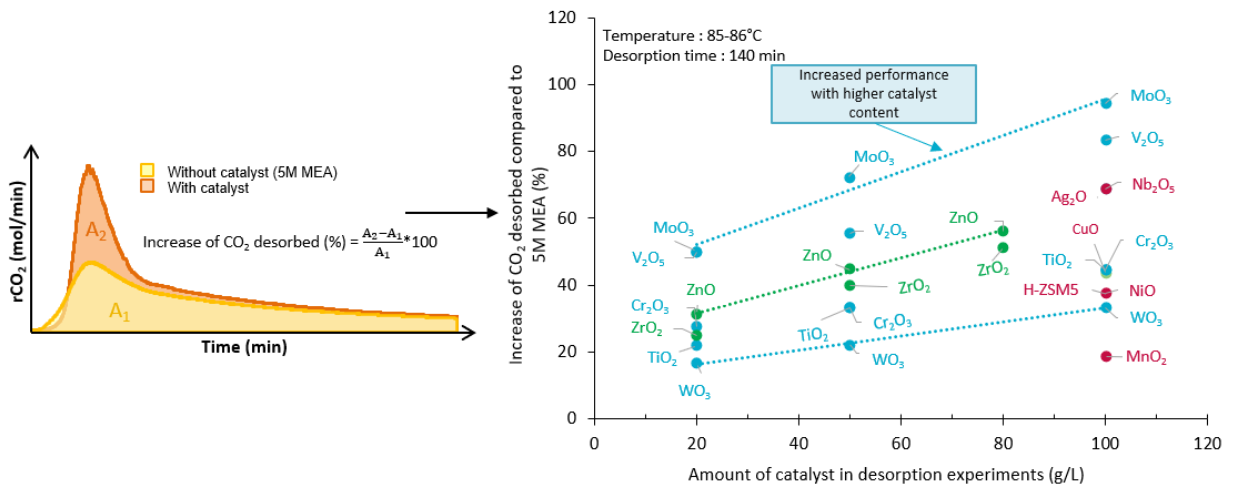


Fig. 4: Increased of $CO_2$ desorbed compared to 5M MEA vs Amount of catalyst. Data from [16] (blue), [27] (red) and [28] (green).

Regarding other materials, since a comparison between studies is not feasible, another strategy must be adopted. H-ZSM5 zeolite is widespread, and several studies experimentally test it under the same conditions as other catalysts. H-ZSM5 can therefore be used as a reference (Table 5). The performance of the metal oxides has just been discussed, but γ-$Al_2O_3$, which is widely used, was not included in the studies that were cross-referenced. Table 5 shows that the

increase in $CO_2$ desorption is similar when either $\gamma$-$Al_2O_3$ or H-ZSM5 is added with 5M MEA or with either a blended amine solvent (3M MEA 2.5 M AMP 0.5M PZ). This time, the results do not move in the same way as the B/L*MSA product, because according to the data from this study, the B/L*MSA product is almost twice as important for H-ZSM5 compared to $\gamma$-$Al_2O_3$. The authors [29] explain the result with the product MSA*TSA but the value of TSA for H-ZSM5 seems much higher compared to data from other studies (Table 2).

In the case of the zeolite group, H-Y does not seem a promising result with an increase of desorbed $CO_2$ of 8.4% compared to 19.5% achieved with H-ZSM5. According to the authors of this study [12], this observation is attributed to the lower MSA of H-Y which reduces the MSA*B/L factor (Table 2). In another paper, H-Mordenite, H-Beta and H-ZSM5 were investigated [13]. H-Beta shows superior performance to H-ZSM5. In fact, although H-Beta has slightly lower MSA than H-ZSM5, it contains many more acidic sites, which explain its promising catalytic effect. SAPO-34 zeolite shows much poorer results than H-ZSM5, due to a lower MSA*TSA factor [29]. However, the solvent is composed of a mixture of MEA, AMP and PZ, which may also have an influence. Moreover, as mentioned previously, the value of TSA for H-ZSM5 seems overestimated compared to data from other studies (Table 2).

