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***Low temperature hybrid plasma-catalytic methanation over Ni-Ce-Zr
hydrotalcite-derived catalysts***

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Abstract

The activity of Ceria and Zirconia-promoted Ni-containing hydrotalcite-derived catalysts was assayed in a hybrid plasma-catalytic process for the hydrogenation of carbon dioxide into methane at low temperatures and in the presence of a cold dielectric barrier discharge (DBD) plasma. High methane yields, around 80%, were measured under hybrid plasma-catalytic conditions, even at very low temperatures (110°C, adiabatic conditions). In the absence of plasma, acceptably high CO₂ conversions and methane yields were only observed at temperatures higher than 330°C. The presence of completely reduced Ni-crystallites of intermediate size, more readily available on the non-promoted catalysts was found to enhance the methanation reaction. Ce and Zr addition did not result in a noticeable improvement of the catalytic activity.

Keywords: CO₂-methanation, plasma, nickel catalysts, hydrotalcites

1. Introduction

In the last decades, several strategies have been proposed in order to stabilize increasing atmospheric CO₂ concentrations [1]. Among them, CO₂ methanation, i.e. Sabatier reaction, is considered as one of the most effective technologies for CO₂ valorization, offering moreover a feasible route for renewable H₂ storage and utilisation [2, 3]. Ni and Ni-Ru supported on diverse porous materials are typically used as catalysts in CO₂ methanation [2, 4-6]. Ni-containing hydrotalcite-derived catalysts can be easily prepared through the incorporation of Ni-cations into their pristine brucite-like structure [7]. Such materials have already shown relatively high activity towards CO₂ methanation, at moderate temperatures, i.e. 350°C [8]. Ce-species can be moreover ion-exchanged into such materials, resulting in an increased reducibility of the Ni-species, and in the introduction of intermediate strength basic sites (Lewis acid-base pairs), which can promote CO₂ adsorption and activate its hydrogenation [7]. The use of a Dielectric barrier discharge (DBD) plasma during the preparation of hydrotalcite-derived catalyst has lately shown to lead to the formation of relatively small Ni particles tightly bonded to the support which, in turn, facilitated the hydrogenation of CO₂ to CH₄ [9]. The *in-situ* use of cold DBD plasmas can furthermore assist the catalytic hydrogenation reaction through the formation of a large variety of active species, as has been recently reported for CO methanation [4, 10].

In the present work, the CO₂ methanation activity of Ce and/or Zr-promoted Ni-Mg-Al hydrotalcite-derived catalysts was assayed in the absence and in the presence of a cold dielectric barrier discharge (DBD) plasma. With the aim of further modifying the basicity of HT-derived catalysts, Ce and Zr were added, either together with the Ni, Mg and Al precursors or, in the case of Ce, through ion exchange from a solution containing [Ce(EDTA)]-complexes.

2. Experimental

2.1. Catalysts synthesis

The Ni-containing Mg-Al hydrotalcites were synthesized through co-precipitation at constant pH from an aqueous solution containing Ni, Mg and Al nitrates (Mg/Ni=3, $M^{2+}/M^{3+}=3$, 20% wt. Ni loading). Zirconium species were introduced into the hydrotalcite structure at the co-precipitation stage, using zirconium oxynitrate at molar ratio Al^{3+}/Zr^{4+} equal to 9/1. Ce-species were introduced by ion exchange with a 3% wt. aqueous solution of [Ce(EDTA)]-complexes [7, 11]. The resulting hydrotalcites were subsequently calcined at 550°C for 4 h. Four different catalysts were prepared: HT-25Ni, Ce-promoted: HTNi-Ce, Zr-promoted: HTNi-Zr, and Ce-Zr-promoted: HTNi-CeZr. The X-ray fluorescence (XRF) analysis of the calcined catalyst confirmed the presence of 20% wt. Ni. The catalysts were reduced under 5% vol. H_2/Ar through temperature-programmed reduction (heating rate 5°C/min) followed by isothermal reduction at 900°C for 2 h.

2.2. Physico-chemical characterization

The specific surface area (BET) of the materials was calculated from their respective N_2 adsorption isotherms acquired at -196°C (degas: 150°C, 4 h, BELSORP MINI II-BEL JAPAN). X-ray diffraction (XRD) patterns were recorded in an Empyrean diffractometer (PANalytical, $CuK\alpha$ source). Temperature-programmed reduction experiments (TPR, BEL Japan BELCAT-M, TCD detector) were performed under 25 mL/min of a 5% vol. H_2/Ar mixture (10°C/min, 25-950°C). CO_2 -TPD experiments were carried out using 50 mg of reduced catalysts, pretreated for 1 h at 500°C, then cooled down to 80°C and fed with 10% vol. CO_2/He for 1h. The catalysts was flushed with He for 20 minutes, then heated to 900°C (10°C/min).

