



## Research Paper

# Upcycling bentonite into nickel sorbent and its subsequent use as a heterogeneous catalyst in CO<sub>2</sub>-assisted pyrolysis of high-density polyethylene

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## ABSTRACT

This study presented a strategy for utilizing sodium aluminosilicate hydrate (NASH), synthesized via alkali activation of bentonite, as a dual-function material for aqueous Ni<sup>2+</sup> removal and subsequent catalytic application in CO<sub>2</sub>-assisted pyrolysis of high-density polyethylene (HDPE). The NASH samples exhibited high Ni sorption capabilities, achieving Ni loadings of 1.0–9.0 wt% through concentration-dependent sorption mechanisms. Subsequent calcination and H<sub>2</sub> reduction successfully converted sorbed Ni<sup>II</sup> species into metallic Ni<sup>0</sup>, as confirmed by XRD and XPS analyses. Pyrolysis experiments with HDPE revealed that 9.0% Ni-Cat. exhibited the highest catalytic activity, promoting syngas (H<sub>2</sub> and CO) production while effectively suppressing coke formation under a CO<sub>2</sub> atmosphere. Increasing the CO<sub>2</sub> concentration from 20 to 80 vol% progressively enhanced cumulative CO yield from 18.2 to 58.9 mmol, with both H<sub>2</sub> and CO yields reaching their maximum at 80 vol% CO<sub>2</sub>. Overall, this approach offered an integrated strategy for simultaneous spent sorbent upcycling, Ni-contaminated wastewater remediation, and thermochemical plastic waste valorization.

## 1. Introduction

Heavy metal contamination of aqueous environments presents persistent ecological and public health risks due to the toxicity, persistence, and bioaccumulation potential of these pollutants (Hama Aziz et al., 2023; Saravanan et al., 2024). Sorption has been widely adopted as an effective treatment strategy, with a broad range of sorbent materials developed for desired remediation purposes (Fouda-Mbanga et al., 2024a; Ismail et al., 2024). However, the large-scale application of sorption processes inevitably generates substantial quantities of metal-laden spent sorbents, the management of which remains a critical yet insufficiently addressed challenge (Bayuo et al., 2024). These materials pose environmental risks due to potential metal leaching while simultaneously representing a concentrated secondary resource (Fouda-Mbanga et al., 2024b). Such challenges highlight the incompleteness of current sorption-based treatment strategies from a circular economy perspective, as these approaches fail to account for the full lifecycle of spent sorbents (Sai Bharadwaj et al., 2025).

Existing approaches to spent sorbent management primarily rely on regeneration or metal recovery. Although regeneration can partially restore sorption capacity, its effectiveness declines over successive cycles and typically requires additional chemical reagents, generating secondary waste streams and increasing operational costs (Chakma et al., 2026; Fouda-Mbanga et al., 2024a). Metal recovery presents an alternative but often involves energy-intensive and costly processes that generate by-products requiring further treatment (Bayuo et al., 2024). Beyond environmental concerns, the disposal of hazardous metal-laden sorbents entails considerable economic burdens on wastewater treatment operations, further limiting the viability of current management practices (Vakili et al., 2024). Critically, neither approach fully aligns with circular economy principles, underscoring the need for innovative strategies that valorize spent sorbents as functional materials.

The functional transformation of spent sorbents into value-added materials represents a promising yet underexplored valorization strategy, wherein metal species retained during the sorption process are leveraged to impart new catalytic functionality (Chen et al., 2025; Yang

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et al., 2021). The sorbed metals can serve as catalytically active sites, while the sorbent matrix provides structural support, effectively converting a waste material into a functional resource without additional metal inputs (Chen et al., 2022). Among candidate metal species, nickel (Ni) is particularly well established for its catalytic activity in thermochemical processes, making Ni-loaded spent sorbents especially attractive for this purpose (Wei et al., 2025). This approach not only eliminates the need for dedicated catalyst synthesis but also reduces material consumption and waste disposal costs, offering a viable circular economy strategy for spent sorbent management.

Catalytic pyrolysis of carbonaceous feedstocks represents a promising application for sorption-derived catalytic materials, providing a practical route for converting waste streams into syngas (Svadlenak et al., 2021). Syngas ( $H_2$  and CO) serves as a key intermediate for hydrogen production and fuel synthesis (Kumar et al., 2022). In this context, the use of  $CO_2$  as a reaction atmosphere has attracted increasing attention owing to its participation in gasification and reforming reactions, which enhances syngas production (Jung et al., 2023; Luo et al., 2022). Moreover,  $CO_2$  can suppress coke formation via carbon- $CO_2$  reactions, thereby improving product quality and potentially extending catalyst lifetime (Lee et al., 2026a). Despite this potential, the direct application of sorption-derived materials as pyrolysis catalysts without additional synthesis steps remains underexplored.

The main objective of this study is to demonstrate a circular valorization pathway of a naturally abundant clay material, bentonite, linking aqueous  $Ni^{2+}$  remediation with thermochemical plastic waste conversion through the upcycling of Ni-laden spent sorbents into functional catalysts. To this end, sodium aluminosilicate hydrate (NASH) was synthesized via alkali activation of this low-cost and readily available material (Toor et al., 2015). NASH was reported to exhibit a high ion-exchange capacity for metal uptake and a thermally stable aluminosilicate framework (Zhang et al., 2023). The synthesized NASH was characterized and employed for  $Ni^{2+}$  removal from aqueous solution, and the resulting Ni-loaded NASH was subsequently applied as a catalyst for the pyrolysis of high-density polyethylene (HDPE) under  $N_2$  and  $CO_2$  atmospheres.

## 2. Materials and methods

### 2.1. Chemical reagents

Bentonite, HDPE (melt index: 2.2 g 10 min<sup>-1</sup>), and silica gel ( $SiO_2$ , pore size: 60 Å, 60–100 mesh) were purchased from Sigma-Aldrich (USA). Nickel(II) nitrate hexahydrate, nitric acid, sodium hydroxide, and dichloromethane (DCM) were supplied from Daejung Chemicals and Metals (Korea). A multi-element standard solution XVI was purchased from Merck (Germany). Ultra-high-purity  $N_2$  (99.99 vol%) and  $CO_2$  (99.99 vol%) gases were supplied by Green Gas Co. (Korea). A calibration gas mixture composed of  $H_2$  (19.99 vol%), CO (19.97 vol%), methane ( $CH_4$ , 20.03 vol%),  $CO_2$  (19.98 vol%), and  $N_2$  (20.03 vol%), together with a reducing gas mixture containing 20 vol%  $H_2$  balanced with  $N_2$ , was obtained from RIGAS (Korea). The  $C_2$  hydrocarbon standard gas mixture, consisting of acetylene ( $C_2H_2$ , 5.1 vol%), ethylene ( $C_2H_4$ , 15.0 vol%), ethane ( $C_2H_6$ , 10.1 vol%), propylene ( $C_3H_6$ , 10.0 vol%),  $CO_2$  (20.0 vol%), and  $N_2$  (39.8 vol%), was supplied by Union-Gas (Korea).

### 2.2. Synthesis of NASH

NASH was synthesized via an alkali activation method (Khalifa et al., 2020; Marsh et al., 2018). Bentonite was mixed with 4 M NaOH solution at a liquid-to-solid ratio of 10 mL g<sup>-1</sup> and stirred at 75 °C for 24 h. The resulting solid was separated by filtration, washed repeatedly with deionized water until neutral pH, and dried at 80 °C for 12 h.

### 2.3. $Ni^{2+}$ sorption and catalyst preparation

Sorption experiments were conducted at initial  $Ni^{2+}$  concentrations of 50, 200, and 1000 mg L<sup>-1</sup> at pH 6.0 to assess the sorption behavior of NASH. Residual  $Ni^{2+}$  and released  $Na^+$  concentrations in the solution were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, 5800, Agilent, USA). An additional aqueous leaching test was conducted using Ni-loaded NASH to evaluate the potential release of sorbed Ni. Detailed sorption and leaching procedures were described in Text S1, while the kinetic analysis was provided in Text S2. Ni-loaded NASH samples for catalytic pyrolysis were prepared by scaling up the sorption process under the same experimental conditions. The resulting solids were dried, calcined under air, and subsequently reduced under 20 vol%  $H_2$  balanced with  $N_2$  to convert sorbed Ni species into metallic Ni-containing catalysts. Detailed catalyst preparation procedures were described in Supplementary Information (Text S3).