The mesoporous silicate MCM-41 don't outperform H-ZSM5, with an increase in the amount of carbon dioxide released of 21.2% compared to 29.4%. This is explained by a low number of acidic sites, which consequently decreases the MSA*B/L factor (Table 2 and Table 3). SBA-15 shows the same results as H-ZSM5. Unfortunately, the chemical and physical properties of H-ZSM5 are not reported in the considered study. No studies testing both KIT-6 and H-ZSM5 were found in the literature. However, compared to the blank test, this mesoporous silicate increases the released $CO_2$ by more than 30%. This data was recorded after 20 min of desorption, while other tests last on average 1.5-2 hours. At this stage, only a small amount of $CO_2$ is generally desorbed, so in relative terms, this may appear significant, whereas in absolute terms, the values are very close. Moreover, the smaller the quantity, the greater the experimental error.

Natural clays also cannot be directly compared to H-ZSM5. Attapulgite shows a huge increase of more than 60%, which may be surprising given its physicochemical properties (Table 4). The same remark as for KIT-6, i.e. in this case desorption only lasted around 20 min. Finally, montmorillonite shows a moderate increase of 13.4%.

Table 5: Increased of $CO_2$ desorbed compared to 5M MEA.

| Catalyst | Solvent | Temperature (°C) | Desorption time (min) | Catalyst concentration (g/L) | Increase of $CO_2$ desorbed compared to blank test (%) | Reference |
|---|---|---|---|---|---|---|
| H-ZSM5 | 5M MEA | 105 | 120 | 15 | 19.5 | Liang et al. (2016) [12] |
| H-Y | | | | | 8.4 | Liang et al. (2016) [12] |
| H-ZSM5 | 5M MEA | 98 | 90 | 12.5 | 20.7 | Zhang et al. (2019) [13] |
| $\gamma$-$Al_2O_3$ | | | | | 19.4 | Zhang et al. (2019) [13] |
| H-Mordenite | | | | | 15.7 | Zhang et al. (2019) [13] |
| H-Beta | | | | | 29.1 | Zhang et al. (2019) [13] |
| H-ZSM5 | 3M MEA | 96 | 120 | 12.5 | 22.8 | Zhang et al. (2018) [29] |
| $\gamma$-$Al_2O_3$ | 2.5 M AMP | | | | 19.0 | Zhang et al. (2018) [29] |
| SAPO-34 | 0.5M PZ | | | | 10.1 | Zhang et al. (2018) [29] |
| H-ZSM5 | 5M MEA | 98 | 90 | 12.5 | 29.4 | Liu et al. (2017) [25] |
| MCM-41 | | | | | 21.2 | Liu et al. (2017) [25] |
| H-ZSM5 | 5M MEA | 97.5 | 60 | 12.5 | 14.8 | Gao et al. (2020) [33] |
| SBA-15 | | | | | 14.8 | Gao et al. (2020) [33] |
| KIT-6 | 5M MEA | 100 | 20 | 12.5 | 31.0 | Zhang et al. (2022) [21] |
| Attapulgite | 5M MEA | 88 | 20.8 | 12.5 | 60.9 | Tan et al. (2023) [34] |
| Montmorillonite | 5M MEA | 86 | 60 | 50 | 13.4 | Bhatti et al. (2021) [35] |

### 3.3. Economic criteria

It is important to consider an economic criterion in order to select a catalyst that offers best performance at the lowest possible cost. Indeed, the price of the catalyst can be a limiting factor for the large-scale deployment of the catalytic $CO_2$ capture. This consideration is not straightforward to address, as prices depend directly on purity, required quantity, suppliers, and therefore on partnerships and geographical locations.

