Research Article

Promotion Effect of CaO Modification on Mesoporous Al_2O_3 -Supported Ni Catalysts for CO_2 Methanation

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The catalysts $\text{Ni}/\text{Al}_2\text{O}_3$ and CaO modified $\text{Ni}/\text{Al}_2\text{O}_3$ were prepared by impregnation method and applied for methanation of CO_2 . The catalysts were characterized by N_2 adsorption/desorption, temperature-programmed reduction of H_2 (H_2 -TPR), X-ray diffraction (XRD), and temperature-programmed desorption of CO_2 and H_2 (CO_2 -TPD and H_2 -TPD) techniques, respectively. TPR and XRD results indicated that CaO can effectively restrain the growth of NiO nanoparticles, improve the dispersion of NiO, and weaken the interaction between NiO and Al_2O_3 . CO_2 -TPD and H_2 -TPD results suggested that CaO can change the environment surrounding of CO_2 and H_2 adsorption and thus the reactants on the Ni atoms can be activated more easily. The modified $\text{Ni}/\text{Al}_2\text{O}_3$ showed better catalytic activity than pure $\text{Ni}/\text{Al}_2\text{O}_3$. $\text{Ni}/\text{CaO}-\text{Al}_2\text{O}_3$ showed high CO_2 conversion especially at low temperatures compared to $\text{Ni}/\text{Al}_2\text{O}_3$, and the selectivity to CH_4 was very close to 1. The high CO_2 conversion over $\text{Ni}/\text{CaO}-\text{Al}_2\text{O}_3$ was mainly caused by the surface coverage by CO_2 -derived species on $\text{CaO}-\text{Al}_2\text{O}_3$ surface.

1. Introduction

In present years, various technological options have been considered to reduce the amount of carbon dioxide emitted in the atmosphere by combustion of fossil fuels [1–7]. In case hydrogen is available or can be produced by renewable energy such as solar energy in order to achieve a low-carbon society [4], the hydrogenation of captured CO_2 is an interesting option as a CO_2 Capture and Storage (CCS) technology [4]. The methane produced can be injected in chemical and petrochemical industries as natural gas use. Thus, the possibility to transform H_2 and CO_2 into CH_4 becomes a real alternative in an environmental and ecological point of view [7–9].

CO_2 methanation, also called the Sabatier reaction [10], has been known for a long time and a great number of metal catalysts have been conducted in the reaction [3, 4, 6–8, 11–14] such as Rh [4, 15–18], Ru [19, 20], Ni [1, 4, 21–26] supported on various oxide solids like Al_2O_3 [1, 2, 4, 15, 22, 27], SiO_2 [1, 4, 28], ZrO_2 [1, 21–24], or TiO_2 [17]. Evidences have shown that CO_2 adsorption and dissociation are the

first steps in the mechanism of CO_2 methanation, and CO_2 dissociation into CO is sometimes considered as a poisoning effect on hydrogen adsorption [4, 29]. Moreover, the increase of catalytic activity was also related to the enhancement of the hydrogen adsorption capacity. Therefore, in order to increase catalytic activity of the methanation, it is necessary to enhance hydrogen supply at the surface of the catalyst [15, 18]. It was suggested that nickel supported catalysts could supply active catalysts in CO_2 methanation to increase the reaction performances [30], and hence this was the principal objective of this work.

The Ni-based catalyst has been extensively investigated under widely varying experimental conditions, and $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts showed moderate catalytic activity in methanation of carbon dioxide with hydrogen [8]. For Ni-based catalysts, the promoters, such as MgO , CeO_2 , and La_2O_3 , have played important roles in the activity for CO_2 methanation. The basic properties, special electronic structure, and strong interaction with Ni could enhance the CO_2 adsorption and dissociation and consequently improve the activity of the catalyst for CO_2 methanation. In our previous study [2],

NiCe/CNTs and NiCe/Al₂O₃ catalysts prepared by impregnation method were found to be highly active and stable for CO₂ methanation. Therefore, it is desired to develop an effectively promoted Ni-based catalyst which exhibits high activity in methanation of carbon dioxide, namely, to combine a well-known catalyst Ni/Al₂O₃ with CaO in CO₂ adsorption and dissociation. The aim of this work was to investigate the effects of CaO-Al₂O₃ as the support and the content of CaO on the catalytic performance of CO₂ methanation over Ni/CaO-Al₂O₃ catalysts and to optimize the reaction temperature.

2. Experimental

2.1. Preparation of CaO-Al₂O₃ Supports and Ni-Based Catalysts. The CaO-Al₂O₃ composite support ($w_{\text{CaO}} = 0, 10, 20, 30\%$) was prepared by the sol-gel method. Ca(NO₃)₂·4H₂O, Al(NO₃)₃·9H₂O, and citric acid with a stoichiometric ratio were dissolved in deionized water and stirred and evaporated at 70°C until the solution became viscous colloids. Subsequently the support was dried in an oven at 120°C for 24 h and placed in the muffle furnace calcined at 600°C in air for 3 h [2, 22, 31, 32].