### 2.4. Characterization of samples

The morphology, elemental composition, crystalline structure, surface chemical states, and textural properties of bentonite and pristine NASH were characterized using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX, CUBE II, Emcrafts, Korea), X-ray diffraction (XRD, D8 ADVANCE, Bruker, Germany), X-ray photoelectron spectroscopy (XPS, K-alpha+, Thermo Scientific, USA), and Brunauer-Emmett-Teller/Barrett-Joyner-Halenda (BET/BJH, BELSORP-max II, MicrotracBEL, Japan) analyses. The reduced samples were denoted as X% Ni-Cat., where X represents the Ni loading (wt%). Additional XRD and XPS analyses were conducted on Ni-loaded and Ni-Cat. samples to track structural and chemical changes during catalyst transformation, while the fresh and spent 9.0% Ni-Cat./ $SiO_2$  catalytic beds were further characterized by XRD and SEM-EDX to evaluate post-pyrolysis phase and morphological changes. Ni loading was quantified by microwave-assisted acid digestion followed by ICP-OES analysis, which was also applied to the spent catalytic beds to evaluate Ni retention after pyrolysis. Transmission electron microscopy and scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy (TEM and STEM-EDX, JEM-2100F, JEOL, Japan) were performed on the fresh 9.0% Ni-Cat. to examine Ni particle size and elemental distribution. BET/BJH analyses were also performed on the fresh and spent 9.0% Ni-Cat./ $SiO_2$  catalytic beds to evaluate changes in their textural properties after pyrolysis. Detailed characterization procedures were described in Supplementary Information (Text S4).

### 2.5. Catalytic pyrolysis experiments

The thermal degradation behavior of HDPE under  $N_2$  and  $CO_2$  atmospheres was examined by thermogravimetric analysis (TGA, 449 F5 Jupiter, NETZSCH, Germany). Ex-situ catalytic pyrolysis experiments were conducted using a two-zone fixed-bed reactor, where HDPE (3 g) and a catalytic bed consisting of Ni-Cat. (2 g) mixed with  $SiO_2$  (1 g) were placed in the first and second heating zones, respectively.  $SiO_2$  was used as an inert diluent to improve bed dispersion (Kim et al., 2022). The first heating zone was heated from 100 to 700 °C at a heating rate of 10 °C min<sup>-1</sup>, while the second heating zone was maintained at 700 °C for catalytic upgrading. Each pyrolysis experiment was terminated when the first heating zone reached 700 °C, corresponding to a total pyrolysis time of 60 min. Pyrolysis experiments were conducted under different  $CO_2$  concentrations (0, 20, 50, and 80 vol%, balanced with  $N_2$ ) at a total flow rate of 200 mL min<sup>-1</sup>. Condensable and non-condensable products were analyzed by gas chromatography-mass spectrometry (GC-MS, 8890/5977B, Agilent, USA) and micro-gas chromatography (micro-GC, 990, Agilent, USA), respectively. After pyrolysis, spent catalysts were subjected to temperature-programmed oxidation (TPO) analysis to quantify carbonaceous deposits. Fresh Ni-Cat. samples were mixed with  $SiO_2$  at a mass ratio of 2:1 prior to TPO analysis to match the catalytic

bed configuration. Detailed experimental conditions for TGA, pyrolysis, product analysis, and TPO are described in Supplementary Information (Texts S5-S7).

### 3. Results and discussion

#### 3.1. Characterization of NASH

The physicochemical properties of the raw bentonite were presented in Figs. 1a and S1a-d. The SEM image revealed a layered and aggregated structure (Fig. S1a), with elemental mapping indicating Si, Al, Na, and O as the dominant elements (21.7, 9.0, 2.3, and 67.0 wt%). The XRD pattern exhibited characteristic reflections corresponding to montmorillonite (JCPDS No. 01-0026) as the dominant phase, along with quartz (JCPDS No. 46-1045), albite (JCPDS No. 10-0393), and cristobalite (JCPDS No. 39-1425) as minor phases (Fig. 1a). The  $N_2$  adsorption-desorption isotherm revealed a mesoporous character, with a specific surface area of  $33.4 \text{ m}^2 \text{ g}^{-1}$ , a total pore volume of  $0.14 \text{ cm}^3 \text{ g}^{-1}$ , and an average pore diameter of 8.1 nm (Fig. S1b). The BJH pore size distribution exhibited a primary peak at approximately 2.0 nm, with a broad secondary distribution in the 20–100 nm range (Fig. S1c). The Si 2p spectrum exhibited two peaks at 102.4 and 103.8 eV, consistent with Si-O-Al and Si-O-Si bonding, respectively (Fig. S1d) (Liu et al., 2018). The Al 2p spectrum showed peaks at 74.3 and 75.6 eV, assigned to octahedrally and tetrahedrally coordinated Al species, respectively, within the aluminosilicate framework (Liu et al., 2018; McIntosh et al., 2017). The Na 1s peak at 1072.4 eV was assigned to interlayer  $\text{Na}^+$  in the montmorillonite structure (Seyama and Soma, 1986). The O 1s spectrum showed components at 531.7 and 533.2 eV, consistent with lattice oxygen and surface hydroxyl groups, respectively (Roy et al., 2023).

Alkali activation induced notable structural and physicochemical changes, confirming the formation of a NASH-containing aluminosilicate phase (Figs. 1b and S1e-h). The SEM image revealed a morphological transition from the layered structure of bentonite to a compact and irregular aggregated structure (Fig. S1e). Elemental mapping showed a marked increase in Na content (14.5 wt%) compared to bentonite, reflecting Na incorporation into the aluminosilicate framework during alkali activation. The contents of Si, Al, and O were 13.7, 11.2, and 60.6 wt%, respectively. The XRD pattern showed that the characteristic low-angle reflection of montmorillonite was still observed after alkali activation, while the quartz reflection was retained and new reflections assigned to hydrosodalite ( $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$ , JCPDS No. 11-

0401) emerged (Fig. 1b). These changes indicated partial transformation of the original bentonite during NASH formation (Marsh et al., 2018; Marsh et al., 2024). The textural properties also underwent notable changes upon NASH formation (Fig. S1f). The specific surface area decreased from  $33.4$  to  $17.5 \text{ m}^2 \text{ g}^{-1}$ , and the total pore volume declined from  $0.14$  to  $0.08 \text{ cm}^3 \text{ g}^{-1}$ , while the average pore diameter increased from 8.1 to 9.1 nm. The BJH pore size distribution retained a similar profile to that of bentonite, with a reduction in peak intensity (Fig. S1g). These changes suggested partial pore collapse and structural densification, likely resulting from gel formation and pore filling during the development of the aluminosilicate network.

Compared to bentonite, the XPS spectra of pristine NASH exhibited notable shifts in binding energies upon alkali activation (Fig. S1h). The Si 2p peaks shifted to 101.9 and 103.1 eV, indicating an increased contribution of Si-O-Al bonding in the NASH network (Liu et al., 2024). The Al 2p spectrum showed two components at 73.8 and 74.8 eV, consistent with an increased contribution of tetrahedrally coordinated Al in the NASH structure (So et al., 2022). The Na 1s peak shifted from 1072.4 to 1071.5 eV, indicating that  $\text{Na}^+$  species were incorporated into the aluminosilicate framework as charge-balancing cations rather than remaining in interlayer environments (Walkley et al., 2018b). The O 1s spectrum displayed a shift to lower binding energies, with two components at 530.9 and 532.0 eV, reflecting an increased contribution of bridging oxygen (Si-O-Al) and a reduction in surface hydroxyl species consistent with enhanced network polymerization (Idriss, 2021; Shamo et al., 2024). Overall, these XPS results confirmed the reorganization of the aluminosilicate network upon alkali activation, corroborating the structural transformation evidenced by XRD.

