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# Design rules for ternary CO<sub>2</sub> hydrogenation catalysts *via* literature-sourced network construction and analysis

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The development of CO<sub>2</sub> hydrogenation catalysts has largely depended on researchers's trial and error efforts. However, exploring unreported ternary catalysts requires substantial time and cost, highlighting the need for more efficient screening strategies. This study adopts a data-driven informatics approach where literature data is restructured into networks to reveal systematic relationships between reaction conditions and CO<sub>2</sub> conversion. Knowledge extracted from the catalyst combination network further enables the identification of promising ternary catalysts. NiMnPr/Al<sub>2</sub>O<sub>3</sub> and NiMnCe/Al<sub>2</sub>O<sub>3</sub> for CO<sub>2</sub> hydrogenation are rapidly identified and experimentally validated, exhibiting higher CO<sub>2</sub> conversion than their corresponding binary catalysts. Moreover, detailed characterization is carried out for NiMnPr/Al<sub>2</sub>O<sub>3</sub>. These findings and analysis demonstrate that mapping multidimensional data into networks provides a powerful strategy for uncovering correlated variables and facilitating intuitive, highly efficient catalyst development and understanding.

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## 1 Introduction

CO<sub>2</sub> hydrogenation, the conversion of carbon dioxide into methane, is a crucial reaction in contexts such as carbon neutrality and space technologies.<sup>1–5</sup> Catalysts centered on Ru and Ni have been explored to date.<sup>6–12</sup> Ru has demonstrated activity at low temperature but is expensive and scarce. Meanwhile, Ni is inexpensive but faces challenges of exhibiting higher reaction temperature and lower catalytic activity compared with Ru.<sup>13–15</sup> Since Ru-based catalysts are limited by high cost and scarcity, developing Ni-based catalysts with high performance at low temperature is a critical strategy for the practical application of CO<sub>2</sub> hydrogenation.<sup>16,17</sup> In particular, previous catalyst explorations have largely centered on binary catalysts *via* trial-and-error approaches, whereas ternary catalysts remain unexplored.<sup>18</sup> Given that specific combinations of elements can generate synergistic interactions, in which the catalytic activity deviates from that of the individual components or their simple average, ternary systems hold strong potential.<sup>19</sup> Therefore, ternary catalysts are explored as they may

realize synergistic performance gains unattainable with binary formulations.

Trial-and-error catalyst development is often inefficient in terms of both cost and time.<sup>20</sup> In contrast, data-driven catalyst informatics can extract hidden trends and patterns from diverse variables in catalysts data, thereby offering opportunities for more efficient and useful catalyst discovery.<sup>21–24</sup> Machine learning has been used to successfully discover previously unreported and potentially promising catalysts.<sup>25,26</sup> However, a major challenge lies in the black-box nature of machine learning, which obscures both the reasoning behind the predictions and the underlying learning process in the dataset.<sup>27</sup> To address this problem, catalyst network analysis utilizing graph theory has emerged. This approach visualizes the relationship between catalytic activity and multidimensional variables, providing human-readable insights.<sup>28–30</sup> Based on the positional relationships within the network, it enables reaction condition optimization, efficient catalyst screening, and catalyst design.

Based on the above context and challenges, multidimensional analysis and ternary catalysts design through catalyst screening are performed for CO<sub>2</sub> hydrogenation dataset. Network construction and analysis are used in order to better understand the relationship between multidimensional factors and CO<sub>2</sub> conversion and to improve the efficiency of ternary catalyst design from binary catalysts data, thereby providing a means for accelerated catalysts exploration.

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## 2 Method

### 2.1 Data details

A dataset comprising 4051 entries collected from 100 papers is used for the network analysis of catalytic studies.<sup>26</sup> Table 1 summarizes the category of the dataset and their features. After removing entries containing missing values, 3531 entries are employed for network construction.

### 2.2 Preprocessing for network construction

To construct the network, the following features are utilized and preprocessed: base, base wt%, base 2, base 2 wt%, support, support wt%, calcination temperature (°C), calcination time (h), temperature (°C), W/F (mg<sub>cat</sub> mL min<sup>-1</sup>), inert% in feed, and CO<sub>2</sub> conversion%. To better understand the relationship between catalyst information and catalyst activity, base wt%, base 2 wt%, support wt%, and CO<sub>2</sub> conversion% are clustered using the one dimensional K-means algorithm. The number of clusters for each dataset is decided based on the distribution of each variables. By this algorithm, base wt% is clustered into 5 bins (0.0–7.0%, 7.5–15.0%, 17.0–26.0%, 27.5–40.0%, 47.0–100.0%), base 2 wt% into 4 bins (0.0–3.0%, 4.0–10.0%, 12.5–17.0%, 25.0–37.5%), support wt% into 4 bins (0.0–60.7%, 62.5–80.0%, 81.0–91.5%, 92.0–100.0%), and CO<sub>2</sub> conversion into 10 bins (0.0–5.61%, 5.63–14.15%, 14.19–24.52%, 24.62–35.37%, 35.4–46.03%, 46.08–56.88%, 57.0–67.53%, 67.59–77.5%, 77.52–88.38%, 88.41–100.0%).

Two networks, N-1 and N-2, are constructed in this work. For N-1 network, each catalyst element is represented as a node along with its respective content. Here, nodes are defined as vertices which represents base, base 2, support, calcination temperature,

calcination time, temperature, W/F, inert gas, CO<sub>2</sub> conversion. Edges are links that are added between CO<sub>2</sub> conversion and each of the other variables (base, base 2, support, calcination temperature (°C), calcination time (h), temperature (°C), W/F, inert% in feed) when the corresponding pair is observed together within the same record in the dataset. Note that this is purely a visualization outcome of the layout algorithm, and the geometric distances should not be interpreted as precise numerical distances since nodes sharing more edges are placed closer to each other. The layouts of both networks are constructed as undirected graphs *via* ForceAtlas2 algorithm within Gephi application to visualize the relationship of between CO<sub>2</sub> conversion and other features.<sup>31,32</sup> The edge weight is set to 1 for both networks. Node size is determined by degree ranking within a range of 10 to 40. Additionally, for visibility purposes, the labels are represented in a simplified manner on the network: base as b, base 2 as b2, support as s, calcination temperature as cTemp, calcination time as cTime, temperature as T, W/F as W/F, inert in feed as inert, and CO<sub>2</sub> conversion as conv. For example, one data (base: Ni, base wt%: 10.0, base 2: none, base 2 wt%: 0.0, support: Al<sub>2</sub>O<sub>3</sub>, support: wt%: 90.0, calcination temperature (°C): 600, calcination time (h): 4.0, temperature (°C): 350, W/F: 5.26, inert in feed%: 21.0, CO<sub>2</sub> conversion%: 25.552) of the network N-1 is represented as nodes: b-Ni: 7.5–15.0, b2-None, s-Al<sub>2</sub>O<sub>3</sub>: 81.0–91.5, cTemp: 600, cTime: 4.0, temp: 350, W/F: 5.26, inert: 21.0, and conv: 24.62–35.37 as shown in Fig. S1. In the network N-2, nodes are constructed by combining base and base 2 to represent the catalyst combinations. For example, one data (base: Ni, base wt%: 10.0, base 2: none, base 2 wt%: 0.0, support: Al<sub>2</sub>O<sub>3</sub>, support: wt%: 90.0, calcination temperature (°C): 600, calcination time (h): 4.0, temperature (°C): 350, W/F: 5.26, inert in feed%: 21.0, CO<sub>2</sub> conversion%: 25.552) is represented as nodes: Ni(7.5–15.0)None(), s-Al<sub>2</sub>O<sub>3</sub>: 81.0–91.5, cTemp: 600, cTime: 4.0, T: 350, W/F: 5.26, inert: 21.0, and conv: 24.62–35.37 as shown in Fig. S2.

Table 1 The features and their explanations in the dataset<sup>26</sup>

Category	Features
Catalyst information	Base Base wt% Base 2 Base 2 wt% Support Support wt% Support 2
Preparation condition	Catalyst preparation method Calcination temperature (°C) Calcination time (h) Reduction temperature (°C) Reduction pressure (bar) Reduction time (h) Reduction H <sub>2</sub> %
Reaction condition	Temperature (°C) Pressure (bar) W/F (mg <sub>cat</sub> mL min <sup>-1</sup> ) Time on stream (h) CO% in feed Inert% in feed CH <sub>4</sub> % in feed H <sub>2</sub> O% in feed H <sub>2</sub> /CO <sub>2</sub> % in feed
Catalyst activity	CO <sub>2</sub> conversion%

### 2.3 Experimental

**2.3.1 Catalyst preparation.** The tested catalysts are prepared by impregnating a support oxide with water-soluble metallic precursors in combinations presented on Table 2.