As previously performed, the comparison is based on a reference, H-ZSM5. Prices are those available at lab scale, excluding VAT and transport costs. The minimum purity of metal oxides is 98%. Fig. 5 shows the ratio between the price of the considered catalyst and that of H-ZSM5. Overall, metal oxides have a reasonable price with a catalyst price/H-ZSM5 price of less than 5. Only $Nb_2O_5$ and $Ag_2O$ are respectively 20 and 34 times more expensive than H-ZSM5. Concerning zeolites, SAPO-34 is the most expensive one. Indeed, H-Y, H-Beta and H-Mordenite have prices very close to H-ZSM5. However, mesoporous silicates have extremely high prices, reaching up to nearly 350 times that of H-ZSM5. Regarding natural clays, the price of montmorillonite is similar to that H-ZSM5, unlike attapulgite, which is significantly more expensive.
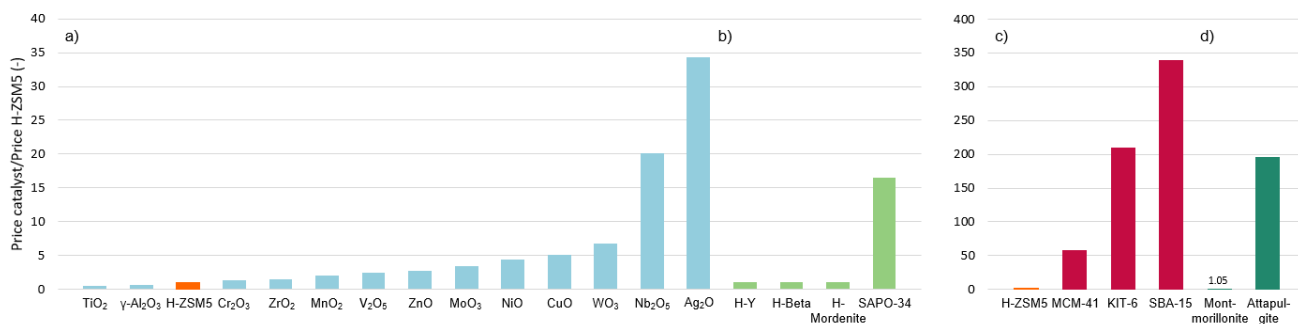


Fig. 5: Price catalyst/Price H-ZSM5 of considered catalysts. (a) metal oxides. (b) zeolites. (c) mesoporous silicas. (d) natural clays.

### 3.4. Safety and environmental considerations

In a more conscientious approach, the impact of the use of the catalyst on human health and the environment must be considered before scaling up the process. Once inserted into the regeneration column, the catalyst is not in contact with people or with the outside environment. However, on one hand, laboratory tests during the research period involve handling these products by humans more frequently. Moreover, residues may be exposed to the external environment, particularly aquatic systems, through the cleaning of laboratory equipment. On the other hand, at industrial scale, the stages of catalyst production/synthesis, transportation, handling to the column, and cleaning of equipment can lead to health and environmental risks. That is why hazard statements associated with catalysts are analyzed and are listed in Table 6 according to the harmonized classification by the European Chemical Agency (ECHA) [36].

Several hazard statements are particularly striking for the human health and the environment: H330, H350, H350i, H362, H372, H400 and H410 (codification is detailed in Table 7). $V_2O_5$, NiO, CuO and ZnO have one or more of these hazard statements and a particular attention is given on this aspect during the selection process. $V_2O_5$ has several (Table 6), so it is eliminated from the selection. Others hazard statements are less compelling, but still deserve attention: H301, H318, H341, H351, H361fd, H373, H411 and H413. Products presenting these hazard statements are not directly excluding, but it is considered in the selection methodology along with performance and cost criteria.

Metal oxides often present risks when they are used, for example $MoO_3$ and $TiO_2$ are suspected of causing cancer (H351), NiO may cause damage to organs through prolonged or repeated exposure if inhaled (H373), etc. Although some metal oxides do not seem to present any particular risk: $Cr_2O_3$, $Nb_2O_5$, $ZrO_2$. Zeolites, mesoporous silicas and natural clays are considered safe.