#### 3.2. $\text{Ni}^{2+}$ sorption behavior

The sorption kinetics of  $\text{Ni}^{2+}$  onto pristine NASH at initial concentrations of 50, 200, and  $1000 \text{ mg L}^{-1}$  were presented in Fig. 2a, and the corresponding parameters were summarized in Table S3. At all concentrations, rapid initial uptake occurred, reflecting the availability of abundant active sorption sites on NASH. At  $50 \text{ mg L}^{-1}$ , equilibrium was rapidly attained with a  $q_{e(\text{exp.})}$  of  $11.0 \text{ mg g}^{-1}$ . At  $200 \text{ mg L}^{-1}$ , the initial rapid uptake was followed by a gradual increase before approaching equilibrium at a  $q_{e(\text{exp.})}$  of  $50.2 \text{ mg g}^{-1}$ . In contrast, at  $1000 \text{ mg L}^{-1}$ , sorption proceeded continuously throughout the experimental period without reaching equilibrium, with  $q_{e(\text{exp.})}$  reaching  $103.2 \text{ mg g}^{-1}$ .

The pseudo-first-order (PFO) model provided a reasonable fit at 50

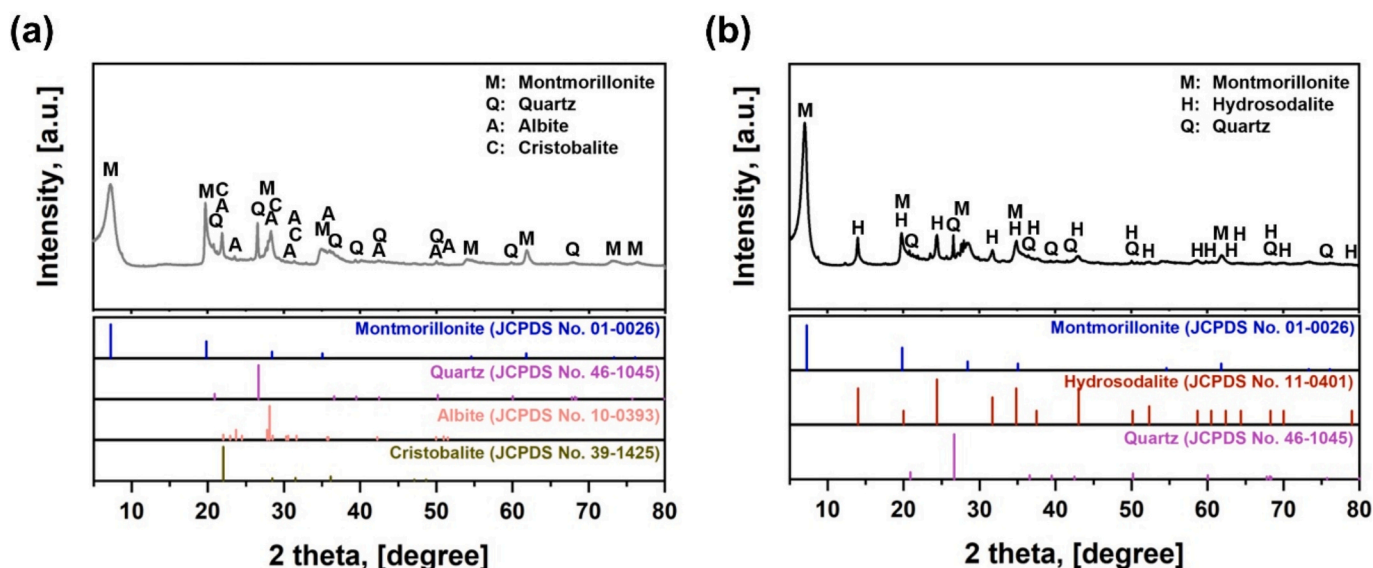


Fig. 1. XRD patterns of (a) bentonite and (b) pristine NASH.

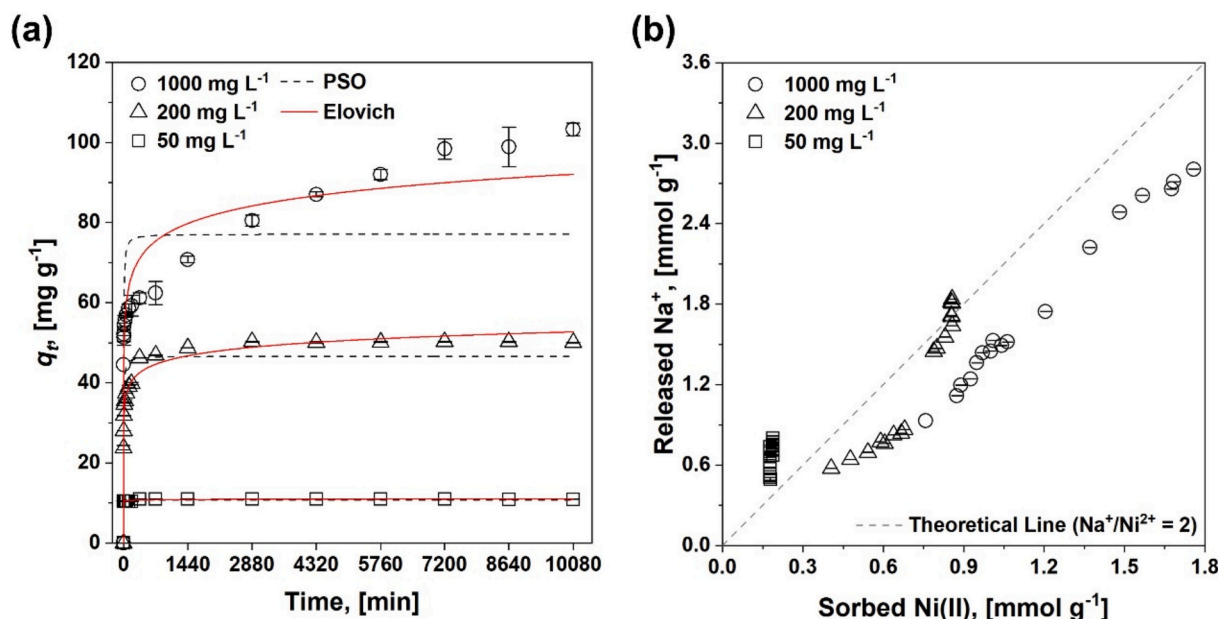


Fig. 2.  $\text{Ni}^{2+}$  sorption behavior of pristine NASH at initial concentrations of 50, 200, and 1000  $\text{mg L}^{-1}$ : (a) sorption kinetics fitted using the PSO and Elovich models and (b) relationship between sorbed  $\text{Ni}^{2+}$  and released  $\text{Na}^{+}$  (experimental conditions: initial pH = 6.0, sample dose = 5  $\text{g L}^{-1}$ , and contact time = 0–10,080 min).

$\text{mg L}^{-1}$ , while the pseudo-second-order (PSO) model yielded higher  $R^2$  values across all concentrations. However, both models showed limitations in describing the  $\text{Ni}^{2+}$  sorption behavior at higher concentrations, as evidenced by the underestimated  $q_{e(\text{cal.})}$  relative to  $q_{e(\text{exp.})}$  at 1000  $\text{mg L}^{-1}$  (Table S3). The Elovich model provided consistently better fits across all concentrations ( $R^2 = 0.9215\text{--}0.9965$ ), suggesting that  $\text{Ni}^{2+}$  sorption occurred on energetically heterogeneous sites (Debord et al., 2022). The Elovich constant  $\beta$  decreased with increasing initial concentration (0.2–10.2  $\text{g mg}^{-1}$ ), indicating that sorption progressively involved sorption sites with different energy levels as surface coverage increased (Schmidt and Martínez, 2016).

To further interpret these concentration-dependent behaviors, the variation of solution pH during sorption was examined (Fig. S2a). At 50  $\text{mg L}^{-1}$ , the pH increased markedly from 6.0 to 10.6, indicating that the alkalinity released from NASH dominated the solution chemistry and created favorable conditions for  $\text{Ni}(\text{OH})_2$  precipitation under alkaline conditions (Gómez Jousse et al., 2025). At 200  $\text{mg L}^{-1}$ , the pH increased to 8.8, suggesting that the higher  $\text{Ni}^{2+}$  concentration partially offset the alkalinity through Ni hydrolysis and surface reactions (da Conceição et al., 2021). In contrast, at 1000  $\text{mg L}^{-1}$ , the pH initially increased to 7.6 and subsequently decreased to 6.7. This behavior may reflect changes in the solution proton balance associated with Ni(II) hydrolysis and surface complexation, while ion-exchange processes continued to contribute to  $\text{Ni}^{2+}$  uptake (Fernando and Zhou, 2019; Silverstein, 2021).