Table 2 M1–M2–M3 combinations of the prepared  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported catalysts

Label	M1	M2	M3
NiMnCe/Al <sub>2</sub> O <sub>3</sub>	Ce	Ni	Mn
NiMnPr/Al <sub>2</sub> O <sub>3</sub>	Pr	Ni	Mn
NiMnBa/Al <sub>2</sub> O <sub>3</sub>	Ba	Mn	Ni
NiMnCo/Al <sub>2</sub> O <sub>3</sub>	Mn	Co	Ni
NiMnNa/Al <sub>2</sub> O <sub>3</sub>	Na	Ni	Mn
NiMnFe/Al <sub>2</sub> O <sub>3</sub>	Mn	Fe	Ni
NiMn/Al <sub>2</sub> O <sub>3</sub>	Mn	Ni	—
NiCe/Al <sub>2</sub> O <sub>3</sub>	Ce	Ni	—
NiPr/Al <sub>2</sub> O <sub>3</sub>	Pr	Ni	—
MnPr/Al <sub>2</sub> O <sub>3</sub>	Pr	Mn	—
Ni/Al <sub>2</sub> O <sub>3</sub>	Ni	—	—
Mn/Al <sub>2</sub> O <sub>3</sub>	Mn	—	—
Pr/Al <sub>2</sub> O <sub>3</sub>	Pr	—	—



$\gamma$ -Alumina ( $\gamma$ - $\text{Al}_2\text{O}_3$ , Kojundo Chemical Laboratory Co., Ltd, 99.0%) is used as support for catalysts. Iron(III) nitrate non-hydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , min. 99.0%) from Junsei Chemical Co., Ltd and nickel(II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Wako Special Grade), manganese(II) acetate tetrahydrate ( $(\text{CH}_3\text{COO})_2\text{Mn}$ , Wako Special Grade), cerium(III) nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , Wako Special Grade), praseodymium(III) nitrate  $n$ -hydrate ( $\text{Pr}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ , 99.5%), barium acetate ( $\text{Ba}(\text{CH}_3\text{COO})_2$ , min. 99.0%), cobalt(II) acetate ( $(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$ , Wako Special Grade), and sodium nitrate ( $\text{NaNO}_3$ , min. 99.0%) from FUJIFILM Wako Pure Chemical Corporation are used as precursors for the impregnated metals in the catalysts.

All catalysts are synthesized according to the following procedure. 2 g of the support ( $\gamma$ - $\text{Al}_2\text{O}_3$ ) are dispersed in 100 mL

of pure water under continuous stirring. Separately, the metallic precursors for M1, M2 and M3 are each dissolved in 50 mL of pure water to achieve 5 wt% each in the final catalyst based on the calculated precursor quantities for complete impregnation. The metallic solutions are sequentially added to the support dispersion at 5 minutes intervals in M1–M2–M3 order. After stirring for 1 hour, the dispersion is aged 24 hours without stirring at room temperature. The stirring is restarted and the water is evaporated. The remaining powder is collected and dried at 80 °C for 12 hours. Finally, the material is ground in a mortar, calcined at 500 °C for 3.0 hours and ground again before testing. For comparison, unary and binary catalysts are also prepared by the same procedure.

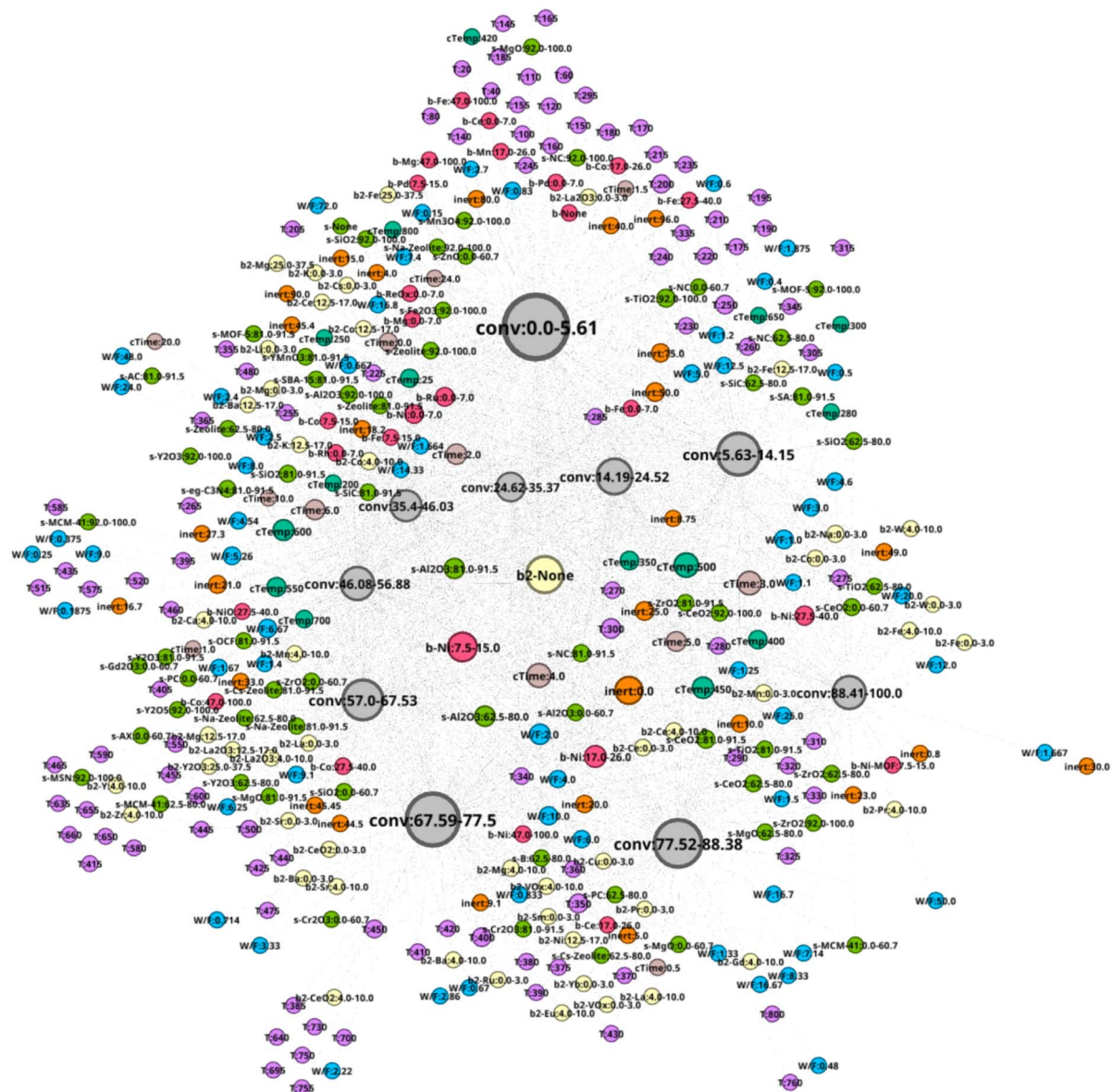


Fig. 1 The N-1 network. Each variable is color-coded: pink (base), yellow (base 2), green (support), emerald (calcination temperature (°C)), light brown (calcination time (h)), light purple (temperature (°C)), light blue (W/F ( $\text{mg}_{\text{cat}} \text{min}^{-1} \text{mL}^{-1}$ )), orange (inert% in feed), and gray ( $\text{CO}_2$  conversion, %). Note that labels are adjusted and node size is determined by degree ranking within a range of 10 to 40 for visualization purposes. A higher resolution of this network can be found in the SI.



**2.3.2 Catalyst activity and characterization.** Catalyst performance is tested in fixed-bed quartz reactor ( $L = 375$  mm,  $ID = 7.5$  mm) under ambient pressure. The catalyst powder (100 mg) is placed between two layers of quartz wool. The reactor temperature is monitored using a K-type thermocouple, with the tip placed near the outer reactor wall of the catalyst bed location. Prior to measurement run, the system is purged at  $50$  °C for 20–30 min under  $N_2$  gas at a flow of  $50$  mL  $min^{-1}$ , then cooled down under a  $N_2/H_2/CO_2$  flow of 25/20/5 mL  $min^{-1}$ . After measuring at room temperature and confirming the absence of impurities in the outlet flow, catalyst performance is studied at 150–450 °C at 50 °C intervals under the same gas flow conditions. The reaction mixture is analyzed by using a Shimadzu GC-2014 chromatograph equipped with a SHINCARBON ST 50/80 mesh column (3 mm  $\times$  2 m, He carrier).  $CO_2$  conversion and yield ( $CO$  and  $CH_4$ ) are estimated using  $N_2$  as an internal standard.  $CO_2$  conversion is calculated in accordance to eqn (1) product P yield for  $CO$  and  $CH_4$  is calculated in accordance to eqn (2), where  $n = 1$  for  $CO$  and  $CH_4$ . To ensure reproducibility, each catalyst is tested twice. The 12 hours durability testing is conducted on  $NiMnPr/Al_2O_3$  under  $H_2/CO_2$  of 4 at 450 °C.

$$CO_{2Conv} = \frac{(CO_{2In}/N_{2In}) - (CO_{2Out}/N_{2Out})}{(CO_{2In}/N_{2In})} \times 100 \quad (1)$$

$$P_{Yield} = \frac{n(P_{Out}/N_{2Out})}{(CO_{2In}/N_{2In})} \times 100 \quad (2)$$

$$P_{selectivity} = \frac{P_{yield}}{CO_{2Conv}} \times 100 \quad (3)$$

Scanning electron microscopy (JEOL Neo-Scope JCM-7000), and X-ray diffraction (Rigaku MiniFlex600-C) are used in order to obtain surface condition of samples and crystal structure.