The Ni-based catalysts were prepared by impregnating the supports (100Al₂O₃, 10CaO-90Al₂O₃, 20CaO-80Al₂O₃, and 30CaO-70Al₂O₃) with an aqueous solution of Ni(NO₃)₂·6H₂O [2, 9, 22]. The Ni loading was fixed at 15 wt.% in the samples. The impregnated granules were dried at 120°C for 12 h and then calcined at 500°C in air for 3 h. The prepared catalysts were denoted as 15Ni/100Al₂O₃, 15Ni/10CaO90Al₂O₃, 15Ni/20CaO80Al₂O₃, and 15Ni/30CaO70Al₂O₃, respectively.

2.2. Characterization of Catalysts. N₂ adsorption/desorption was carried out using a Quantachrome Nova 1000e apparatus at 77 K. Before measurement, the samples were degassed at 120°C for 3 h [2, 9].

Temperature-programmed reduction of H₂ (H₂-TPR) was performed in a fixed bed reactor to observe the catalyst reducibility [2, 31, 32]. 100 mg sample was loaded in the middle of the reactor tube. The temperature of the reactor was raised from 100°C to 800°C at a heating rate of 10°C/min under 5% H₂/95% N₂ with a flow rate of 30 mL/min. The H₂ consumption was analyzed online by a SC-200 gas chromatograph with a thermal conductivity detector (TCD).

The crystalline phases of the catalysts were characterized by a Rigaku D/MAX-2500 X-ray diffractometer (XRD) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ scanning range of 10°–90° [2, 32].

Experiments of temperature-programmed desorption of CO₂ (CO₂-TPD) were conducted employing an automated gas sorption analyser TP-5080 [22]. The samples were pretreated at 500°C (5°C/min) under N₂ flow (30 mL/min) for 1 h and reduced at the same temperature under H₂ flow (30 mL/min) for 1 h. After that, the materials were cooled and exposed to CO₂ (30 mL/min) for 1 h at 50°C. CO₂-TPD measurements were carried out up to 750°C with the heating rate of 10°C/min under N₂ flow (30 mL/min).

Measurements of temperature-programmed desorption of H₂ (H₂-TPD) were performed with the same procedure as CO₂-TPD, only the adsorption gas changing from CO₂ to 5% H₂/95% N₂ [2, 22].

2.3. Catalytic Performance. The catalytic performance of the catalyst was conducted under atmospheric pressure in a fixed bed reactor with an interior diameter of 6 mm. 100 mg of catalyst was pretreated at 500°C in 30 mL/min H₂ flow for 1 h and then cooled down to room temperature in N₂. Next, a mixture of H₂ and CO₂ (molar ratio = 4.0) was switched to the reactor. The catalyst was then heated to the reaction temperature at a rate of 5°C/min. The composition of the outlet gases was analyzed online by a GC-1690 model gas chromatograph with a TDX-01 column and a thermal conductivity detector (TCD). The CO₂ conversion (X_{CO_2}) and CH₄ yield (Y_{CH_4}) were estimated by the following:

$$X_{\text{CO}_2} = \frac{(F_{\text{CH}_4\text{out}} + F_{\text{COout}})}{(F_{\text{CH}_4\text{out}} + F_{\text{COout}} + F_{\text{CO}_2\text{out}})}, \quad (1)$$

$$Y_{\text{CH}_4} = \frac{F_{\text{CH}_4\text{out}}}{(F_{\text{CH}_4\text{out}} + F_{\text{COout}} + F_{\text{CO}_2\text{out}})}.$$

3. Results and Discussion

3.1. Textural Properties of the Catalysts. The textural properties of the catalysts were characterized by N₂ adsorption/desorption analysis, and the N₂ adsorption/desorption isotherms and pore size distributions obtained by the BJH equation were shown in Figure 1. The pristine Ni/Al₂O₃ catalyst had a large pore size (average pore diameter) of 3.60 nm. After modification, the pore sizes of the catalysts changed significantly. The increase of pore size was attributed to deposition of nanoparticles in the pores of the Al₂O₃, which formed new porosity and extra surface area. As seen from Figure 1(b), the pristine catalyst exhibited the pore size distribution centered at about 3.60 nm. After the modification, the small pores below 20 nm were formed by the self-organization of nanoparticles inside the large pores of Al₂O₃. The formation of the pore structure by CaO modification would improve the dispersion of Ni species.

Specific surface area, pore volume, and pore diameter of the Ni/CaO-Al₂O₃ catalysts with different CaO contents calcined at 500°C were presented in Table 1. It could be seen that the addition of CaO resulted in slight increases in specific surface area and pore volume of the catalysts. Among the samples, 15Ni/10CaO90Al₂O₃ exhibited the largest specific surface area of 9.59 m²/g. This could be mainly attributed to the blocking of part of mesopores of the catalysts and the change in NiO and Al₂O₃ structures through their interactions with CaO. Furthermore, the pore diameters of the catalysts had changed.