The intraparticle diffusion (IPD) model plots were presented in Fig. S3, and the corresponding parameters were summarized in Table S4. The multi-linear nature of the plots indicated multiple diffusion stages (Hu et al., 2024). At 50  $\text{mg L}^{-1}$ , two stages were observed, likely reflecting rapid equilibrium attainment and the contribution of pH-induced precipitation (Zhao et al., 2017). In contrast, three stages were identified at 200 and 1000  $\text{mg L}^{-1}$ , suggesting increased diffusion resistance at higher concentrations (Liu et al., 2022). For these concentrations, Stages I and II were attributed to external mass transfer and intraparticle diffusion within the porous structure, respectively (Silva et al., 2021). Stage III reflected the approach to equilibrium at 200  $\text{mg L}^{-1}$ , while sorption continued without attaining equilibrium at 1000  $\text{mg L}^{-1}$  (Hu et al., 2024). Overall, these results indicated that  $\text{Ni}^{2+}$  sorption onto NASH involved multiple diffusion stages, with external mass transfer and intraparticle diffusion as the primary rate-controlling steps.

The relationship between sorbed  $\text{Ni}^{2+}$  and released  $\text{Na}^{+}$  was presented in Fig. 2b to evaluate the contribution of ion exchange. The experimental  $\text{Na}^{+}$  release was compared with the theoretical ion-exchange line ( $\text{Na}^{+}/\text{Ni}^{2+} = 2$ ) (Allahdin et al., 2022). At 50  $\text{mg L}^{-1}$ , the experimental  $\text{Na}^{+}$  release exceeded the theoretical value, likely attributable to the highly alkaline conditions (Fig. S2a) that facilitated both  $\text{Na}^{+}$  release and  $\text{Ni}(\text{OH})_2$  precipitation. At 200  $\text{mg L}^{-1}$ , the experimental  $\text{Na}^{+}$  release was initially lower than the theoretical value but gradually approached and slightly exceeded the theoretical line at later stages, suggesting that ion exchange was a primary removal pathway while additional mechanisms contributed, particularly during the initial and intermediate stages. The moderately alkaline conditions may further allow a minor contribution from precipitation (Fig. S2a). At 1000  $\text{mg L}^{-1}$ , the experimental data were consistently below the theoretical ion-exchange line, indicating that ion exchange alone could not account for the observed  $\text{Ni}^{2+}$  removal.  $\text{Na}^{+}$  release continuously increased throughout the reaction period (Fig. S2b), demonstrating that ion exchange remained active. These results collectively demonstrated that ion exchange was a primary but concentration-dependent mechanism for  $\text{Ni}^{2+}$  uptake onto NASH, with additional contributions from pH-induced precipitation and surface complexation (Islam et al., 2019; Mo et al., 2021; Villafranca et al., 2024; Zhao et al., 2017).

The sorbed  $\text{Ni}^{2+}$  contents determined from solution-phase analysis were  $1.092 \pm 0.001$ ,  $5.004 \pm 0.007$ , and  $10.32 \pm 0.16$  wt% at 50, 200, and 1000  $\text{mg L}^{-1}$ , respectively, while the corresponding Ni loading values determined by solid-phase acid digestion were  $0.968 \pm 0.011$ ,  $3.87 \pm 0.16$ , and  $8.99 \pm 0.15$  wt% (mean  $\pm$  standard error). The slight discrepancy between the two measurements was attributed to the inherent differences between solution-based estimation and solid-phase quantification, including potential contributions from surface-adsorbed or precipitated Ni species not fully incorporated into the solid matrix. Nevertheless, the overall agreement between the two approaches indicated that solution-based sorption data reasonably estimated the Ni loading of NASH, providing a basis for its subsequent use as a Ni-containing catalyst precursor. An additional aqueous leaching test of the 9.0% Ni-NASH showed only trace Ni release ( $0.007 \text{ mg L}^{-1}$ ) after 24 h of contact with deionized water, indicating limited leaching of sorbed Ni under the tested conditions.

### 3.3. Structural transformation into Ni-based catalyst

Prior to reduction, the reducibility of the calcined 9.0% Ni-NASH was evaluated by H<sub>2</sub>-TPR analysis to identify an appropriate reduction temperature for catalyst activation (Fig. S4). Two reduction peaks were observed at approximately 380 and 645 °C, attributed to the reduction of NiO species with weak and strong metal-support interactions, respectively (Ahmad et al., 2021). Accordingly, a reduction temperature of 800 °C was selected to ensure sufficient reduction of NiO species. The structural transformation arising from this thermal treatment was subsequently examined by XRD as a function of Ni loading.

The XRD patterns of Ni-NASH and Ni-Cat. samples were presented in Fig. 3. For the Ni-NASH samples (Fig. 3a), the characteristic reflections of hydrosodalite remained detectable across all Ni loadings, indicating that the aluminosilicate framework was largely preserved following Ni<sup>2+</sup> sorption. However, the progressive decrease in overall reflection intensity with increasing Ni loading suggested a gradual reduction in the crystallinity of the hydrosodalite framework following Ni<sup>2+</sup> uptake. A weak reflection emerged at approximately 29.4° and increased in intensity with increasing Ni loading, suggesting a possible association with Ni-containing species. However, the absence of additional characteristic reflections precluded a definitive phase assignment. Given that the equilibrium pH decreased from 10.6 to 6.7 with increasing initial Ni concentration, bulk Ni(OH)<sub>2</sub> precipitation was unlikely to be the dominant contributor under these conditions.

Following calcination and H<sub>2</sub> reduction, the XRD patterns of the Ni-Cat. samples differed markedly from those of the Ni-NASH precursors (Fig. 3b). The hydrosodalite phase was completely transformed, and new reflections corresponding to carnegieite (NaAlSiO<sub>4</sub>, JCPDS No. 11-0220) emerged in the 1.0% and 3.9% Ni-Cat. samples, suggesting a thermally induced phase transition of the aluminosilicate framework (Walkley et al., 2018a). Additionally, reflections corresponding to face-centered cubic (FCC) metallic Ni<sup>0</sup> (JCPDS No. 04-0850) were observed in all Ni-Cat. samples. In the 9.0% Ni-Cat. sample, the carnegieite reflections were absent and the metallic Ni<sup>0</sup> reflections were dominant, suggesting that high Ni loading hindered the crystallization of the aluminosilicate phase during thermal treatment. This behavior may be attributed to Ni<sup>2+</sup>-induced changes in the local charge balance and Na-Al-Si environment of NASH, which could have interfered with the structural rearrangement required for crystallization.

The surface chemical states of the 9.0% Ni-NASH and 9.0% Ni-Cat.

samples were examined by XPS analysis. The Si 2p spectrum of the 9.0% Ni-NASH sample exhibited only minor shifts relative to pristine NASH (Figs. S1h and S5a), suggesting that the Si chemical state was largely preserved following Ni<sup>2+</sup> uptake. The Na 1s peak intensity decreased markedly compared to pristine NASH, indicating that Na<sup>+</sup> was released from the aluminosilicate framework upon Ni<sup>2+</sup> sorption, corroborating the ion exchange mechanism discussed in Section 3.2. The Ni 2p<sub>3/2</sub> spectrum displayed a main peak at 855.8 eV with a prominent satellite feature at 861.4 eV, consistent with the presence of Ni<sup>II</sup> species (Yadav et al., 2023).