*Table 6: Hazard statements of considered catalysts.*

| Catalyst | Hazard statement codes | Catalyst | Hazard statement codes | Catalyst | Hazard statement codes |
|---|---|---|---|---|---|
| $MoO_3$ | H319; H335; H351 | CuO | H400; H410 | H-Beta | / |
| $V_2O_5$ | H301; H330; H335; H341; H350; H361fd; H362; H372; H411 | $MnO_2$ | H302; H332 | SAPO-34 | / |
| $Cr_2O_3$ | / | ZnO | H400; H410 | MCM-41 | / |
| $TiO_2$ | H351 | $ZrO_2$ | / | SBA-15 | / |
| $WO_3$ | / | $\gamma$-$Al_2O_3$ | / | KIT-6 | / |
| $Nb_2O_5$ | / | H-ZSM5 | / | Attapulgite | / |
| $Ag_2O$ | / | H-Y | / | Montmorillonite | / |
| NiO | H317; H350i; H372; H413 | H-Mordenite | / | | |

*Table 7: Codification of hazard statements.*

| | Hazard statements |
|---|---|
| H301: Toxic if swallowed. | H351: Suspected of causing cancer. |
| H302: Harmful if swallowed. | H361fd: Suspected of damaging fertility. Suspected of damaging the unborn child. |
| H317: May cause an allergic skin reaction. | H362: May cause harm to breast-fed children. |
| H319: Cause serious eye irritation. | H372: Causes damage to organs to prolonged or repeated exposure. |
| H330: Fatal if inhaled. | H400: Very toxic to aquatic life. |
| H332: Harmful if inhaled. | H410: Very toxic to aquatic life with long lasting effects. |
| H335: May cause respiratory irritation. | H411: Toxic to aquatic life with long lasting effects. |
| H341: Suspected of causing genetic defects | H413: May cause long lasting harmful effects to aquatic life. |
| H350: May cause cancer. H350i: May cause cancer by inhalation. | |

## 3.5. Discussion

The previous paragraphs aimed to collect the available data on the various catalysts in terms of physical and chemical properties, performances, cost and the risks to people and the environment associated with their use. Based on this information, the least interesting catalysts are discarded in order to retain the most promising ones. The pros and cons of the different catalysts and the final selection are summarised in Table 8.

### Metal oxides

Firstly, $MnO_2$, NiO and $WO_3$ were excluded due to their poor performance (Fig. 4). Moreover, from a safety perspective, NiO presents increased risks to human health (H372). Although $WO_3$ presents no particular risk, it is more expensive than $TiO_2$ and $Cr_2O_3$ (Fig. 5). Additionally, $TiO_2$ and $Cr_2O_3$ allow the desorption of a greater amount of $CO_2$ than $WO_3$ following the study of Bhatti et al. [27] (Fig. 4). That is why $WO_3$ is rejected. Whatever the catalyst concentration, $TiO_2$ and $Cr_2O_3$ consistently exhibit very close performance in the middle of the ranking. In addition, at a concentration of 100 g/L, CuO also shows similar performance. Furthermore, their prices are entirely affordable. However, CuO poses increased risks to aquatic life (H410) and $TiO_2$ is suspected of causing cancer (H351). Therefore, $Cr_2O_3$, which poses no particular risk, has been selected. ZnO and $ZrO_2$ perform well. However, ZnO presents risks for the aquatic ecosystem (H410) and is more expensive. Between these two metal oxides, $ZrO_2$ was chosen. Then, $Ag_2O$ demonstrated good results, but this compound is the most expensive metal oxide. $Nb_2O_5$, which performs similarly to $Ag_2O$, presents no particular risk and is less expensive, so $Nb_2O_5$ is retained. $V_2O_5$ demonstrates very good performance and a reasonable price. However, as previously outlined it is highly toxic and dangerous. Indeed, it can be carcinogenic (H350), fatal if inhaled (H330), cause damage to organs on prolonged or repeated exposure (H372). Afterwards, $MoO_3$ achieves the highest amount of $CO_2$ release (Fig. 4) despite an extremely low MSA (Table 1), which is somewhat surprising. Additionally, the cost of this material is reasonable. The only drawback is that it is