3.2. Crystal Phase Analysis of the Catalysts. The XRD patterns of the catalysts calcined at 500°C were displayed in Figure 2, from which the diffraction peaks at 37.2°, 43.3°, 62.9°, 75.4°, 77.4°, 78.1°, 78.5°, 79.1°, 79.5°, 79.9°, 80.3°, 80.7°, 81.1°, 81.5°, 81.9°, 82.3°, 82.7°, 83.1°, 83.5°, 83.9°, 84.3°, 84.7°, 85.1°, 85.5°, 85.9°, 86.3°, 86.7°, 87.1°, 87.5°, 87.9°, 88.3°, 88.7°, 89.1°, 89.5°, 89.9°, 90.3°, 90.7°, 91.1°, 91.5°, 91.9°, 92.3°, 92.7°, 93.1°, 93.5°, 93.9°, 94.3°, 94.7°, 95.1°, 95.5°, 95.9°, 96.3°, 96.7°, 97.1°, 97.5°, 97.9°, 98.3°, 98.7°, 99.1°, 99.5°, 99.9°, 100.3°, 100.7°, 101.1°, 101.5°, 101.9°, 102.3°, 102.7°, 103.1°, 103.5°, 103.9°, 104.3°, 104.7°, 105.1°, 105.5°, 105.9°, 106.3°, 106.7°, 107.1°, 107.5°, 107.9°, 108.3°, 108.7°, 109.1°, 109.5°, 109.9°, 110.3°, 110.7°, 111.1°, 111.5°, 111.9°, 112.3°, 112.7°, 113.1°, 113.5°, 113.9°, 114.3°, 114.7°, 115.1°, 115.5°, 115.9°, 116.3°, 116.7°, 117.1°, 117.5°, 117.9°, 118.3°, 118.7°, 119.1°, 119.5°, 119.9°, 120.3°, 120.7°, 121.1°, 121.5°, 121.9°, 122.3°, 122.7°, 123.1°, 123.5°, 123.9°, 124.3°, 124.7°, 125.1°, 125.5°, 125.9°, 126.3°, 126.7°, 127.1°, 127.5°, 127.9°, 128.3°, 128.7°, 129.1°, 129.5°, 129.9°, 130.3°, 130.7°, 131.1°, 131.5°, 131.9°, 132.3°, 132.7°, 133.1°, 133.5°, 133.9°, 134.3°, 134.7°, 135.1°, 135.5°, 135.9°, 136.3°, 136.7°, 137.1°, 137.5°, 137.9°, 138.3°, 138.7°, 139.1°, 139.5°, 139.9°, 140.3°, 140.7°, 141.1°, 141.5°, 141.9°, 142.3°, 142.7°, 143.1°, 143.5°, 143.9°, 144.3°, 144.7°, 145.1°, 145.5°, 145.9°, 146.3°, 146.7°, 147.1°, 147.5°, 147.9°, 148.3°, 148.7°, 149.1°, 149.5°, 149.9°, 150.3°, 150.7°, 151.1°, 151.5°, 151.9°, 152.3°, 152.7°, 153.1°, 153.5°, 153.9°, 154.3°, 154.7°, 155.1°, 155.5°, 155.9°, 156.3°, 156.7°, 157.1°, 157.5°, 157.9°, 158.3°, 158.7°, 159.1°, 159.5°, 159.9°, 160.3°, 160.7°, 161.1°, 161.5°, 161.9°, 162.3°, 162.7°, 163.1°, 163.5°, 163.9°, 164.3°, 164.7°, 165.1°, 165.5°, 165.9°, 166.3°, 166.7°, 167.1°, 167.5°, 167.9°, 168.3°, 168.7°, 169.1°, 169.5°, 169.9°, 170.3°, 170.7°, 171.1°, 171.5°, 171.9°, 172.3°, 172.7°, 173.1°, 173.5°, 173.9°, 174.3°, 174.7°, 175.1°, 175.5°, 175.9°, 176.3°, 176.7°, 177.1°, 177.5°, 177.9°, 178.3°, 178.7°, 179.1°, 179.5°, 179.9°, 180.3°, 180.7°, 181.1°, 181.5°, 181.9°, 182.3°, 182.7°, 183.1°, 183.5°, 183.9°, 184.3°, 184.7°, 185.1°, 185.5°, 185.9°, 186.3°, 186.7°, 187.1°, 187.5°, 187.9°, 188.3°, 188.7°, 189.1°, 189.5°, 189.9°, 190.3°, 190.7°, 191.1°, 191.5°, 191.9°, 192.3°, 192.7°, 193.1°, 193.5°, 193.9°, 194.3°, 194.7°, 195.1°, 195.5°, 195.9°, 196.3°, 196.7°, 197.1°, 