The XPS spectra of the 9.0% Ni-Cat. sample exhibited distinct changes in chemical states relative to the 9.0% Ni-NASH sample following calcination and H<sub>2</sub> reduction (Fig. S5b). The Si 2p components exhibited a reduced separation with a relative increase in the Si-O-Si component (102.5 eV), suggesting enhanced silicate network polymerization following thermal treatment (Vasconcelos et al., 2025). The Na 1s binding energy shifted from 1071.3 to 1071.8 eV, reflecting modifications in the Na<sup>+</sup> chemical environment associated with thermal transformation of the aluminosilicate framework. In the Ni 2p<sub>3/2</sub> spectrum, peaks at 852.0 and 854.6 eV were assigned to metallic Ni<sup>0</sup> and Ni<sup>II</sup>, respectively, accompanied by a satellite feature at 860.3 eV characteristic of Ni<sup>II</sup> (Sánchez-González et al., 2025). The metallic Ni<sup>0</sup> peak at 852.0 eV confirmed successful reduction of Ni<sup>II</sup>, consistent with the XRD results and the reduction behavior indicated by H<sub>2</sub>-TPR (Figs. 3b and S4). TEM analysis was further performed to examine the particle size and spatial distribution of Ni particles in the 9.0% Ni-Cat. Nanoscale Ni particles were distributed over the NASH-derived aluminosilicate support, with some localized aggregation (Fig. S6). The particles exhibited an average diameter of 37.1 ± 12.7 nm (*n* = 73), and approximately 82.2% of the particles were distributed within the 20–50 nm range. STEM-EDX elemental mapping further confirmed the broad spatial distribution of Ni over the support, together with Si, Al, O, and Na.

### 3.4. Thermal degradation and pyrolysis of HDPE

Prior to evaluating the catalytic performance of Ni-Cat. during pyrolysis, the thermal degradation behavior of HDPE was investigated using TGA (Fig. S7a). Under an N<sub>2</sub> atmosphere, the primary thermal degradation of HDPE occurred between 390 and 520 °C, with the maximum degradation rate observed at 473 °C. This was attributed to the volatilization of condensable and non-condensable hydrocarbons

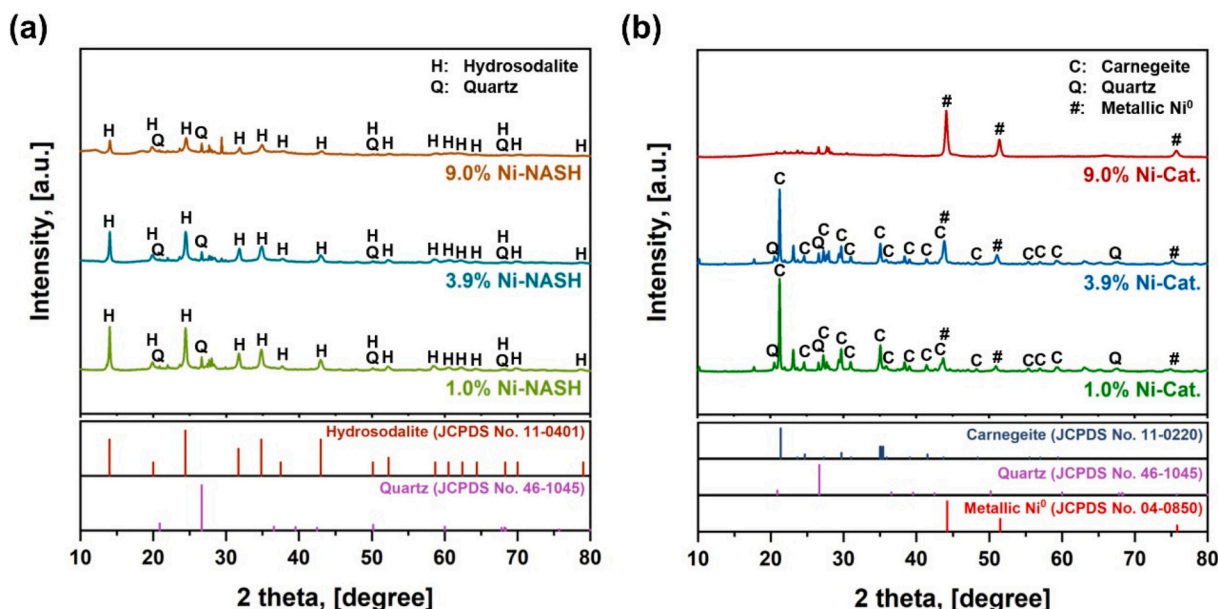


Fig. 3. XRD patterns of (a) Ni-NASH and (b) Ni-Cat. samples at different Ni loadings.

(HCs) through C—C and C—H bond scission (Wang et al., 2025). HDPE was completely volatilized by 700 °C, indicating its conversion into volatile products. The thermal degradation profile under a CO<sub>2</sub> atmosphere closely resembled that under an N<sub>2</sub> atmosphere, suggesting that CO<sub>2</sub> did not significantly influence the thermal decomposition of HDPE.

To characterize the pyrolysis products derived from HDPE, lab-scale conventional pyrolysis was conducted at 700 °C under N<sub>2</sub> and CO<sub>2</sub> atmospheres, as determined by TGA. Under an N<sub>2</sub> atmosphere, pyrolysis of HDPE predominantly produced liquid HCs with a carbon-number distribution ranging from C<sub>7</sub> to C<sub>37</sub> (Fig. S7b and Table S5). The broad distribution of HCs was attributed to random chain scission reactions occurring along the chemically uniform HDPE backbone (Li et al., 2025). Given that saturated HCs with a carbon number of 17 have melting points of approximately 20–22 °C, the liquid pyrolysates were categorized into three carbon-number ranges based on their physical state: C<sub>7</sub>–C<sub>16</sub> (oil), C<sub>17</sub>–C<sub>20</sub> (semi-wax), and C<sub>21</sub>–C<sub>37</sub> (wax) (Li et al., 2019). Under a CO<sub>2</sub> atmosphere, the liquid pyrolysates exhibited similar chemical compositions to those under an N<sub>2</sub> atmosphere

(Table S5), but with a shift toward shorter-chain HCs. The cumulative peak areas of C<sub>21</sub>–C<sub>37</sub> (wax) and C<sub>17</sub>–C<sub>20</sub> (semi-wax) decreased by 19.9 and 9.5%, respectively, relative to an N<sub>2</sub> atmosphere, whereas the C<sub>7</sub>–C<sub>16</sub> fraction showed only a 3.8% reduction (Fig. S7c). The observed slight increase in C<sub>7</sub>–C<sub>10</sub> HC intensities suggested that CO<sub>2</sub> may have participated in gas-phase homogeneous reactions (GHRs) with high-molecular-weight HCs, promoting lighter HC formation (Lee et al., 2026a). Nevertheless, the influence of CO<sub>2</sub> on the overall conversion of pyrolysis products into gaseous species was negligible (Fig. S7d). This limited influence may be associated with restricted interactions between CO<sub>2</sub> and long-chain HCs, which have relatively low volatility.

### 3.5. Catalytic pyrolysis performance under N<sub>2</sub> and CO<sub>2</sub>

To promote the conversion of HDPE-derived volatiles into gaseous products, Ni-Cat. samples were introduced into the ex-situ pyrolysis system operated with an additional high-temperature reaction zone. A previous study demonstrated enhanced syngas production during HDPE