XRD is performed to obtain diffraction pattern over the  $2\theta$  of 3–90 with a step size  $0.01^\circ$  and a scan of  $10^\circ$  per min.

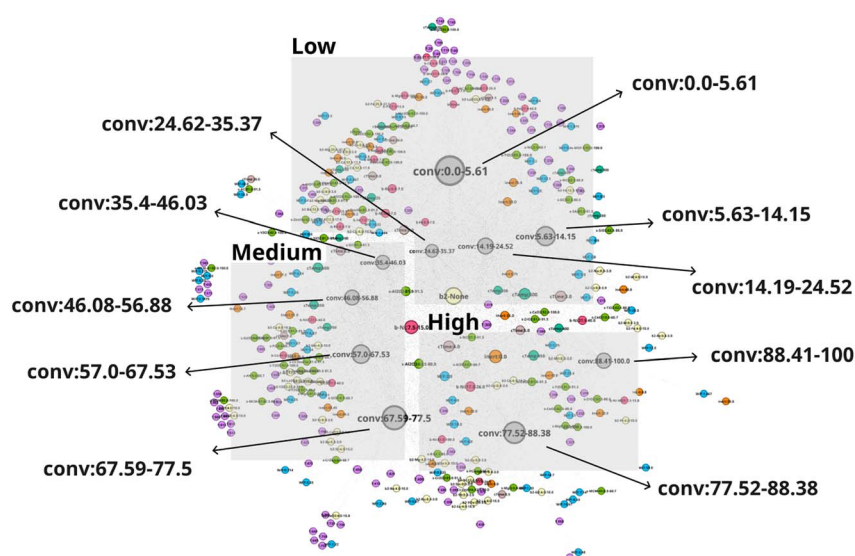
$CO_2$  uptake is performed to evaluate the  $CO_2$  adsorption-desorption properties. After degassing the samples at 300 °C for 2 h under vacuum to remove adsorbed moisture and surface impurities,  $CO_2$  adsorption-desorption measurements are carried out using a BELSORP MINI X.  $CO_2$  adsorption isotherms are obtained at room temperature (25 °C) by increasing the pressure from 0 to 100 kPa, and desorption are subsequently recorded by decreasing the pressure.

TPR profile is monitored with a TCD detector by BELCAT II system (MicrotracBEL, Co., Osaka, Japan). 50 mg of sample is pretreated under an He flow ( $30.0$  mL  $min^{-1}$ ) at 500 °C for 1 h, and cooled to 45 °C.  $H_2$ -TPR profile is observed under a 10 vol%  $H_2/Ar$  flow ( $30.0$  mL  $min^{-1}$ ) from 50 °C to 900 °C at the ramping rate of  $10.0$  °C  $min^{-1}$ . A molecular sieves 4A trap is placed at the line between an out-let of the sample bed and a TCD detector.

## 3 Result and discussion

### 3.1 Network construction and analysis

The network N-1 is constructed and analyzed to investigate the relationship between  $CO_2$  conversion and other features as shown in Fig. 1. Construction of the N-1 network results in an undirected network which has 360 nodes and 28 248 edges. The edge weight is set to 1. Node size is determined by degree ranking within a range of 10 to 40. Node placement is determined by the relationship of a node against all other nodes within the network. As seen in Fig. 2, the network structure reveals that nodes for  $CO_2$  conversion are placed in groups that can be interpreted as areas of low, medium, and high  $CO_2$  conversion. The nodes for  $CO_2$  conversion are defined as follows: low conversion: 0.00–5.61% and 5.63–14.15%; medium conversion: 35.40–46.03%, 46.08–56.88%, and 57.00–67.53%; high conversion: 35.40–46.03%, 46.08–56.88%, and 57.00–67.53%, as



**Fig. 2** A large picture of N-1. Each variable is color-coded: pink (base), yellow (base 2), green (support), emerald (calcination temperature (°C)), light brown (calcination time (h)), light purple (temperature (°C)), light blue ( $W/F$  ( $mg_{cat} min^{-1} mL^{-1}$ )), orange (inert% in feed), and gray ( $CO_2$  conversion, %). Areas up to 35.37% is defined as low  $CO_2$  conversion area, 35.4% to 77.5% is defined as medium  $CO_2$  conversion area, and greater than 77.52% is defined as high  $CO_2$  conversion area. A higher resolution of this network can be found in the SI.



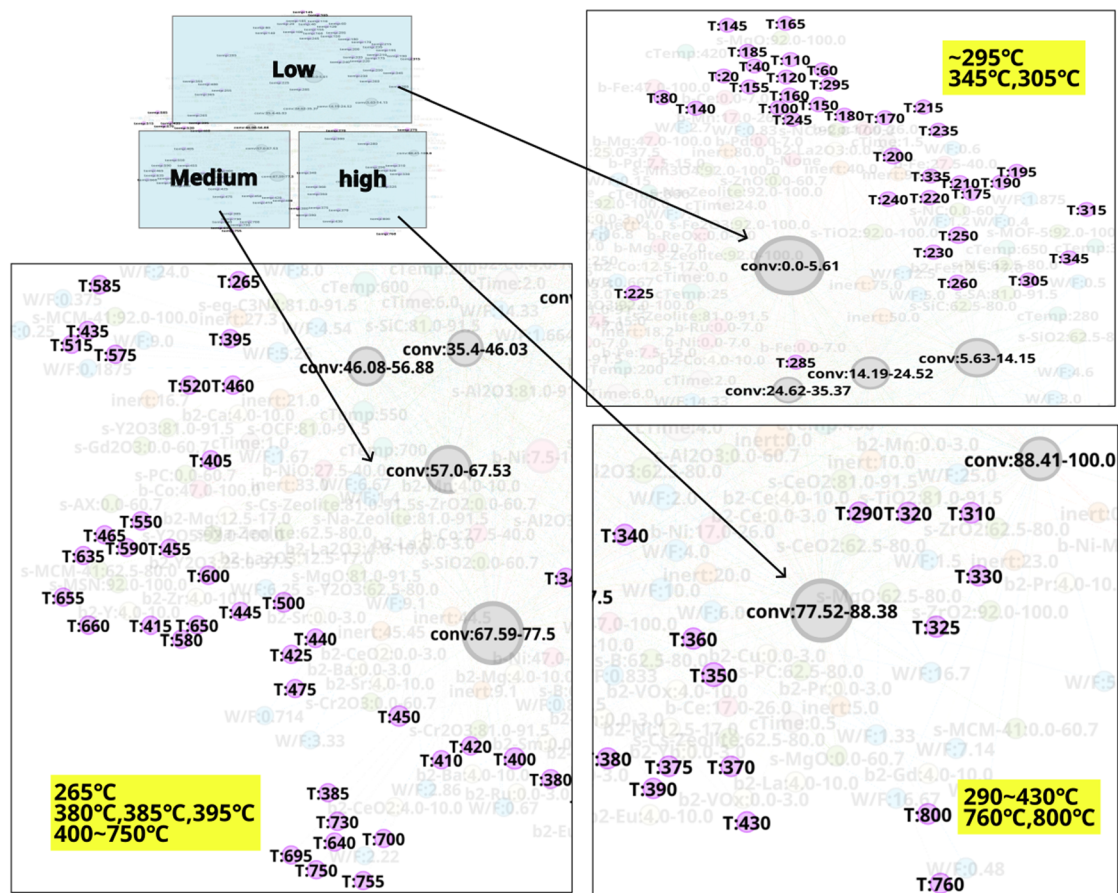


Fig. 3 Relationship between temperature ( $^{\circ}\text{C}$ ) and  $\text{CO}_2$  conversion (%) based on the N-1 network which shows enlarged views of regions where temperatures are concentrated. Nodes of temperature (light purple) and  $\text{CO}_2$  conversion (gray) are highlighted. Areas up to 35.37% is defined as low  $\text{CO}_2$  conversion area, 35.4% to 77.5% is defined as medium  $\text{CO}_2$  conversion area, and greater than 77.52% is defined as high  $\text{CO}_2$  conversion area. Note that labels are adjusted, and node size is determined by degree ranking within a range of 10 to 40 for visualization purposes. A higher resolution of this network can be found in the SI.

well as 67.59–77.5%; high conversion: 77.52–88.38% and 88.41–100%. By looking at nodes found within each  $\text{CO}_2$  conversion area, it becomes possible to understand the factors associated with that range of  $\text{CO}_2$  conversion, thereby making it possible to include multidimensionality during analysis.