197.5°, 197.9°, 198.3°, 198.7°, 199.1°, 199.5°, 199.9°, 200.3°, 200.7°, 201.1°, 201.5°, 201.9°, 202.3°, 202.7°, 203.1°, 203.5°, 203.9°, 204.3°, 204.7°, 205.1°, 205.5°, 205.9°, 206.3°, 206.7°, 207.1°, 207.5°, 207.9°, 208.3°, 208.7°, 209.1°, 209.5°, 209.9°, 210.3°, 210.7°, 211.1°, 211.5°, 211.9°, 212.3°, 212.7°, 213.1°, 213.5°, 213.9°, 214.3°, 214.7°, 215.1°, 215.5°, 215.9°, 216.3°, 216.7°, 217.1°, 217.5°, 217.9°, 218.3°, 218.7°, 219.1°, 219.5°, 219.9°, 220.3°, 220.7°, 221.1°, 221.5°, 221.9°, 222.3°, 222.7°, 223.1°, 223.5°, 223.9°, 224.3°, 224.7°, 225.1°, 225.5°, 225.9°, 226.3°, 226.7°, 227.1°, 227.5°, 227.9°, 228.3°, 228.7°, 229.1°, 229.5°, 229.9°, 230.3°, 230.7°, 231.1°, 231.5°, 231.9°, 232.3°, 232.7°, 233.1°, 233.5°, 233.9°, 234.3°, 234.7°, 235.1°, 235.5°, 235.9°, 236.3°, 236.7°, 237.1°, 237.5°, 237.9°, 238.3°, 238.7°, 239.1°, 239.5°, 239.9°, 240.3°, 240.7°, 241.1°, 241.5°, 241.9°, 242.3°, 242.7°, 243.1°, 243.5°, 243.9°, 244.3°, 244.7°, 245.1°, 245.5°, 245.9°, 246.3°, 246.7°, 247.1°, 247.5°, 247.9°, 248.3°, 248.7°, 249.1°, 249.5°, 249.9°, 250.3°, 250.7°, 251.1°, 251.5°, 251.9°, 252.3°, 252.7°, 253.1°, 253.5°, 253.9°, 254.3°, 254.7°, 255.1°, 255.5°, 255.9°, 256.3°, 256.7°, 257.1°, 257.5°, 257.9°, 258.3°, 258.7°, 259.1°, 259.5°, 259.9°, 260.3°, 260.7°, 261.1°, 261.5°, 261.9°, 262.3°, 262.7°, 263.1°, 263.5°, 263.9°, 264.3°, 264.7°, 265.1°, 265.5°, 265.9°, 266.3°, 266.7°, 267.1°, 267.5°, 267.9°, 268.3°, 268.7°, 269.1°, 269.5°, 269.9°, 270.3°, 270.7°, 271.1°, 271.5°, 271.9°, 272.3°, 272.7°, 273.1°, 273.5°, 273.9°, 274.3°, 274.7°, 275.1°, 275.5°, 275.9°, 276.3°, 276.7°, 277.1°, 277.5°, 277.9°, 278.3°, 278.7°, 279.1°, 279.5°, 279.9°, 280.3°, 280.7°, 281.1°, 281.5°, 281.9°, 282.3°, 282.7°, 283.1°, 283.5°, 283.9°, 284.3°, 284.7°, 285.1°, 285.5°, 285.9°, 286.3°, 286.7°, 287.1°, 287.5°, 287.9°, 288.3°, 288.7°, 289.1°, 289.5°, 289.9°, 290.3°, 290.7°, 291.1°, 291.5°, 291.9°, 292.3°, 292.7°, 293.1°, 293.5°, 293.9°, 294.3°, 294.7°, 295.1°, 295.5°, 295.9°, 296.3°, 296.7°, 297.1°, 297.5°, 297.9°, 298.3°, 298.7°, 299.1°, 299.5°, 299.9°, 300.3°, 300.7°, 301.1°, 301.5°, 301.9°, 302.3°, 302.7°, 303.1°, 303.5°, 303.9°, 304.3°, 304.7°, 305.1°, 305.5°, 305.9°, 306.3°, 306.7°, 307.1°, 307.5°, 307.9°, 308.3°, 308.7°, 309.1°, 309.5°, 309.9°, 310.3°, 310.7°, 311.1°, 311.5°, 311.9°, 312.3°, 312.7°, 313.1°, 313.5°, 313.9°, 314.3°, 314.7°, 315.1°, 315.5°, 315.9°, 316.3°, 316.7°, 317.1°, 317.5°, 317.9°, 318.3°, 318.7°, 319.1°, 319.5°, 319.9°, 320.3°, 320.7°, 321.1°, 321.5°, 321.9°, 322.3°, 322.7°, 323.1°, 323.5°, 