suspected of being carcinogenic (H351). However, $MoO_3$ is selected due to its impressive performance. Obviously, specialized protective equipment must be used to mitigate any risks. Finally, $\gamma$-$Al_2O_3$ was not studied under the same conditions as the other metal oxides but is extensively investigated in $CO_2$ catalytic desorption and offers similar performance to H-ZSM5. In summary, the following metal oxides are selected: $Cr_2O_3$, $ZrO_2$, $Nb_2O_5$, $MoO_3$, and $\gamma$-$Al_2O_3$.

### Zeolites

First of all, the H-Y zeolite has good SSA but low MSA (Table *2*), and the experiments (Table 5) clearly showed poorer performance compared to H-ZSM5. Therefore, H-Y does not appear to be a promising candidate. Furthermore, similarly to H-Y, H-Mordenite exhibits a large SSA but a low MSA. However, it possesses a high concentration of TAS, resulting in a high B/L ratio of 42.7 (Table 2). The price is quite similar to H-ZSM5, but the performance of H-Mordenite is slightly lower (Table 5). Nonetheless, it would be worthwhile to explore this zeolite further. Regarding H-Beta, it has a good mesoporous surface area and a very high concentration of Brønsted acid sites (and a B/L ratio) (Table 2). Moreover, H-Beta showed better performance than H-ZSM5 (Table 5) at a similar price. Consequently, H-beta is retained in this selection. SAPO-34 has a very large surface area but a lower number of acid sites compared to H-Mordenite and H-Beta (Table 2). In terms of increase of desorbed amount of CO2, SAPO-34 is significantly less effective than H-ZSM5 (even though, as previously mentioned, the TAS of H-ZSM5 reported in the study is much higher than that reported in other studies (Table 2) [29] ) (Table 5). Additionally, SAPO-34 is much more expensive than H-ZSM5. Hence, this zeolite is not selected. Finally, H-ZSM5 is logically selected, as it is widely used in literature and serves as a reference in the present selection.

### Mesoporous silicates

MCM-41 has an excellent total and mesoporous specific area but very few acid sites, which leads to poorer performance than H-ZSM5 under identical conditions. SBA-15 is slightly more acidic than MCM-41 but much less than several zeolites such as H-Beta or H-mordenite. Regarding the amount of $CO_2$ released during a desorption test, SBA-15 and H-ZSM5 shows the same results. The last mesoporous silica studied is KIT-6, which has an excellent MSA and a good number of acid sites. As discussed previously, results obtained with this catalyst are encouraging but the desorption time was very short. Therefore, this result should be treated with caution. Finally, a common characteristic of these three candidates is their extremely high cost: they are 50 to almost 350 times more expensive than H-ZSM5. The performance of these catalysts is not high enough to accept such a price difference. Consequently, no mesoporous silica was retained in this selection.

### Natural clays

Attapulgite, the first natural clay considered in this study, has a moderate MSA but an extremely low concentration of acid sites and is expensive. In terms of performance, it appears to be very encouraging but once again the desorption time is very short, which may inflate the increase in the amount of $CO_2$ released compared with the case without the catalyst. The second one is montmorillonite which has no particularly good properties. This material is safe to use and has a reasonable price. As with attapulgite, there is no comparison with H-ZSM5 but compared to the base case without catalyst, the amount of desorbed $CO_2$ is slightly higher. In view of these arguments, the natural clays group is not retained in this selection.