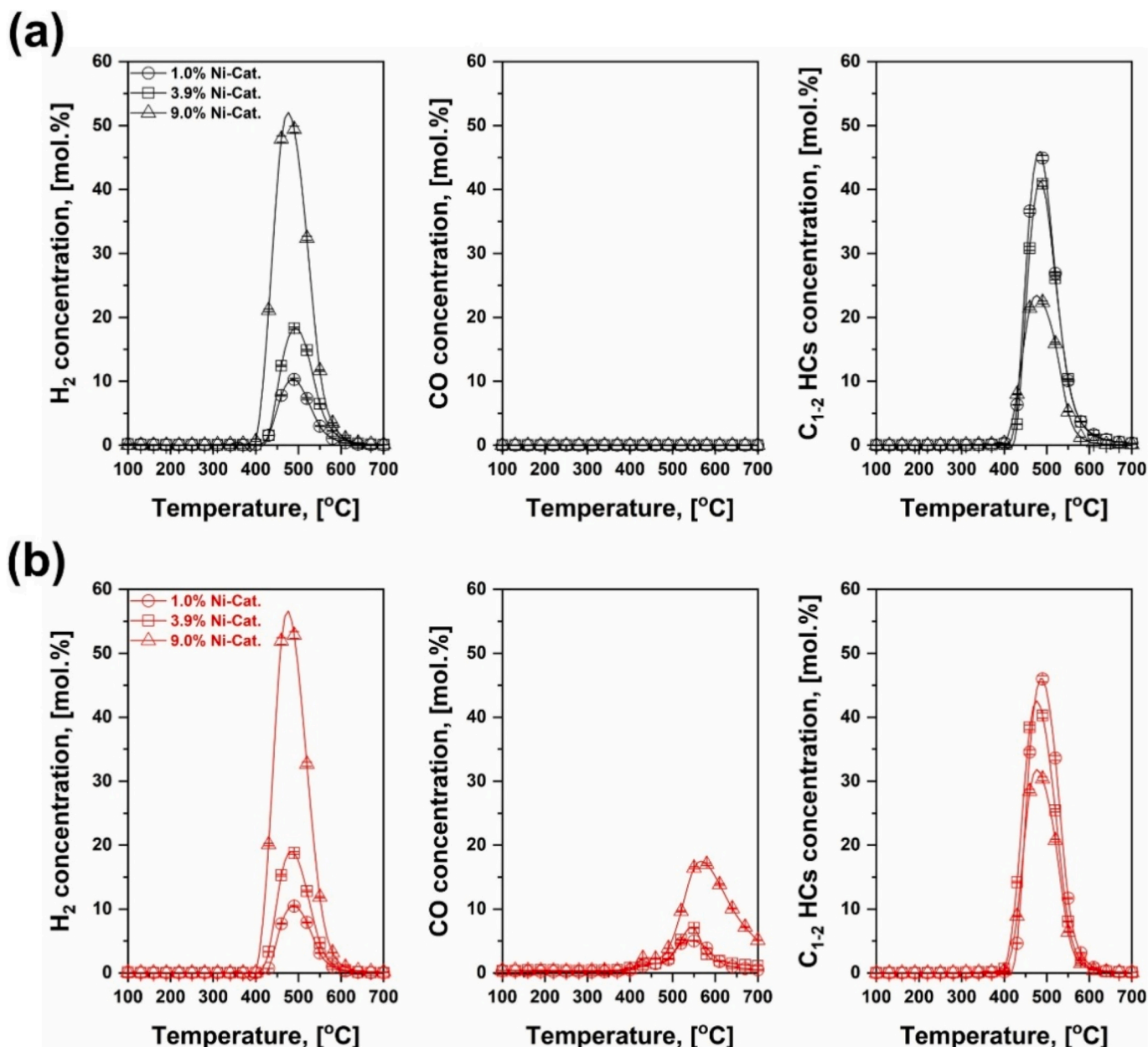


Fig. 4. Concentration profiles of H<sub>2</sub>, CO, and C<sub>1–2</sub> HCs during ex-situ catalytic pyrolysis of HDPE under (a) N<sub>2</sub> and (b) 80 vol% CO<sub>2</sub> atmospheres.

pyrolysis in the presence of a Ni-based catalyst at 700 °C (Lee et al., 2025). Accordingly, the second heating zone was maintained at 700 °C to evaluate the catalytic performance of the sorption-derived Ni-Cat. samples with three Ni loadings (1.0%, 3.9%, and 9.0% Ni-Cat.), targeting the cracking and reforming of HDPE-derived long-chain volatile compounds (VCs) into syngas.

The resulting gas evolution profiles under an N<sub>2</sub> atmosphere were presented in Fig. 4a. The H<sub>2</sub> and C<sub>1–2</sub> HC evolution was initiated at approximately 390 °C, consistent with the thermal degradation behavior observed in the TGA results (Fig. S7a). In contrast, CO formation was not observed due to the absence of oxygen-containing functional groups in HDPE. The H<sub>2</sub> concentration increased progressively with Ni loading, with 9.0% Ni-Cat. exhibiting the highest H<sub>2</sub> production among the catalysts evaluated. The enhanced H<sub>2</sub> production over 9.0% Ni-Cat. may be associated with its higher Ni loading and the presence of metallic Ni<sup>0</sup> (Fig. 3b), which provided active sites for C–H bond activation and dehydrogenation reactions (Min et al., 2021).

The gas evolution profiles obtained under a CO<sub>2</sub> atmosphere were presented in Fig. 4b. Compared to the N<sub>2</sub> atmosphere, the introduction of CO<sub>2</sub> markedly altered the gas composition, particularly by promoting CO formation. Since HDPE did not contain oxygen, the observed CO generation suggested the involvement of CO<sub>2</sub> in GHRs with HDPE-derived VCs (Lee et al., 2024). The onset temperature of H<sub>2</sub> and C<sub>1–2</sub> HC evolution (~390 °C) was consistent with that observed under an N<sub>2</sub> atmosphere. Notably, both H<sub>2</sub> and CO production increased with increasing Ni loading, with 9.0% Ni-Cat. exhibiting the highest gas production. Although reverse water-gas shift reactions (rWGS; H<sub>2</sub> + CO<sub>2</sub> → CO + H<sub>2</sub>O) may have partially consumed H<sub>2</sub>, the simultaneous increase in both H<sub>2</sub> and CO suggested that catalytic cracking of HDPE-derived VCs remained the dominant H<sub>2</sub>-generating pathway.

The cumulative gas production and mass distributions of pyrolysis products were presented in Fig. S8a and b, respectively. Under an N<sub>2</sub> atmosphere, ex-situ catalytic pyrolysis considerably increased gaseous product formation compared to conventional pyrolysis, while wax formation was not observed (Fig. S8b). This result was attributed to the enhanced cracking of heavy HCs into lighter gaseous products over the Ni-Cat. samples (Lee et al., 2026b). Furthermore, the cumulative gas yield increased progressively with Ni loading (Fig. S8a), demonstrating that metallic Ni<sup>0</sup> promoted the conversion of HDPE-derived VCs into gaseous products. The liquid pyrolysates were predominantly composed of monocyclic aromatic hydrocarbons (MAHs) and polycyclic aromatic hydrocarbons (PAHs) (Table S6), likely formed through secondary repolymerization and aromatization reactions under high-temperature conditions (Akhtar et al., 2024). Nevertheless, the cumulative peak areas of MAHs and PAHs decreased with increasing Ni loading (Fig. S9), suggesting that higher Ni loading may have further facilitated the cracking of aromatic intermediates into gaseous products.

Under a CO<sub>2</sub> atmosphere, the cumulative gas production further increased compared to that under an N<sub>2</sub> atmosphere (Fig. S8a). In particular, CO formation was significantly enhanced, which was likely associated with GHRs between CO<sub>2</sub> and HDPE-derived VCs. In these reactions, CO<sub>2</sub> could serve as an oxygen source for the conversion of carbon-containing intermediates into CO. A possible mechanism could involve radical-mediated interactions between CO<sub>2</sub> and HDPE-derived VCs. Thermal decomposition of HDPE-derived VCs could generate chain carbon radicals (R<sub>n</sub>·) through C–C and C–H bond cleavage (Li et al., 2018). These radical species could interact with CO<sub>2</sub> to form oxygen-containing intermediates (R<sub>n</sub>-O-C-O) (Luo et al., 2022), contributing to subsequent dissociation of C–O bonds to yield CO as the primary gaseous product. Increasing the Ni loading from 1.0 to 9.0 wt% could increase the availability of accessible metallic Ni<sup>0</sup> sites, which may facilitate the catalytic cracking of primary VCs into lighter gaseous species. These species could subsequently participate more readily in CO<sub>2</sub>-assisted reactions, thereby contributing to enhanced CO formation. In addition, the formation of MAHs and PAHs was further suppressed under a CO<sub>2</sub> atmosphere, with cumulative peak areas decreasing by 7.3,

41.5, and 30.1% for the 1.0, 3.9, and 9.0% Ni-Cat. samples, respectively (Fig. S9 and Table S6). These results collectively indicated that the combined effects of catalytic cracking and CO<sub>2</sub>-assisted GHRs promoted the conversion of HDPE-derived VCs into gaseous products.