323.9°, 324.3°, 324.7°, 325.1°, 325.5°, 325.9°, 326.3°, 326.7°, 327.1°, 327.5°, 327.9°, 328.3°, 328.7°, 329.1°, 329.5°, 329.9°, 330.3°, 330.7°, 331.1°, 331.5°, 331.9°, 332.3°, 332.7°, 333.1°, 333.5°, 333.9°, 334.3°, 334.7°, 335.1°, 335.5°, 335.9°, 336.3°, 336.7°, 337.1°, 337.5°, 337.9°, 338.3°, 338.7°, 339.1°, 339.5°, 339.9°, 340.3°, 340.7°, 341.1°, 341.5°, 341.9°, 342.3°, 342.7°, 343.1°, 343.5°, 343.9°, 344.3°, 344.7°, 345.1°, 345.5°, 345.9°, 346.3°, 346.7°, 347.1°, 347.5°, 347.9°, 348.3°, 348.7°, 349.1°, 349.5°, 349.9°, 350.3°, 350.7°, 351.1°, 351.5°, 351.9°, 352.3°, 352.7°, 353.1°, 353.5°, 353.9°, 354.3°, 354.7°, 355.1°, 355.5°, 355.9°, 356.3°, 356.7°, 357.1°, 357.5°, 357.9°, 358.3°, 358.7°, 359.1°, 359.5°, 359.9°, 360.3°, 360.7°, 361.1°, 361.5°, 361.9°, 362.3°, 362.7°, 363.1°, 363.5°, 363.9°, 364.3°, 364.7°, 365.1°, 365.5°, 365.9°, 366.3°, 366.7°, 367.1°, 367.5°, 367.9°, 368.3°, 368.7°, 369.1°, 369.5°, 369.9°, 370.3°, 370.7°, 371.1°, 371.5°, 371.9°, 372.3°, 372.7°, 373.1°, 373.5°, 373.9°, 374.3°, 374.7°, 375.1°, 375.5°, 375.9°, 376.3°, 376.7°, 377.1°, 377.5°, 377.9°, 378.3°, 378.7°, 379.1°, 379.5°, 379.9°, 380.3°, 380.7°, 381.1°, 381.5°, 381.9°, 382.3°, 382.7°, 383.1°, 383.5°, 383.9°, 384.3°, 384.7°, 385.1°, 385.5°, 385.9°, 386.3°, 386.7°, 387.1°, 387.5°, 387.9°, 388.3°, 388.7°, 389.1°, 389.5°, 389.9°, 390.3°, 390.7°, 391.1°, 391.5°, 391.9°, 392.3°, 392.7°, 393.1°, 393.5°, 393.9°, 394.3°, 394.7°, 395.1°, 395.5°, 395.9°, 396.3°, 396.7°, 397.1°, 397.5°, 397.9°, 398.3°, 398.7°, 399.1°, 399.5°, 399.9°, 400.3°, 400.7°, 401.1°, 401.5°, 401.9°, 402.3°, 402.7°, 403.1°, 403.5°, 403.9°, 404.3°, 404.7°, 405.1°, 405.5°, 405.9°, 406.3°, 406.7°, 407.1°, 407.5°, 407.9°, 408.3°, 408.7°, 409.1°, 409.5°, 409.9°, 410.3°, 410.7°, 411.1°, 411.5°, 411.9°, 412.3°, 412.7°, 413.1°, 413.5°, 413.9°, 414.3°, 414.7°, 415.1°, 415.5°, 415.9°, 416.3°, 416.7°, 417.1°, 417.5°, 417.9°, 418.3°, 418.7°, 419.1°, 419.5°, 419.9°, 420.3°, 420.7°, 421.1°, 421.5°, 421.9°, 422.3°, 422.7°, 423.1°, 423.5°, 423.9°, 424.3°, 424.7°, 425.1°, 425.5°, 425.9°, 426.3°, 426.7°, 427.1°, 427.5°, 427.9°, 428.3°, 428.7°, 429.1°, 429.5°, 429.9°, 430.3°, 430.7°, 431.1°, 431.5°, 431.9°, 432.3°, 432.7°, 433.1°, 433.5°, 433.9°, 434.3°, 434.7°, 435.1°, 435.5°, 435.9°, 436.3°, 436.7°, 437.1°, 437.5°, 437.9°, 438.3°, 438.7°, 439.1°, 439.5°, 439.9°, 440.3°, 440.7°, 441.1°, 441.5°, 441.9°, 442.3°, 442.7°, 443.1°, 443.5°, 443.9°, 444.3°, 444.7°, 445.1°, 445.5°, 445.9°, 446.3°, 446.7°, 447.1°, 447.5°, 447.9°, 448.3°, 448.7°, 449.1°, 449.5°, 449.9°, 