N-1 is analyzed to investigate the relationship between experiment conditions and  $\text{CO}_2$  conversion. Temperature is found to exhibit a pronounced trend with  $\text{CO}_2$  conversion as shown in Fig. 3. Low temperature range below  $200\text{ }^{\circ}\text{C}$  strongly correlates to low  $\text{CO}_2$  conversion area. On the other hand,  $300\text{--}400\text{ }^{\circ}\text{C}$  temperature range is dispersed among low, medium, and high  $\text{CO}_2$  conversion area. This suggests that  $\text{CO}_2$  conversion may vary significantly depending on the catalyst composition and other experimental conditions within a temperature range of  $300\text{--}400\text{ }^{\circ}\text{C}$ ; in this situation, temperature may have less impact on  $\text{CO}_2$  conversion in comparison to other experimental factors. Temperature range of  $400\text{--}750\text{ }^{\circ}\text{C}$  mainly correlates to medium  $\text{CO}_2$  conversion range, whereas  $430\text{ }^{\circ}\text{C}$ ,  $800\text{ }^{\circ}\text{C}$ , and  $760\text{ }^{\circ}\text{C}$  is included to the high  $\text{CO}_2$  conversion area. The relationship between other variables and  $\text{CO}_2$  conversion is shown in Fig. 4. It can be seen that calcination temperatures

(cTemp) of  $400$  or  $450\text{ }^{\circ}\text{C}$  and calcination times (cTime) of  $0.5$ ,  $4.0$ , or  $5.0\text{ h}$  are associated with high  $\text{CO}_2$  conversion, whereas low or high calcination conditions (e.g.  $25\text{ }^{\circ}\text{C}$ ,  $650\text{ }^{\circ}\text{C}$ , or  $800\text{ }^{\circ}\text{C}$  and  $0$  or  $24$  hours) are included in the area of low  $\text{CO}_2$  conversion area. Therefore, intermediate calcination temperatures and times such as  $400\text{--}450\text{ }^{\circ}\text{C}$  and  $4\text{--}5$  hours, rather than low or high calcination temperatures and time, are possibly ideal conditions to consider for catalyst synthesis. As shown in Fig. 4, nodes with a high inert% in feed(inert) are associated with low  $\text{CO}_2$  conversion, thereby showing these conditions are likely to be undesirable for achieving efficient  $\text{CO}_2$  conversion. In this way, by converting literature data into a network and focusing on experimental conditions, it becomes possible to identify conditions that are effective for  $\text{CO}_2$  conversion as well as those that should be avoided.

The high  $\text{CO}_2$  conversion area in the N-1 network is focused to investigate the relationship between catalysts and  $\text{CO}_2$  conversion. As shown in Fig. 5, Ni, Ce, and Ni-MOF used as “base 1” exhibit high  $\text{CO}_2$  conversion. Na, Co, W, Fe, Mn, Pr, Ce,  $\text{VO}_x$ , Cu, Sm, Ni, Yb, La, Eu, Gd, and Ru are also included as “base 2.” Supports include  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$ , MgO, MCM-41, B,



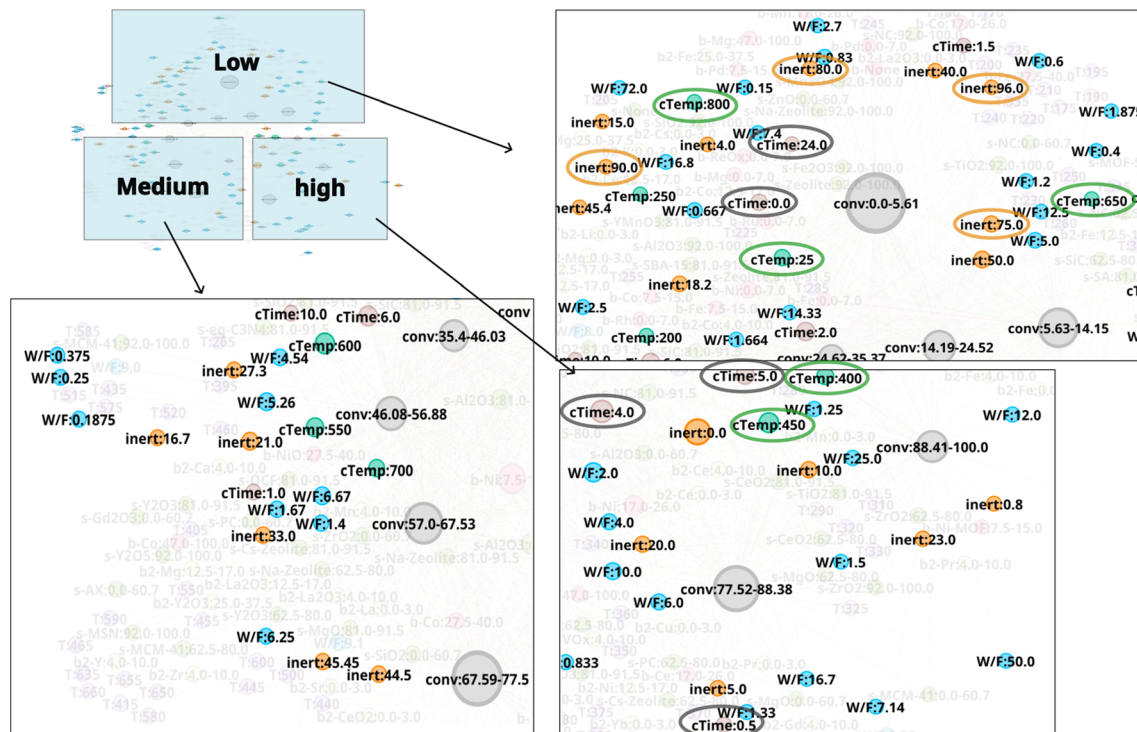


Fig. 4 Relationship between CO<sub>2</sub> conversion (%) and experimental conditions (W/F, inert%; calcination temperature (°C), cTemp; calcination time (h), cTime) based on the N-1 network. Areas up to 35.37% is defined as low CO<sub>2</sub> conversion area, 35.4% to 77.5% is defined as medium CO<sub>2</sub> conversion area, and greater than 77.52% is defined as high CO<sub>2</sub> conversion area. Note that labels are adjusted, and node size is determined by degree ranking within a range of 10 to 40 for visualization purposes. A higher resolution of this network can be found in the SI.

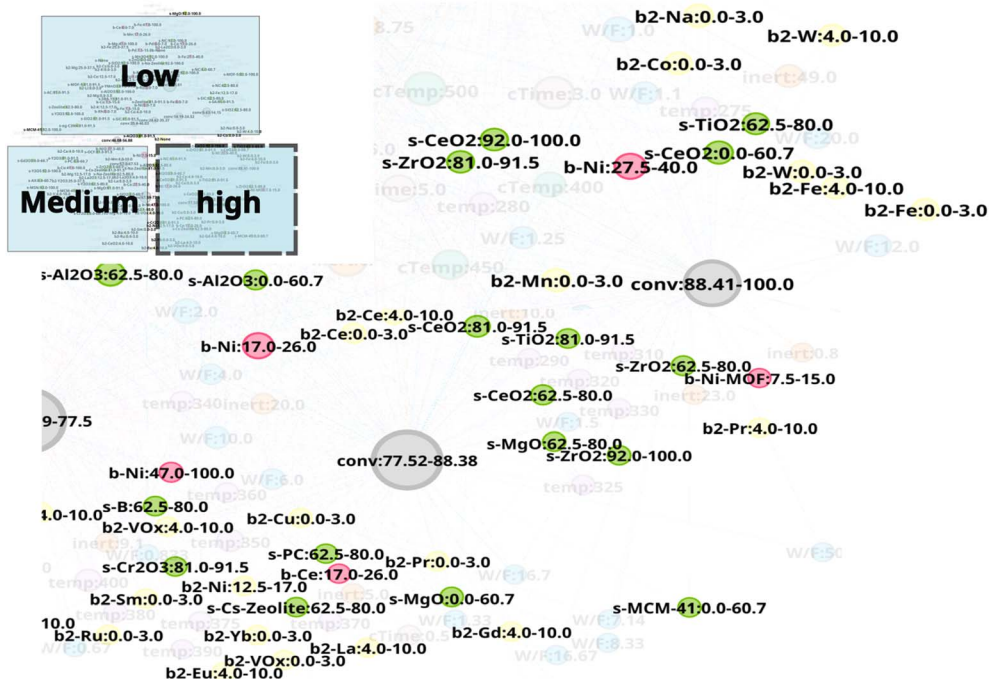


Fig. 5 Relationship between CO<sub>2</sub> conversion (%) and catalyst elements (base 1, b1, base 2, b2; support, s) based on the N-1 network. High CO<sub>2</sub> conversion area is enlarged. Areas up to 35.37% is defined as low CO<sub>2</sub> conversion area, 35.4% to 77.5% is defined as medium CO<sub>2</sub> conversion area, and greater than 77.52% is defined as high CO<sub>2</sub> conversion area. Note that labels are adjusted, and node size is determined by degree ranking within a range of 10 to 40 for visualization purposes. A higher resolution of this network can be found in the SI.