*Table 8: Summary of the strengths and weaknesses of the different catalysts and selected candidates.*

| Catalyst | Physicochemical properties | $CO_2$ desorption performances | Economic criteria | Safety aspect | Selected |
|---|---|---|---|---|---|
| **MoO₃** | - - | ++ | + | - | **Yes** |
| V₂O₅ | - | ++ | + | - - | No |
| **Cr₂O₃** | - | + | + | ++ | **Yes** |
| TiO₂ | - | + | ++ | - | No |
| WO₃ | - | - - | - | ++ | No |
| **Nb₂O₅** | / | + | - | ++ | **Yes** |
| Ag₂O | / | + | - - | ++ | No |
| NiO | / | - | + | - - | No |
| CuO | / | + | + | - - | No |
| MnO₂ | / | - - | + | - | No |
| ZnO | - | + | + | - - | No |
| **ZrO₂** | - | + | + | ++ | **Yes** |
| **γ-Al₂O₃** | + | - | ++ | ++ | **Yes** |
| **H-ZSM5** | + | + | + | ++ | **Yes** |
| H-Y | + | - - | + | ++ | No |
| **H-Mordenite** | + | - | + | ++ | **Yes** |
| **H-Beta** | + + | + | + | ++ | **Yes** |
| SAPO-34 | + | - - | - | ++ | No |
| MCM-41 | - | - | - - | ++ | No |
| SBA-15 | - | - | - - | ++ | No |
| KIT-6 | + | - | - - | ++ | No |
| Attapulgite | - - | + | - - | ++ | No |
| Montmorillonite | - | - - | + | ++ | No |

## 4. Conclusion

In the context of Carbon Capture Utilization and Storage (CCUS) development, the use of solid acid catalysts (SACs) for the regeneration of amine solvents represents a significant advancement in reducing the energy costs associated with this process. This work evaluated various SAC candidates, including metal oxides, zeolites, mesoporous silicas and natural clays, based on four main criteria: physicochemical properties, performance, cost, and associated risks.

Among the physicochemical properties, a large mesoporous surface area is necessary to allow chemical species to reach the catalytic sites. Additionally, the catalytic mechanism is governed by Lewis and Brønsted sites whose number must be maximized on the catalyst. Moreover, several experimental studies have shown that the performance of a catalyst is directly related to the product MSA*B/L. However, comparing performances across different studies is difficult due to the variability in operational conditions (e.g. temperature, experiment duration, catalyst concentration…). Therefore, most catalysts have been compared to the H-ZSM5 zeolite, which is widely referenced in the literature. Some materials, such as MoO₃, V₂O₅, Nb₂O₅, H-Beta, have shown promising results. From an economic standpoint, it has been found that prices vary significantly across different material categories. Indeed, metal oxides and zeolites are reasonably priced, whereas mesoporous silicates are extremely expensive. Finally, the hazard statements from the harmonized classification established by the European Chemical Agency (ECHA) led to the elimination of certain materials, such as V₂O₅, which presented both good performance and cost but posed significant

risks. As a final point, when considering all the criteria, the most promising candidates are metal oxides such as $\gamma$-$Al_2O_3$, $ZrO_2$, $Cr_2O_3$, $Nb_2O_5$, and $MoO_3$, along with the zeolites H-ZSM5, H-Mordenite, and H-Beta.

Ultimately, the integration of these catalysts in industrial amine-based $CO_2$ capture processes could lower energy demands, enhance solvent stability, and reduce operational costs. As next step, the different selected catalysts will be tested at lab and micro-pilot scales. The purpose is to compare their performances at the same operating conditions and on the similar experimental device and associated operating conditions, which is still missing in the existing literature. Further research should also focus on other aspects such as catalyst stability, recyclability, and the potential poisoning from other compounds like SOx and NOx present in flue gases. Additionally, techno-economic studies should be conducted on larger-scale installations to fully harness the benefits of catalytic solvent regeneration, especially for applications involving varying $CO_2$ concentrations.

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