450.3°, 450.7°, 451.1°, 451.5°, 451.9°, 452.3°, 452.7°, 453.1°, 453.5°, 453.9°, 454.3°, 454.7°, 455.1°, 455.5°, 455.9°, 456.3°, 456.7°, 457.1°, 457.5°, 457.9°, 458.3°, 458.7°, 459.1°, 459.5°, 459.9°, 460.3°, 460.7°, 461.1°, 461.5°, 461.9°, 462.3°, 462.7°, 463.1°, 463.5°, 463.9°, 464.3°, 464.7°, 465.1°, 465.5°, 465.9°, 466.3°, 466.7°, 467.1°, 467.5°, 467.9°, 468.3°, 468.7°, 469.1°, 469.5°, 469.9°, 470.3°, 470.7°, 471.1°, 471.5°, 471.9°, 472.3°, 472.7°, 473.1°, 473.5°, 473.9°, 474.3°, 474.7°, 475.1°, 475.5°, 475.9°, 476.3°, 476.7°, 477.1°, 477.5°, 477.9°, 478.3°, 478.7°, 479.1°, 479.5°, 479.9°, 480.3°, 480.7°, 481.1°, 481.5°, 481.9°, 482.3°, 482.7°, 483.1°, 483.5°, 483.9°, 484.3°, 484.7°, 485.1°, 485.5°, 485.9°, 486.3°, 486.7°, 487.1°, 487.5°, 487.9°, 488.3°, 488.7°, 489.1°, 489.5°, 489.9°, 490.3°, 490.7°, 491.1°, 491.5°, 491.9°, 492.3°, 492.7°, 493.1°, 493.5°, 493.9°, 494.3°, 494.7°, 495.1°, 495.5°, 495.9°, 496.3°, 496.7°, 497.1°, 497.5°, 497.9°, 498.3°, 498.7°, 499.1°, 499.5°, 499.9°, 500.3°, 500.7°, 501.1°, 501.5°, 501.9°, 502.3°, 502.7°, 503.1°, 503.5°, 503.9°, 504.3°, 504.7°, 505.1°, 505.5°, 505.9°, 506.3°, 506.7°, 507.1°, 507.5°, 507.9°, 508.3°, 508.7°, 509.1°, 509.5°, 509.9°, 510.3°, 510.7°, 511.1°, 511.5°, 511.9°, 512.3°, 512.7°, 513.1°, 513.5°, 513.9°, 514.3°, 514.7°, 515.1°, 515.5°, 515.9°, 516.3°, 516.7°, 517.1°, 517.5°, 517.9°, 518.3°, 518.7°, 519.1°, 519.5°, 519.9°, 520.3°, 520.7°, 521.1°, 521.5°, 521.9°, 522.3°, 522.7°, 523.1°, 523.5°, 523.9°, 524.3°, 524.7°, 525.1°, 525.5°, 525.9°, 526.3°, 526.7°, 527.1°, 527.5°, 527.9°, 528.3°, 528.7°, 529.1°, 529.5°, 529.9°, 530.3°, 530.7°, 531.1°, 531.5°, 531.9°, 532.3°, 532.7°, 533.1°, 533.5°, 533.9°, 534.3°, 534.7°, 535.1°, 535.5°, 535.9°, 536.3°, 536.7°, 537.1°, 537.5°, 537.9°, 538.3°, 538.7°, 539.1°, 539.5°, 539.9°, 540.3°, 540.7°, 541.1°, 541.5°, 541.9°, 542.3°, 542.7°, 543.1°, 543.5°, 543.9°, 544.3°, 544.7°, 545.1°, 545.5°, 545.9°, 546.3°, 546.7°, 547.1°, 547.5°, 547.9°, 548.3°, 548.7°, 549.1°, 549.5°, 549.9°, 550.3°, 550.7°, 551.1°, 551.5°, 551.9°, 552.3°, 552.7°, 553.1°, 553.5°, 553.9°, 554.3°, 554.7°, 555.1°, 555.5°, 555.9°, 556.3°, 556.7°, 557.1°, 557.5°, 557.9°, 558.3°, 558.7°, 559.1°, 559.5°, 559.9°, 560.3°, 560.7°, 561.1°, 561.5°, 561.9°, 562.3°, 562.7°, 563.1°, 563.5°, 563.9°, 564.3°, 564.7°, 565.1°, 565.5°, 565.9°, 566.3°, 566.7°, 567.1°, 567.5°, 567.9°, 568.3°, 568.7°, 569.1°, 569.5°, 569.9°, 570.3°, 570.7°, 571.1°, 571.5°, 571.9°, 572.3°, 572.7°, 573.1°, 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623.5°, 623.9