Cr<sub>2</sub>O<sub>3</sub>, PC (porous carbon), Al<sub>2</sub>O<sub>3</sub>, and Cs-zeolite. Although these elements and supports are correlated with high CO<sub>2</sub> conversion, it is necessary to investigate the relationship between CO<sub>2</sub> conversion and catalyst combinations of base 1 and base 2 for a better understanding.

### 3.2 Catalyst screening

Another network, N-2, is constructed to explore catalyst combinations and screen for promising combinations. The N-2 network is constructed to investigate the relationship between catalyst combinations and CO<sub>2</sub> conversion as shown in Fig. 6. As shown in Fig. S2, base 1 and base 2 are represented as single nodes, and the relationship between element pairs and CO<sub>2</sub> conversion clarifies whether those pairs are effective in improving CO<sub>2</sub> conversion. It results in an undirected network

which has 379 nodes and 24 717 edges. The edge weight is set to 1. Node size is determined by degree ranking within a range of 10 to 40. Similarly to the case of the N-1 network, the network structure reveals that nodes for CO<sub>2</sub> conversion are placed in groups that can be interpreted as areas of low, medium, and high CO<sub>2</sub> conversion as shown in Fig. 7. The nodes for CO<sub>2</sub> conversion are defined as follows: low conversion: 0.00–5.61% and 5.63–14.15%; medium conversion: 35.40–46.03%, 46.08–56.88%, and 57.00–67.53%, as well as 67.59–77.50%; and high conversion: 77.52–88.38% and 88.41–100%. By looking at nodes included in each CO<sub>2</sub> conversion area, it becomes possible to understand chemical element combinations associated with that particular range of CO<sub>2</sub> conversion. This, therefore, makes it possible to include compatibility of each combination during analysis.

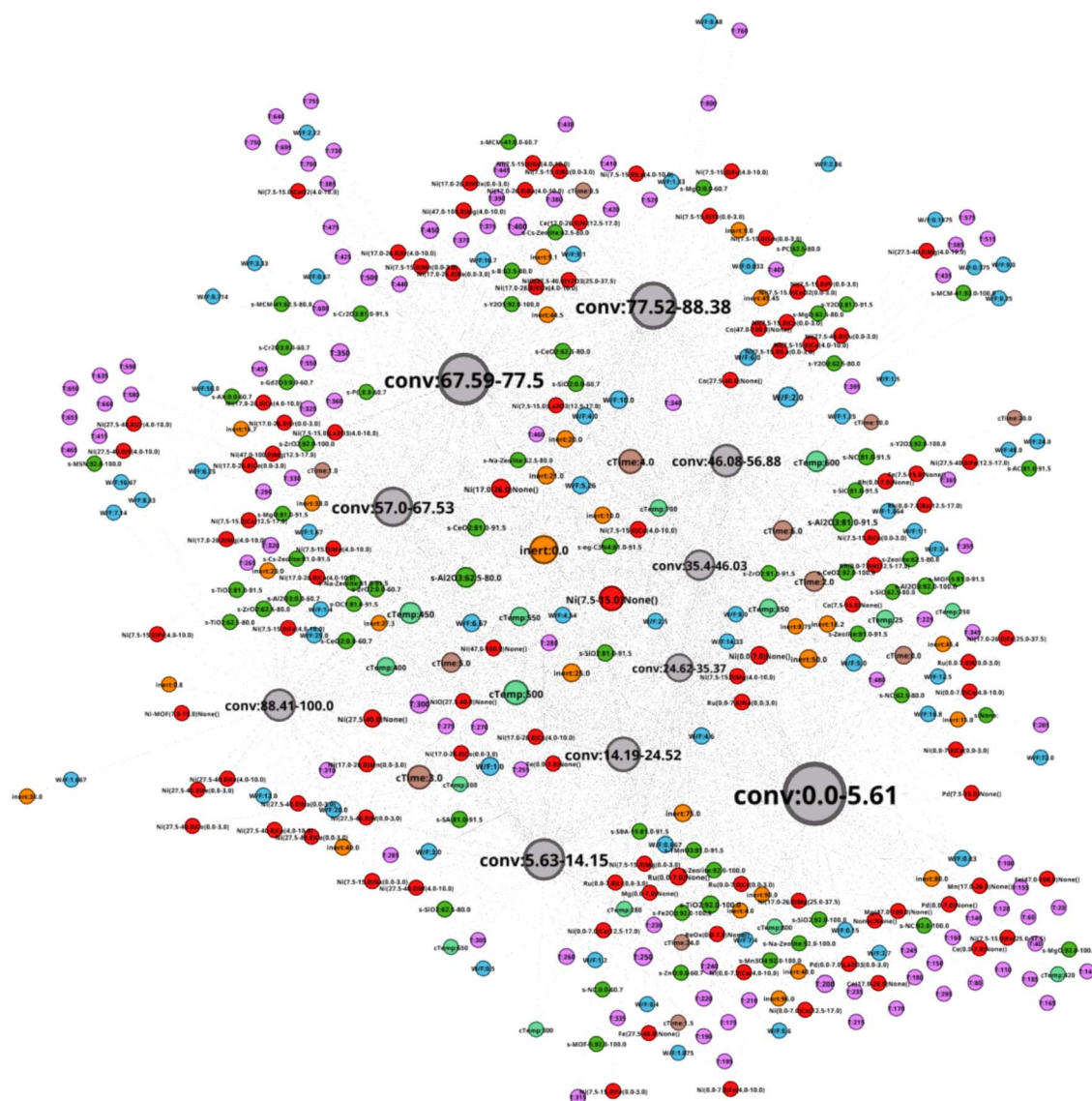


Fig. 6 The N-2 network. Each variables is color-coded: red (catalyst), green (support), emerald (calcination temperature (°C)), light brown (calcination time (h)), light purple (temperature (°C)), light blue (W/F (mg<sub>cat</sub> min<sup>-1</sup> mL<sup>-1</sup>)), orange (inert% in feed), and gray (CO<sub>2</sub> conversion, %). Note that labels are adjusted and node size is determined by degree ranking within a range of 10 to 40 for visualization purposes. A higher resolution of this network can be found in the SI.



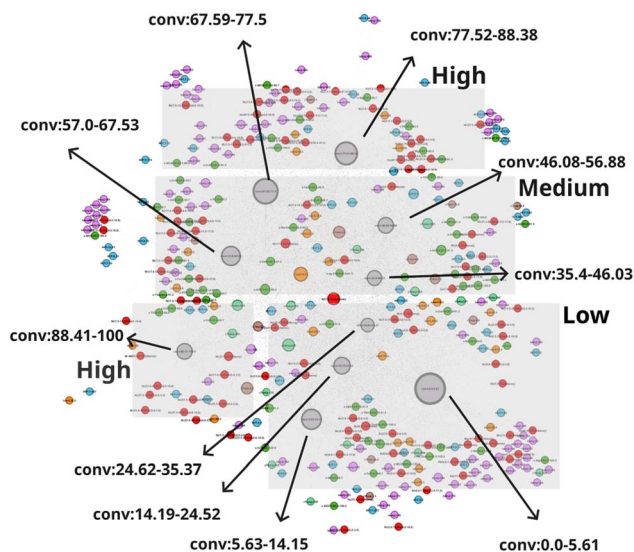


Fig. 7 A large picture of N-2. Each variables is color-coded: red (catalyst), green (support), emerald (calcination temperature ( $^{\circ}\text{C}$ )), light brown (calcination time (h)), light purple (temperature ( $^{\circ}\text{C}$ )), light blue (W/F ( $\text{mg}_{\text{cat}} \text{min}^{-1} \text{mL}^{-1}$ )), orange (inert% in feed), and gray ( $\text{CO}_2$  conversion, %). Areas up to 35.37% is defined as low  $\text{CO}_2$  conversion area, 35.4% to 77.5% is defined as medium  $\text{CO}_2$  conversion area, and greater than 77.52% is defined as high  $\text{CO}_2$  conversion area. A higher resolution of this network can be found in the SI.