Coke formation on metallic Ni<sup>0</sup> surfaces was expected during catalytic pyrolysis involving extensive C–C and C–H bond scission (Wu et al., 2025). Coke deposition on the catalyst surfaces could significantly influence catalytic performance by covering accessible metallic Ni<sup>0</sup> sites, thereby contributing to catalyst deactivation (Ong et al., 2022). To quantify coke deposition, TPO analysis was performed on the fresh and spent catalysts under N<sub>2</sub> and CO<sub>2</sub> atmospheres using a TGA system (Fig. S10). The spent catalysts exhibited notable mass losses compared to the fresh catalysts, corresponding to the combustion of carbonaceous deposits above 400 °C (Kumar et al., 2026). Accordingly, the lower extent of mass loss under a CO<sub>2</sub> atmosphere relative to an N<sub>2</sub> atmosphere suggested that CO<sub>2</sub> suppressed carbon deposition on the Ni catalysts. This could be attributed to CO<sub>2</sub>-assisted GHRs, which converted potential carbon precursors into CO, thereby inhibiting coke formation (Jung et al., 2020). In addition, the higher H<sub>2</sub> yields observed under a CO<sub>2</sub> atmosphere may be partially attributed to reduced coke formation, which preserved the metallic Ni<sup>0</sup> active sites for dehydrogenation reactions (Nyambura et al., 2026). Notably, the differences in carbon deposition between N<sub>2</sub> and CO<sub>2</sub> atmospheres increased with Ni loading, reaching 3.3, 3.9, and 20.6 wt% for the 1.0, 3.9, and 9.0% Ni-Cat. samples, respectively. The pronounced difference observed at 9.0% Ni-Cat. suggested a greater contribution of CO<sub>2</sub>-assisted reactions at higher Ni loading, which may have enhanced the conversion of carbon precursors into gaseous products.

To further characterize the effects of coke deposition on the catalysts, the phase composition and surface morphology of the fresh and spent 9.0% Ni-Cat./SiO<sub>2</sub> catalytic beds were examined by XRD and SEM-EDX analyses (Figs. S11 and S12), respectively. The reflection associated with graphitic carbon became markedly more intense in both spent catalytic beds than in the fresh catalytic bed, while the characteristic reflections of metallic Ni<sup>0</sup> remained detectable after pyrolysis under both N<sub>2</sub> and CO<sub>2</sub> atmospheres (Fig. S11). No distinct reflections attributable to crystalline Ni oxide phases were observed in either spent catalytic bed. In particular, the catalyst spent under N<sub>2</sub> exhibited a stronger graphitic carbon reflection than that spent under CO<sub>2</sub>, indicating greater accumulation of crystalline carbonaceous deposits under the N<sub>2</sub> atmosphere. This observation further supported the suppression of carbonaceous deposit accumulation under the CO<sub>2</sub> atmosphere, which may be associated with GHRs between CO<sub>2</sub> and coke precursors. SEM analysis (Fig. S12) showed that the overall particulate morphology of the 9.0% Ni-Cat./SiO<sub>2</sub> catalytic bed was retained after pyrolysis, although the spent samples exhibited more heterogeneous and aggregated surface features than the fresh catalytic bed. EDX analysis further revealed differences in the relative Ni and C contents depending on the reaction atmosphere. Specifically, the catalytic bed spent under N<sub>2</sub> exhibited a lower relative Ni content (2.3 wt%) and a higher relative C content (66.2 wt%) than that spent under 80 vol% CO<sub>2</sub> (7.1 wt% Ni and 49.3 wt % C). This inverse trend was consistent with greater accumulation of carbonaceous deposits under N<sub>2</sub>, which may have partially covered Ni-containing regions of the catalyst surface. Combined with the TPO results, these observations suggested that CO<sub>2</sub> suppressed carbon deposition and may have reduced the coverage of Ni-containing surface regions during pyrolysis.

The textural properties of the fresh and spent 9.0% Ni-Cat./SiO<sub>2</sub> catalytic beds were evaluated by BET/BJH analysis (Fig. S13). The fresh catalytic bed exhibited a specific surface area of 192.3 m<sup>2</sup> g<sup>−1</sup>, a total pore volume of 0.32 cm<sup>3</sup> g<sup>−1</sup>, and an average pore diameter of 3.3 nm. After pyrolysis under N<sub>2</sub> and 80 vol% CO<sub>2</sub>, the specific surface area slightly decreased to 176.5 and 182.7 m<sup>2</sup> g<sup>−1</sup>, respectively, whereas the total pore volume increased to 0.35 and 0.38 cm<sup>3</sup> g<sup>−1</sup> and the average pore diameter increased to 4.0 and 4.2 nm, respectively. These results suggested that the textural properties of the catalytic beds were largely

retained after pyrolysis, although some redistribution of the pore structure occurred. The catalytic bed spent under 80 vol% CO<sub>2</sub> exhibited a slightly higher specific surface area and total pore volume than that spent under N<sub>2</sub>, consistent with the lower coke deposition observed under the CO<sub>2</sub> atmosphere. Overall, the relatively small decrease in specific surface area indicated that substantial deterioration of the textural properties did not occur during pyrolysis.

Ni retention after catalytic application was assessed by microwave-assisted acid digestion followed by ICP-OES analysis. After correction for the SiO<sub>2</sub> content in the catalytic beds, the Ni contents were  $7.568 \pm 0.064$  wt% under N<sub>2</sub> and  $8.658 \pm 0.099$  wt% under 80 vol% CO<sub>2</sub>. These results indicated that a substantial fraction of Ni was retained in the catalytic beds after pyrolysis under both atmospheres.

### 3.6. Effect of CO<sub>2</sub> concentration on catalytic pyrolysis

Given the highest catalytic performance demonstrated by 9.0% Ni-Cat. under a CO<sub>2</sub> atmosphere (Section 3.5), ex-situ catalytic pyrolysis of HDPE was conducted using this catalyst at varying CO<sub>2</sub> concentrations (0, 20, 50, and 80 vol%) to systematically investigate the effect of CO<sub>2</sub> concentration on syngas production and product distribution. The cumulative gas production and product mass distribution were presented in Fig. S14. The cumulative gaseous product yield increased with CO<sub>2</sub> concentration (Fig. S14a). In particular, the cumulative CO yield increased from 18.2 to 58.9 mmol as the CO<sub>2</sub> concentration increased from 20 to 80 vol%. At 20 and 50 vol% CO<sub>2</sub>, H<sub>2</sub> yield decreased while CO yield increased compared to the 0 vol% CO<sub>2</sub> atmosphere, reflecting a shift in the relative contribution of CO<sub>2</sub>-assisted reaction pathways. This decrease in H<sub>2</sub> yield could be attributed to the rWGS, which consumes H<sub>2</sub> to produce CO (Chen et al., 2024). Nevertheless, the increase in CO yield was not stoichiometrically equivalent to the decrease in H<sub>2</sub> yield, suggesting additional CO sources other than rWGS. These observations were consistent with CO<sub>2</sub>-induced suppression of coke formation (Fig. S15), which likely helped preserve accessible metallic Ni<sup>0</sup> active sites and further promoted the conversion of pyrolytic volatiles into gaseous products (Jung et al., 2022; Song et al., 2023). This was further corroborated by the increased gaseous product yield and the corresponding decrease in liquid product yield with increasing CO<sub>2</sub> concentration (Fig. S14b).

To further elucidate the effects of CO<sub>2</sub> concentration across different Ni loadings, ex-situ catalytic pyrolysis was conducted using 1.0 and 3.9% Ni-Cat. samples, and the cumulative syngas production and coke deposition were presented in Fig. 5a and b, respectively. Coke deposition was estimated from the TPO profiles based on the difference in mass loss

between fresh and spent catalysts. A similar trend was observed across all Ni loadings (Fig. 5a), with H<sub>2</sub> yield decreasing and CO yield increasing at 20 and 50 vol% CO<sub>2</sub> relative to the 0 vol% CO<sub>2</sub> atmosphere. In contrast, both H<sub>2</sub> and CO yields reached their maximum values at 80 vol% CO<sub>2</sub>, suggesting an increasing contribution of CO<sub>2</sub>-assisted GHRs relative to the rWGS at higher CO<sub>2</sub> concentrations. Moreover, coke deposition on the spent catalysts decreased with increasing CO<sub>2</sub> concentration (Fig. 5b). The reduced coke formation under a CO<sub>2</sub> atmosphere suggested decreased coverage of accessible metallic Ni<sup>0</sup> sites by carbonaceous deposits, which may help mitigate coke-induced catalyst deactivation (Abdel-Fatah and Amin, 2025).