FIGURE 1: N₂ adsorption/desorption isotherms (77 K) (a) and pore size distributions obtained applying the BJH equation (b) corresponding to the catalysts.

TABLE 1: Textural properties of Ni/CaO-Al₂O₃ catalysts with different CaO contents.

Sample	Specific surface area ^a (m ² /g)	Pore volume ^b (×10 ⁻² cm ³ /g)	Pore diameter ^c (nm)
15Ni/100Al ₂ O ₃	4.53	1.73	3.60
15Ni/10CaO90Al ₂ O ₃	9.59	2.97	3.98
15Ni/20CaO80Al ₂ O ₃	7.17	2.03	3.62
15Ni/30CaO70Al ₂ O ₃	5.73	2.42	6.68

^aSpecific surface area evaluated using the Brunauer-Emmett-Teller (BET) method. ^bPore volume calculated from the volume of nitrogen held at $p/p_0 = 0.98 \sim 0.99$. ^cBJH desorption average pore diameter.

and 79.4° corresponding to NiO species were observed. In addition, no clear characteristic diffraction peaks of CaO or CaCO₃ phases can be detected, indicating that CaO was highly dispersed on the surface of Al₂O₃ or formed micromorphology grain which was below the detection limit of XRD. Furthermore, it was found that the peak intensities of the NiO phase became weaker in the modified catalysts than that in the pure catalyst, probably due to the superior dispersion of the NiO species induced by CaO addition.

The XRD patterns of the catalysts reduced at 500°C were displayed in Figure 3. There was a new phase assigned to metallic Ni crystallites corresponding to the diffraction peaks at 44.5°, 51.8°, and 76.4°, and the diffraction peaks corresponding to NiO phase were not observed, as well as the diffraction peaks of CaO or CaCO₃, indicating that Ni²⁺ ions in the NiO phase were fully reduced to metallic Ni and Ca²⁺ ions in the CaO phase were not reduced.

3.3. Temperature-Programmed Reduction and Reducibility of the Catalysts. H₂-TPR measurements were performed to

investigate the reducibility of the catalysts and to examine the interaction between nickel species and the supports. Figure 4 showed H₂-TPR profiles of the catalysts with different CaO contents calcined at 500°C for 3 h. It was clear that all the samples showed a H₂ consumption peak in the range of 350°C~600°C corresponding to the reduction of NiO species. For the catalyst 15Ni/100Al₂O₃, main reduction peak was located at 435°C. After CaO modification, the reduction peak was shifted to lower temperatures, which was attributed to the reduction of NiO species that interacted weakly with the CaO-Al₂O₃ supports and the improvement of the catalyst reducibility. This behavior indicated that the incorporation of CaO into Al₂O₃ supports promoted the reduction of NiO species. However, it was found that, relative to that of 15Ni/20CaO80Al₂O₃, the reduction temperature peak of 15Ni/30CaO70Al₂O₃ shifted slightly to higher temperature, which was resulted from the high coverage of CaO on the surface of active sites. This meant that CaO content had an optimal range in the Ni/Al₂O₃ catalyst to affect its catalytic performance.

□ NiO

FIGURE 2: XRD profiles for the catalysts calcined at 500°C for 3 h. (a) 15Ni/100Al₂O₃, (b) 15Ni/10CaO90Al₂O₃, (c) 15Ni/20CaO80Al₂O₃, and (d) 15Ni/30CaO70Al₂O₃.

▽ Metallic Ni

FIGURE 3: XRD profiles for the catalysts reduced at 500°C for 1 h. (a) 15Ni/100Al₂O₃, (b) 15Ni/10CaO90Al₂O₃, (c) 15Ni/20CaO80Al₂O₃, and (d) 15Ni/30CaO70Al₂O₃.

3.4. Temperature-Programmed Desorption of the Catalysts.

The H₂-TPD profiles of the catalysts were presented in Figure 5. The sample 15Ni/100Al₂O₃ exhibited one peak located at 50~400°C. With CaO modification, the catalysts 15Ni/10CaO90Al₂O₃ and 15Ni/20CaO80Al₂O₃ showed two peaks, of which the low-temperature peak corresponded to the physical adsorption of H₂ weakly adsorbed on the metal surface, and the high-temperature peak located at 250~550°C could be originated from chemisorbed H₂. Compared to 15Ni/10CaO90Al₂O₃ and 15Ni/20CaO80Al₂O₃, the sample 15Ni/30CaO70Al₂O₃ only owning the low-temperature peak showed a great difference.

Temperature-programmed desorption of CO₂ (CO₂-TPD) was performed to determine the basicity of the tested

(a) 15Ni/100Al₂O₃(b) 15Ni/10CaO90Al₂O₃(c) 15Ni/20CaO80Al₂O₃(d) 15Ni/30CaO70Al₂O₃

FIGURE 4: H₂-TPR profiles of the catalysts with different CaO contents calcined at 500°C for 3 h.

FIGURE 5: H₂-TPD profiles of the studied catalysts. (a) 15Ni/100Al₂O₃, (b) 15Ni/10CaO90Al₂O₃, (c) 15Ni/20CaO80Al₂O₃, and (d) 15Ni/30CaO70Al₂O₃.

catalysts, and the results were shown in Figure 6. For these catalysts, the peak at about 120°C was assigned to the weak basicity related to CO₂ weakly adsorbed on the support surface. For the CaO modified catalysts 15Ni/10CaO90Al₂O₃ and 15Ni/20CaO80Al₂O₃, there were two low-temperature desorption peaks centered at 120°C and 350°C, respectively. Furthermore, there was a high-temperature desorption peak of all the samples corresponding to the formation of HCO₃⁻ or CO₃²⁻, leading to the strong basicity, and the catalytic performance was correlated with the strength of basicity of the catalyst.