The high  $\text{CO}_2$  conversion area in the N-2 network is investigated further to better understand the relationship between catalyst combinations and  $\text{CO}_2$  conversion as shown in Fig. 8. It can be seen that metal combinations such as NiNa, NiCo, NiFe,

NiMn, NiPr, NiCe, NiVO<sub>x</sub>, NiSm, NiBa, and NiSr are associated with high  $\text{CO}_2$  conversion area and are located near nodes of high  $\text{CO}_2$  conversion. Elements such as Ni, Na, Co, Fe, Sm, Mn, Ce, Pr, and VO<sub>x</sub> are also included in Fig. 5, while elements such as Ba and Sr seem to correlate with high  $\text{CO}_2$  conversion rates when combined with Ni. In particular, the introduction of manganese into nickel-based catalysts has been demonstrated to enhance  $\text{CO}_2$  conversion.<sup>33–37</sup> Furthermore, other combinations such as NiCe, NiPr, NiBa, NiFe, and NiCo, which are screened from Fig. 8, have also been reported to improve  $\text{CO}_2$  conversion.<sup>38–42</sup> Therefore, such catalytic networks appropriately represent the trends observed in literature data across different  $\text{CO}_2$  conversion areas. Catalyst combinations associated with low  $\text{CO}_2$  conversion are also examined as shown in Fig. S3. In this area, combinations such as NiCo, NiCe, NiMg, and NiFe are observed. Notably, Co, Ce, and Fe also appear in the high  $\text{CO}_2$  conversion area, suggesting that the apparent overlap is largely governed by the elemental composition rather than by the presence of a given element alone. As shown in Fig. 8, the promoter contents in the high  $\text{CO}_2$  conversion area remain limited to a few percent relative to Ni such as Ni(27.5–40.0)Co(0.0–3.0), Ni(27.5–40.0)Ce(4.0–10.0), and Ni(27.5–40.0)Fe(4.0–10.0). In contrast, Fig. S3 indicates that low  $\text{CO}_2$  conversion catalysts often involve comparatively excessive promoter loadings relative to Ni such as Ni(0.0–7.0)Co(12.5–17.0), Ni(0.0–7.0)Ce(12.5–17.0), and Ni(7.5–15.0)Fe(25.0–37.5). It should be noted, however, that the low  $\text{CO}_2$  conversion area also includes compositions with low promoter contents such as Ni(7.5–15.0)Fe(0.0–3.0) and Ni(17.0–26.0)Co(4.0–10.0). Taken together, these observations indicate that excessive promoter addition is an unfavorable condition for achieving high  $\text{CO}_2$

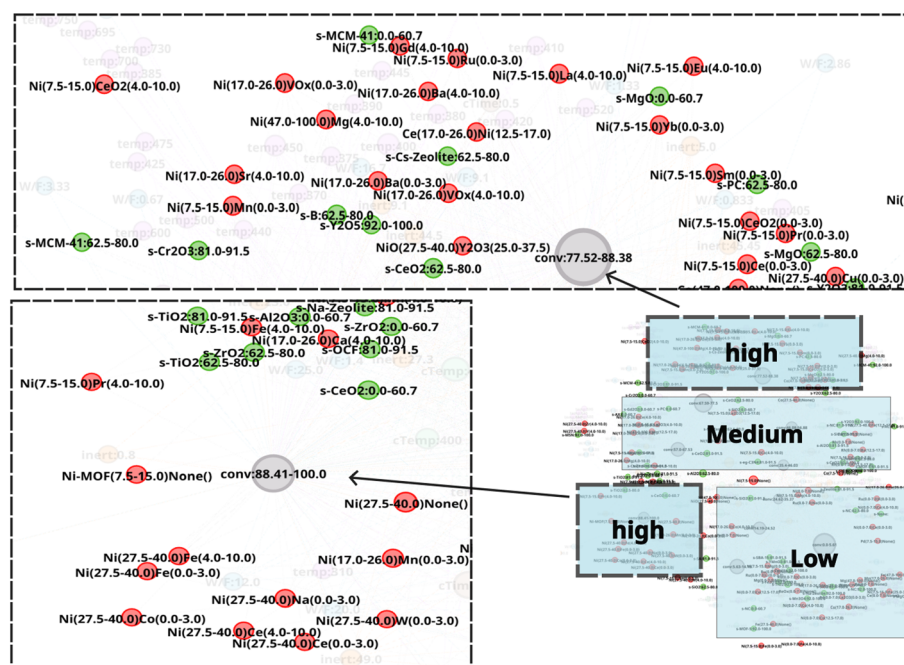


Fig. 8 Details of high  $\text{CO}_2$  conversion area in the N-2 network. Catalyst (pink), support (green), and  $\text{CO}_2$  conversion (gray) are highlighted. Note that labels are adjusted and node size is determined by degree ranking within a range of 10 to 40 for visualization purposes. A higher resolution of this network can be found in the SI.



conversion. The network analysis reveals that certain metal combinations and compositions are systematically associated with CO<sub>2</sub> conversion. Therefore, employing these combinations and compositions may contribute to improving CO<sub>2</sub> conversion based off the trends and information present in these networks. In this study, a systematic screening of metal combinations to identify promising ternary catalysts is performed. To evaluate whether the knowledge extracted from the binary catalysts data can be extended to the design of ternary catalysts, a representative subset of screened ternary candidates (NiMnPr, NiMnCe, NiMnBa, NiMnFe, and NiMnCo) are selected. Al<sub>2</sub>O<sub>3</sub> is selected as the standard support in all catalysts for comparing the activity of element pairs.

### 3.3 Catalyst performance

To evaluate the activity of the screened catalysts, the performance of ternary catalysts is tested at a temperature range of 150–450 °C. For comparison, CO<sub>2</sub> conversion of NiMn/Al<sub>2</sub>O<sub>3</sub>, NiCe/Al<sub>2</sub>O<sub>3</sub>, NiPr/Al<sub>2</sub>O<sub>3</sub>, and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts are also examined. All three element catalysts exhibit better activity compared to Ni/Al<sub>2</sub>O<sub>3</sub>. Furthermore the effectiveness of three element catalysts become more pronounced when compared to NiMn/Al<sub>2</sub>O<sub>3</sub>. At 400 °C, the CO<sub>2</sub> conversion follows the order: NiMnCe/Al<sub>2</sub>O<sub>3</sub> (58.02%) > NiMnPr/Al<sub>2</sub>O<sub>3</sub> (57.33%) > NiMnBa/Al<sub>2</sub>O<sub>3</sub> (49.61%) > NiMn/Al<sub>2</sub>O<sub>3</sub> (48.65%) > NiMnCo/Al<sub>2</sub>O<sub>3</sub> (36.70%) > NiMnNa/Al<sub>2</sub>O<sub>3</sub> (31.68%) > NiMnFe/Al<sub>2</sub>O<sub>3</sub> (27.99%). The CH<sub>4</sub> yield follows the order: NiMnPr/Al<sub>2</sub>O<sub>3</sub> (40.53%) > NiMnCe/Al<sub>2</sub>O<sub>3</sub> (39.24%) > NiMn/Al<sub>2</sub>O<sub>3</sub> (30.21%) ≈ NiMnBa/Al<sub>2</sub>O<sub>3</sub> (30.07%) > NiMnCo/Al<sub>2</sub>O<sub>3</sub> (16.66%) > NiMnFeAl<sub>2</sub>O<sub>3</sub> (8.99%) > NiMnNa/

Al<sub>2</sub>O<sub>3</sub> (6.67%). Interestingly, NiMnCe/Al<sub>2</sub>O<sub>3</sub> and NiMnPr/Al<sub>2</sub>O<sub>3</sub> exhibit higher CO<sub>2</sub> conversion than NiCe/Al<sub>2</sub>O<sub>3</sub> (39.22%) and NiPr/Al<sub>2</sub>O<sub>3</sub> (10.86%), possibly due to additional effects among the three elements, as shown in Fig. 9(a). Furthermore, a 12 h durability testing is conducted on NiMnPr/Al<sub>2</sub>O<sub>3</sub>, which exhibits the highest CH<sub>4</sub> yield, and it demonstrated excellent stability as

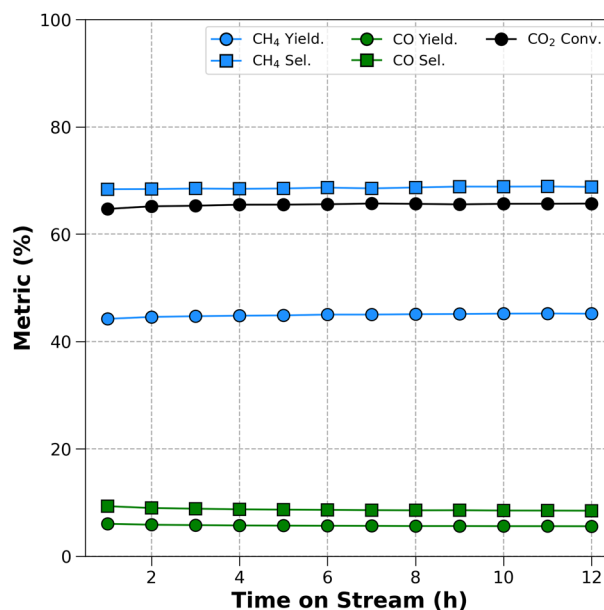


Fig. 10 A 12 h durability test for NiMnPr/Al<sub>2</sub>O<sub>3</sub> at 450° under H<sub>2</sub>/CO<sub>2</sub> of 4.