### 3.7. Practical and environmental implications

The circular valorization pathway developed in this study, in which Ni(II)-laden spent NASH was directly transformed into a catalyst for CO<sub>2</sub>-assisted pyrolysis of HDPE, was illustrated in Fig. 6. The catalytic performance of Ni-Cat. was compared with that reported for other thermochemical systems (Table S7). Under present conditions, the 9.0% Ni-Cat. produced 56.8 mmol g<sub>sample</sub><sup>-1</sup> of syngas with a coke formation of 6.0 wt%. The syngas production was comparable to that reported for other Ni-based plastic conversion systems, while coke formation remained within the lower range of the reported values. These results indicated that the sorption-derived catalyst could achieve comparable syngas production with relatively limited coke formation, highlighting the potential of spent sorbents as catalyst precursors for thermochemical conversion processes.

The proposed approach could reduce the need for conventional catalyst synthesis and additional metal precursor inputs because the sorbed Ni species were directly converted into catalytically active metallic Ni<sup>0</sup> through calcination and H<sub>2</sub> reduction. From an economic perspective, this strategy may reduce the material and disposal burdens associated with conventional catalyst preparation and spent-sorbent management by directly valorizing the Ni-laden sorbent as a catalyst precursor. However, additional energy and material inputs are required for calcination and H<sub>2</sub> reduction, and quantitative techno-economic and life-cycle assessments based on process-scale cost and energy data should be considered in future scale-up studies. Furthermore, the use of CO<sub>2</sub> as a reactive atmosphere suppressed coke formation during catalytic pyrolysis, suggesting a reduced potential for coke-induced deactivation. However, prolonged catalyst stability remains to be verified through repeated-cycle or continuous operation experiments. Overall, this study demonstrated an integrated waste valorization strategy linking aqueous Ni<sup>2+</sup> removal with thermochemical plastic waste

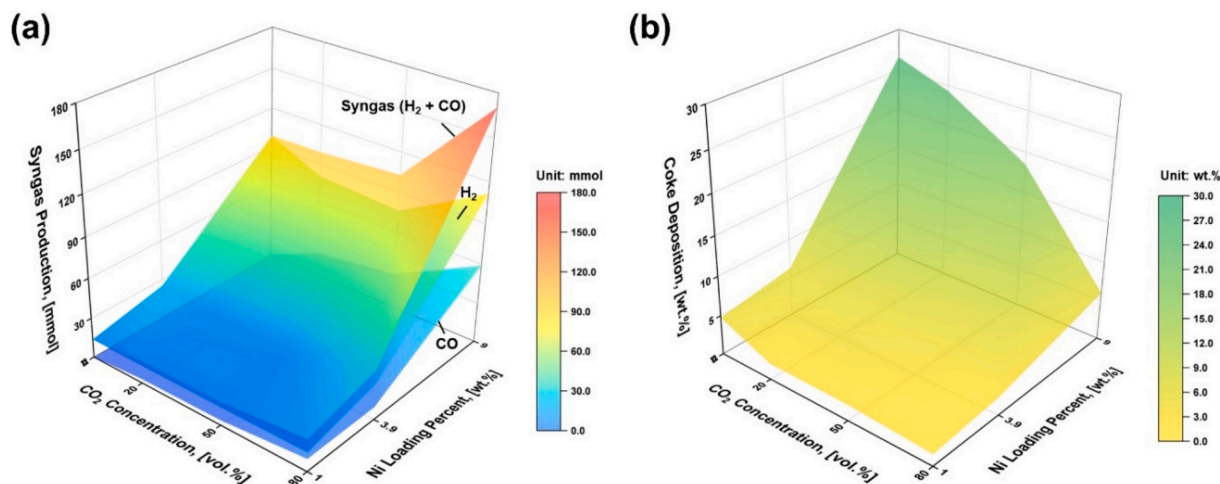
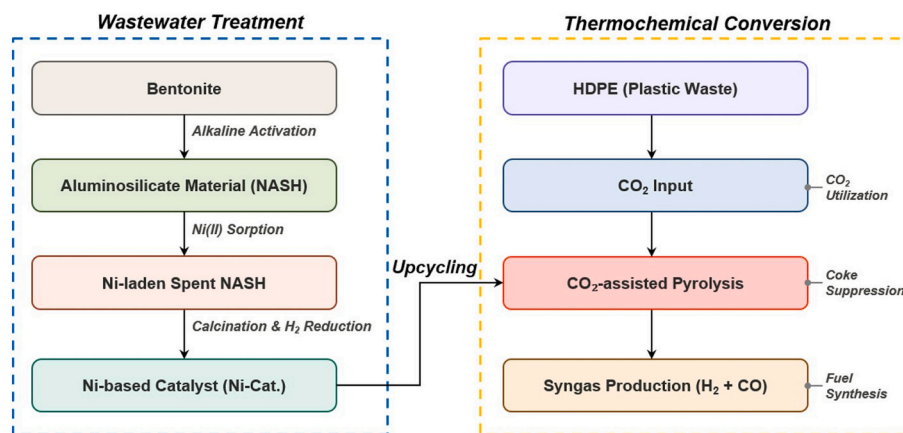


Fig. 5. Effects of CO<sub>2</sub> concentration and Ni loading on catalytic performance during ex-situ pyrolysis of HDPE over Ni-Cat. samples: (a) cumulative syngas production and (b) coke deposition.



**Fig. 6.** Schematic illustration of the proposed circular valorization pathway integrating aqueous  $\text{Ni}^{2+}$  removal by NASH with the conversion of Ni-laden spent sorbents into catalysts for  $\text{CO}_2$ -assisted pyrolysis of plastic waste.

conversion. By converting Ni-laden spent sorbents into functional catalysts, the proposed pathway could provide an alternative to conventional disposal-oriented management while simultaneously enabling syngas production from plastic waste under  $\text{CO}_2$ -assisted conditions.

#### 4. Conclusions

This study demonstrated a circular valorization pathway linking aqueous  $\text{Ni}^{2+}$  removal with thermochemical plastic waste conversion. Ni-laden spent NASH was transformed into a heterogeneous catalyst for  $\text{CO}_2$ -assisted pyrolysis of HDPE. NASH synthesized via alkali activation of bentonite exhibited effective  $\text{Ni}^{2+}$  uptake through concentration-dependent mechanisms, including ion exchange, surface complexation, and pH-induced precipitation, yielding Ni loadings of 1.0, 3.9, and 9.0 wt%. Subsequent calcination and  $\text{H}_2$  reduction converted sorbed  $\text{Ni}^{\text{II}}$  species into metallic  $\text{Ni}^0$ , as confirmed by XRD and XPS analyses. Among the tested catalysts, 9.0% Ni-Cat. exhibited the highest catalytic activity. Under a  $\text{CO}_2$  atmosphere, the combined effects of catalytic cracking and  $\text{CO}_2$ -assisted GHRs enhanced syngas production while suppressing coke formation relative to an  $\text{N}_2$  atmosphere. Increasing the  $\text{CO}_2$  concentration from 20 to 80 vol% progressively increased CO yield from 18.2 to 58.9 mmol, while both  $\text{H}_2$  and CO yields reached their maximum values at 80 vol%  $\text{CO}_2$ , suggesting an increasing contribution of  $\text{CO}_2$ -assisted GHRs relative to the rWGSr at higher  $\text{CO}_2$  concentrations. These findings demonstrated the potential of spent sorbent upcycling as an integrated strategy for wastewater treatment and thermochemical plastic waste valorization. Further repeated-cycle and continuous-operation tests are required to establish the long-term catalytic stability, while in situ spectroscopic and kinetic studies are needed to further validate the proposed  $\text{CO}_2$ -assisted reaction pathways. Techno-economic and life-cycle assessments are also needed to evaluate the feasibility of the proposed upcycling strategy at larger scales.

#### CRedit authorship contribution statement

**Kwangsuk Yoon:** Writing – original draft, Investigation, Conceptualization. **Hoyeon Cha:** Visualization, Formal analysis. **Heuiyun Lee:** Investigation, Formal analysis. **Eilhann E. Kwon:** Methodology, Data curation. **Taewoo Lee:** Writing – review & editing, Validation. **Hocheol Song:** Writing – review & editing, Supervision.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.clay.2026.108401>.

#### Data availability

Data will be made available on request.

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