3.5. Catalytic Performance. The effect of the reaction temperature on the CO₂ conversion and CH₄ selectivity, as well as CH₄ yield, was studied and the result was shown in Figure 7. The unmodified catalyst 15Ni/100Al₂O₃ was

FIGURE 6: CO₂-TPD profiles of the catalysts with different CaO contents. FIGURE 7: CO₂ conversion and CH₄ selectivity (a) and CH₄ yield (b) versus reaction temperature over the catalysts.

almost not active at 240°C; with the reaction temperature increasing up to 360°C, its catalytic activity was slightly improved; after that, its CO₂ conversion was increased from 10.3% at 360°C to 56.6% at 450°C; and with the reaction temperature further increasing, the CO₂ conversion was declined to 52.1% at 510°C. However, with modification, the catalysts became more active at low temperatures (<450°C). It was seen that the addition of CaO content had an appropriate amount in the Ni/Al₂O₃ catalyst for the CO₂ methanation performance. For the modified catalysts, the activities possessed a maximum at the CaO content of 20 wt.% and then decreased with increasing CaO content to 30 wt.%. Namely, the 15Ni/20CaO80Al₂O₃ catalyst presented the best catalytic performance over the investigated temperature range, and the CO₂ conversion ranged from 6.1% at 240°C to 66.6% at 450°C. This result indicated that the superior dispersion of the NiO

species and more available CO₂ adsorption sites induced by CaO addition finally promoted the catalytic performance of CO₂ methanation for the modified catalysts.

As shown in [2], the 12Ni5Ce/Al₂O₃ catalyst displayed better catalytic activity with CH₄ yield of 62.4% than the catalyst 12Ni/Al₂O₃ (47.0% CH₄ yield) at 350°C. As shown in [33], Ni15La/Al₂O₃ displayed the CH₄ yield of 87.5%, and the pristine catalyst Ni/Al₂O₃ possessed 80.0% CH₄ yield at 320°C. In addition, as shown in [34], the 12Ni5Ca/CNTs catalyst displayed 85.0% CH₄ yield at 350°C, but the unmodified catalyst 12Ni/CNTs revealed CH₄ yield of 71.9%. However, in this work, with CaO modification, the sample 15Ni/20CaO80Al₂O₃ exhibited the CH₄ yield of 63.2% at 450°C, while the catalyst 15Ni/100Al₂O₃ presented the CH₄ yield of 53.1%. Hence, compared with the above literatures (displayed in Figure 8), CaO as the promoter,

FIGURE 8: Comparison of the results in this work with the previous literature.

FIGURE 9: CO₂ conversion and CH₄ yield versus reaction time at 450°C.

owing to its relative low price and high activity, has more advantages than adding CeO₂ and La₂O₃.

Figure 9 showed the CO₂ conversion and CH₄ yield versus the reaction time on stream in the CO₂ methanation at 450°C, and it was seen that the catalytic performance of 15Ni/20CaO80Al₂O₃ was better than that of the 15Ni/100Al₂O₃ catalyst. For the catalyst 15Ni/100Al₂O₃, it was observed that CO₂ conversion decreased from 56.6% at 40 min to 36.7% at 360 min, while the catalyst 15Ni/20CaO80Al₂O₃ exhibited better stability under the selected operating conditions than the pristine catalyst, decreasing from 66.6% at 40 min to 53.7% at 360 min. From the XRD analysis of the reduced catalyst before and after reaction shown in [2], it was found that the Ni particles became bigger and the sintering of nickel occurred during the reaction, which could be probably due to the weakened

interaction between Ni species and the support; that is, as the CO₂ methanation proceeded, the catalyst with bigger Ni particles was deactivated. Hence, with CaO modification, the catalysts could apparently possess higher activity and better stability than the unmodified catalyst.

4. Conclusions

The CO₂ methanation has been studied over Ni/CaO-Al₂O₃ catalysts prepared by impregnating CaO-Al₂O₃ composite support with an aqueous solution of nickel nitrate. The presence of CaO was found to be beneficial for improving the catalytic activity and exhibited excellent activity for CO₂ methanation in a low-temperature range. The catalyst activity strongly depended on the addition amount of CaO for the CaO-Al₂O₃ support. A suitable CaO content could cause a significantly effect on the interaction between Ni and Al₂O₃ support, leading to an excellent catalytic performance. The results showed that, among the studied catalysts, the catalyst 15Ni/20CaO80Al₂O₃ showed optimal catalytic performance (highest CO₂ conversion and CH₄ yield) under the tested reaction conditions, which was mainly attributed to the fact that the highly dispersed CaO inhibited the incorporation of nickel species into the lattice of Al₂O₃.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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