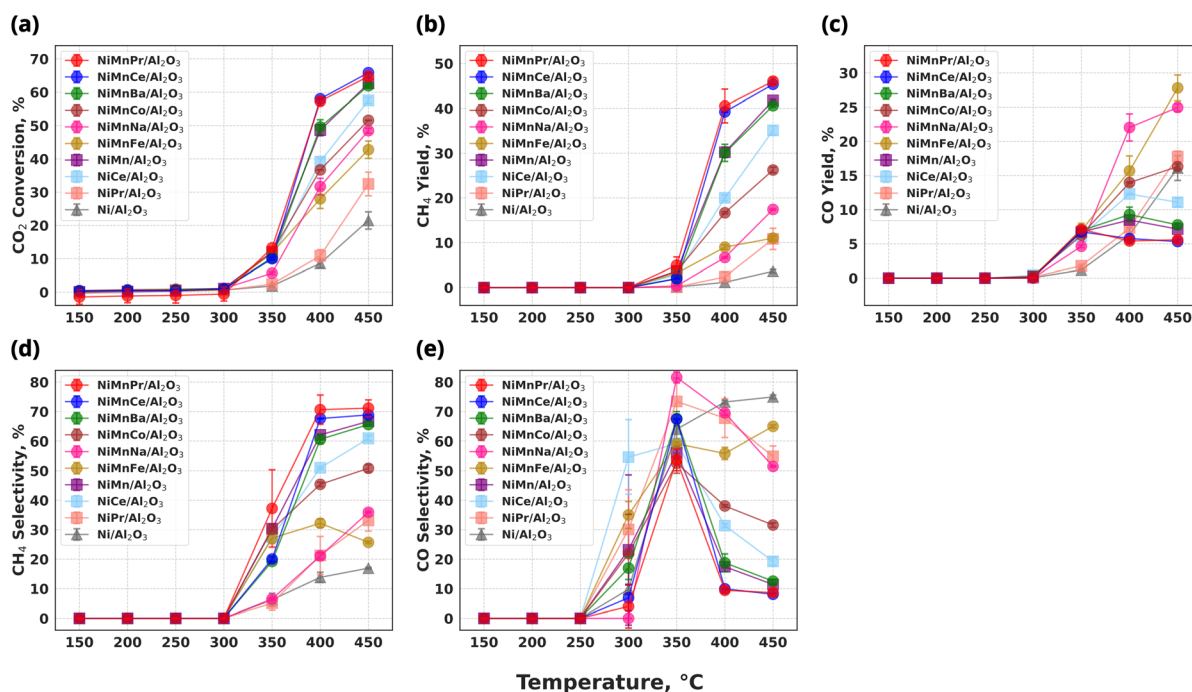


Fig. 9 (a) CO<sub>2</sub> conversion, %, (b) CH<sub>4</sub> yield, %, (c) CO yield, %, (d) CH<sub>4</sub> selectivity, %, and (e) CO selectivity, % as a function of temperature. Ternary, binary, and unary catalysts are represented by circles, squares, and triangles, respectively. Note that the plots and error bars at each temperature represent the average and standard deviation of two measurements to ensure reproducibility.



shown in Fig. 10. More detailed results for catalysts containing Ni, Mn, and/or Pr are shown in Fig. S4, and a comparison with previously reported catalysts is shown in Table S1. CO<sub>2</sub> conversion and CH<sub>4</sub> yield of NiMnBa/Al<sub>2</sub>O<sub>3</sub> are comparable to those of NiMn/Al<sub>2</sub>O<sub>3</sub>, whereas NiMnCo/Al<sub>2</sub>O<sub>3</sub>, NiMnNa/Al<sub>2</sub>O<sub>3</sub>, and NiMnFe/Al<sub>2</sub>O<sub>3</sub> reduce CO<sub>2</sub> conversion and suppress methane formation as shown in Fig. 9(a), (b) and (d). Furthermore, as shown in Fig. 9(c) and (e), NiMnCe/Al<sub>2</sub>O<sub>3</sub>, NiMnPr/Al<sub>2</sub>O<sub>3</sub>, and NiMnBa/Al<sub>2</sub>O<sub>3</sub> can suppress CO formation, whereas NiMnCo/Al<sub>2</sub>O<sub>3</sub>, NiMnFe/Al<sub>2</sub>O<sub>3</sub>, and NiMnNa/Al<sub>2</sub>O<sub>3</sub> exhibit increased CO yield with rising temperature. Consequently, the activity for CO<sub>2</sub> hydrogenation changes significantly depending on the element added to NiMn. In other words, pairing Ni–Mn with a lanthanoid element resulted in higher yields compared to transition (Fe, Co) and basic metals (Na, Ba). In particular, NiMnCe/Al<sub>2</sub>O<sub>3</sub> and NiMnPr/Al<sub>2</sub>O<sub>3</sub> exhibit higher CO<sub>2</sub> conversion than corresponding binary catalysts, demonstrating their potential as promising catalysts.

### 3.4 Characterization on NiMnPr/Al<sub>2</sub>O<sub>3</sub>

The NiMnPr/Al<sub>2</sub>O<sub>3</sub> catalyst, which exhibits the highest CH<sub>4</sub> yield, is selected for detailed characterization to identify the physicochemical features responsible for its superior performance. XRD is investigated to confirm the crystal structure. The XRD patterns of catalysts containing Ni, Mn, and/or Pr are shown in Fig. 11(a), while those of the other catalysts are provided in Fig. S5. As shown in Fig. 11(a), XRD patterns show the characteristic diffraction peaks of  $\gamma$ -alumina, whereas no peaks corresponding to the Ni, Mn, and Pr are detected. The absence of peaks indicates that either the concentration of the crystalline phase of the species containing the impregnated elements is very low or they are not forming crystalline phases. Furthermore, no differences in peak intensity or shift are observed among catalysts.

SEM-EDS analyses is conducted to confirm morphology and surface compositions of the synthesized catalysts. As shown in Fig. 11(b), although no peaks related to Mn, Ni, or Pr are

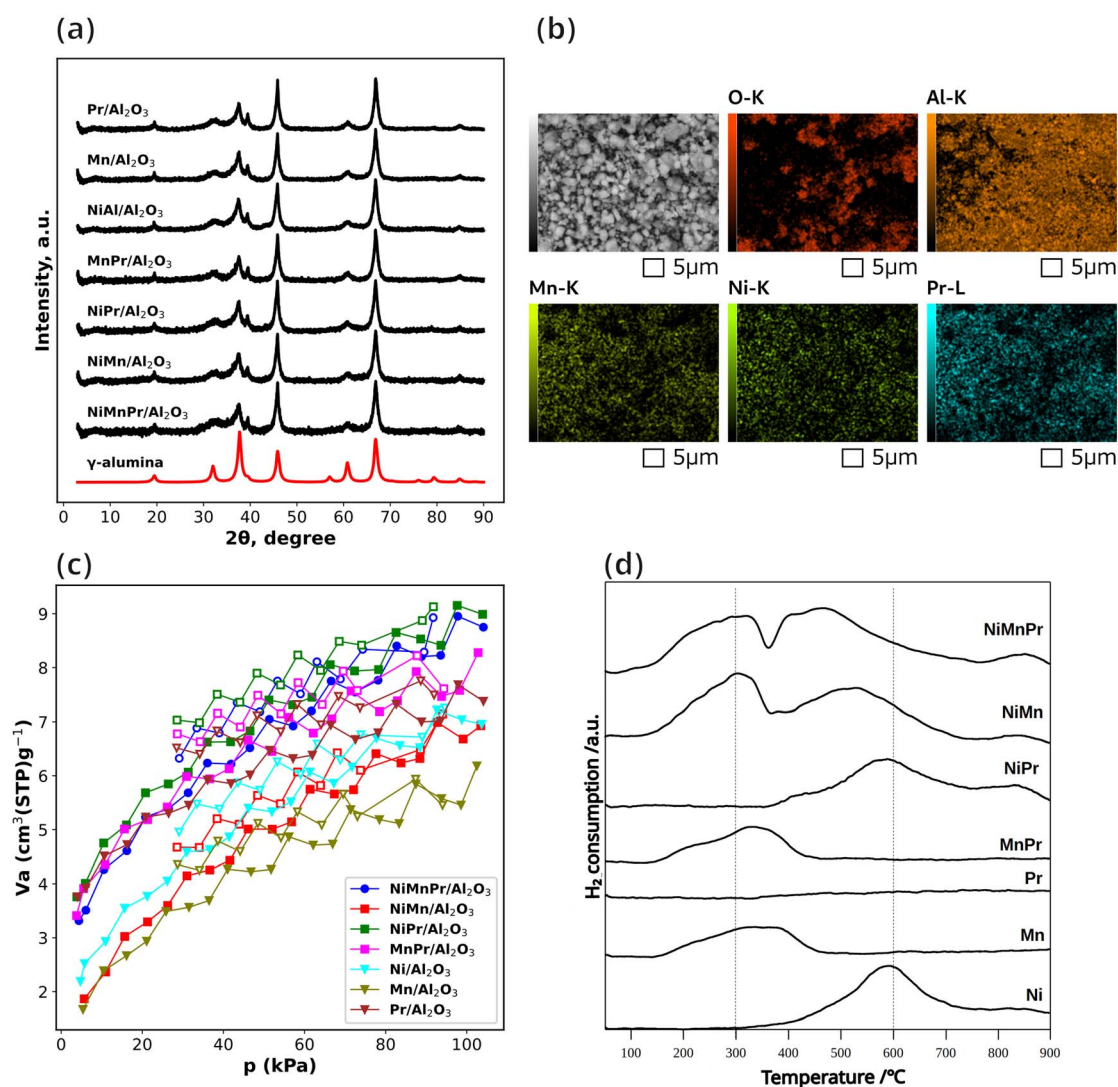


Fig. 11 (a) XRD for catalysts with Ni, Pr, or Mn. The reference pattern shown in red is obtained from the built-in database of the Rigaku Miniflex 600-C software. (b) The SEM-EDS image for NiMnPr/Al<sub>2</sub>O<sub>3</sub>. (c) CO<sub>2</sub> adsorption and desorption for catalysts with Ni, Pr, or Mn. (d) H<sub>2</sub>-TPR profiling for catalysts with Ni, Pr, or Mn.



observed in XRD, SEM-EDS confirms the presence of these three elements. The catalyst appears as an agglomeration with an average diameter of approximately 5  $\mu\text{m}$ . SEM-EDS elemental mapping confirms the presence of Ni, Mn, and Pr on the  $\gamma\text{-Al}_2\text{O}_3$  support. The Ni-K, Mn-K, and Pr-L maps show broadly distributed signals over the observed area indicating good dispersion at the micrometer scale. SEM-EDS for other catalysts also shows in Fig. S6–S8.

$\text{CO}_2$  adsorption–desorption measurements are performed to investigate the  $\text{CO}_2$  related properties of the catalysts. As shown in Fig. 11(c), the  $\text{CO}_2$  uptake is in the order of  $\text{Pr}/\text{Al}_2\text{O}_3$ ,  $\text{NiAl}_2\text{O}_3$ ,  $\text{MnAl}_2\text{O}_3$  for the unary catalysts.  $\text{NiPr}/\text{Al}_2\text{O}_3$  exhibits the highest  $\text{CO}_2$  uptake, followed by  $\text{NiMnPr}/\text{Al}_2\text{O}_3$  with a nearly comparable value, and then by  $\text{MnPr}/\text{Al}_2\text{O}_3$  and  $\text{Pr}/\text{Al}_2\text{O}_3$ , whereas other Pr-free catalysts have relatively lower  $\text{CO}_2$  uptake. It is considered that Pr-containing catalyst systems enhance  $\text{CO}_2$  adsorption and activation.<sup>43</sup> In other words, the addition of Pr to Ni or Ni–Mn catalysts increases  $\text{CO}_2$  uptake. This result is consistent with the higher  $\text{CO}_2$  conversion and  $\text{CH}_4$  yield observed for the  $\text{NiMnPr}$  and  $\text{NiPr}$  catalysts compared with the  $\text{NiMn}$  and  $\text{Ni}$  catalysts at 400  $^\circ\text{C}$ , as shown in Fig. 9(a) and (b). Therefore, the Pr in the ternary catalyst may also contribute to changes in surface properties related to  $\text{CO}_2$ .

The results of  $\text{H}_2$ -TPR profile are shown in Fig. 11(d).  $\text{Ni}/\text{Al}_2\text{O}_3$  indicates a large reduction peak at 600  $^\circ\text{C}$  from 300  $^\circ\text{C}$  to 800  $^\circ\text{C}$ , attributed to the reduction of  $\text{NiO}$  to  $\text{Ni}$  metal.  $\text{Mn}/\text{Al}_2\text{O}_3$  gives broad peak at around 150–500  $^\circ\text{C}$ , derived from sequential reduction steps of Mn oxides such as  $\text{MnO}_2$  to  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}$ .  $\text{Pr}/\text{Al}_2\text{O}_3$  does not serve any obvious reduction profile below 900  $^\circ\text{C}$ . The addition of Pr to Mn or Ni slightly increases the shoulder peak area at lower temperature, which is likely due to an increase in the number of easily reduced Mn or Ni species. There are significant differences in binary  $\text{NiMn}$  and ternary  $\text{NiMnPr}$  catalysts in comparison to unary Ni and Mn catalysts. Both  $\text{NiMn}$  and  $\text{NiMnPr}$  catalysts possess two-humped reduction peak. It is considered that the lower temperature profile at 100–350  $^\circ\text{C}$  from  $\text{MnO}_2$  into  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$  into  $\text{MnO}$  whereas the higher temperature profile 350–750  $^\circ\text{C}$  from  $\text{NiO}$  into  $\text{Ni}$  origin, respectively.<sup>36</sup> It is very interesting that the peak at higher temperature derived from Ni origin gives gradual shift to the lower temperature at the top peak from 585  $^\circ\text{C}$  ( $\text{NiAl}_2\text{O}_3$ ), 530  $^\circ\text{C}$  ( $\text{NiMnAl}_2\text{O}_3$ ) to 475  $^\circ\text{C}$  ( $\text{NiMnPrAl}_2\text{O}_3$ ). The improved reducibility of  $\text{NiO}$  contributes to the fine dispersion of the as-generated Ni. As the result, higher catalytic activity is observed in the binary  $\text{NiMn}/\text{Al}_2\text{O}_3$  systems in earlier studies.<sup>44,45</sup> This trend is consistent with the enhanced  $\text{CO}_2$  conversion and  $\text{CH}_4$  yield observed for these catalysts as shown in Fig. 9(a) and (b). Overall, considering  $\text{CO}_2$  uptake and  $\text{H}_2$ -TPR profile, the unique  $\text{NiMnPr}$  catalyst, which is experimentally validated as facilitating  $\text{CO}_2$  methanation at lower temperatures, clearly indicates the effect of additive Pr for further improvement of  $\text{NiMn}$  nature.

## 4 Conclusions

$\text{CO}_2$  hydrogenation dataset is utilized to structure multidimensional data *via* network analysis. The constructed networks

provide insights into which experimental conditions are effective or not for the catalysts data across multidimensional variables. Furthermore, the networks are applied to catalyst screening, identifying useful catalyst combinations. Six ternary element catalysts selected from high  $\text{CO}_2$  conversion area are developed and experimentally validated.  $\text{NiMnPr}/\text{Al}_2\text{O}_3$  and  $\text{NiMnCe}/\text{Al}_2\text{O}_3$  demonstrate activity exceeding that of their respective binary element catalysts. This result demonstrates that network-based trends and knowledge can efficiently discover new catalysts. This approach not only uncovers key trends and relationships across multidimensional variables in complex heterogeneous reactions but also establishes a generalizable strategy for guiding the design of efficient catalysts. These findings highlight the potential of data-driven network methodologies to accelerate catalyst discovery and provide a framework for exploring complex catalytic systems.

## Author contributions

Y. H.: Conceptualization, network construction and analysis, experimental investigation and analysis. F. G.-E.: Experimental investigation and analysis, validation. S. N.: Experimental investigation and analysis. K. T.: Supervision, validation, funding. L. T.: Supervision, network analysis, validation, funding. All authors were involved in reviewing and editing the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

All data is provided in the manuscript.

Supplementary information (SI): source dataset (xlsx), support information (pdf), high-resolution Fig. 1 (png), and high-resolution Fig. 6 (png). Raw chromatograms and calculated catalyst activities from activity test. See DOI: <https://doi.org/10.1039/d6sc00563b>.

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