2.3. Hybrid Plasma-Catalytic Methanation

The activity of the different catalysts in CO₂-methanation was evaluated at temperatures from 110 to 430°C, in a dielectric barrier discharge (DBD) plasma reactor operating at atmospheric pressure. It consisted of two coaxial tubes (quartz/alumina tubes), having internal diameters of 10 and 3 mm (2,5 mm gap), and 10 mm of effective length [11]. A high-voltage alternating current in the range of 14 kV (41 kHz) was applied in order to create DBD plasma, corresponding to a power between 3-9 W. Around 300 mg (0.6 cm³) of catalyst were placed at the annular space of the discharge zone in DBD reactor. A reactant gas containing 20% vol. CO₂ and 80% vol. H₂ was fed at 200 mL/min (GHSV = 20,000h⁻¹). The gas temperature inside the catalytic bed was measured with the aid of a K-type thermocouple. The DBD plasma reactor was used either under adiabatic conditions or under isothermal conditions, using an electric furnace to reach the desired temperature in this last case. The gaseous products exiting the reactor were analyzed in a gas chromatograph (IGC-120-ML, Delsi Intersmat). CO₂ conversion (X_{CO_2} , %), CH₄ and CO selectivity (S_{CH_4} and S_{CO} , %), and CH₄ and CO yield (Y_{CH_4} and Y_{CO} , %), were calculated as follows:

$$X_{CO_2} = \frac{(n_{CO_2}^{in} - n_{CO_2}^{out})}{n_{CO_2}^{in}} \times 100 \quad (\text{eq. 1})$$

$$S_{CH_4} = \frac{n_{CH_4}^{out}}{(n_{CH_4}^{out} + n_{CO}^{out})} \times 100 \quad (\text{eq. 2})$$

$$Y_{CH_4} = X_{CO_2} \times S_{CH_4} \quad (\text{eq. 3})$$

$$S_{CO} = \frac{n_{CO}^{out}}{(n_{CH_4}^{out} + n_{CO}^{out})} \times 100 \quad (\text{eq. 4})$$

$$Y_{CO} = X_{CO_2} \times S_{CO} \quad (\text{eq. 5})$$

A blank on-plasma test was performed in the absence of catalysts at 430°C. This test yielded almost no CO₂ conversion and zero selectivity to CH₄. Off-plasma experiments were performed in the presence of each catalyst, at temperatures from 130 to 430°C. The results of these off-plasma experiments are discussed in detail below.

3. Results and discussion

3.1. Characterization of the HTNi-derived catalysts

The XRD diffractograms acquired for the reduced HTNi-catalysts, (Fig. not shown), evidence the typical reflections of hydrotalcite-derived mixed-oxides having a periclase-type structure (2θ : 43°, 62.5°; JCDPS00-045-0946) [12]. Several diffraction peaks corresponding to metallic nickel are as well present (2θ : 44°, 51°, 76°; JCDSP01-089-7128). In the case of Ce and/or Zr promoted catalysts, additional phases of segregated ceria (JCDSP00-043-1002) and/or zirconia (JCDSP00-049-1642) can be observed. Ni crystal sizes were estimated using Scherrer equation and are presented in Table 1. Crystal size notably decreases as a consequence of the presence of Zr, i.e. from 20.7 nm in HTNi-Ce to 8.1 nm in HTNi-ZrCe. Table 1 shows as well the results of the textural characterization. The addition of Zr seems to increase the final porosity of the HT-derived mixed oxide, whereas Ce results in a certain extent of pore blockage, related to its incorporation through ion-exchange using [Ce(EDTA)]-complexes.

The H₂-TPR profiles for these catalysts, Fig. 1, evidence a single wide and asymmetric reduction peak centered between 810-860°C, arising from the reduction of nickel oxide in strong interaction with the Mg-Al mixed oxide matrix [7]. The shoulders appearing at about 600°C can be assigned to segregated NiO-species, as already observed before [11]. For the Ce-promoted catalysts, i.e. HTNi-Ce and HTNi-ZrCe, the main reduction peak is shifted to lower temperatures, pointing to enhanced reducibility of Ni-species in the presence of this

promoter. Additional reduction peaks at 300 and 415°C arising from the reduction of Ce⁴⁺ to Ce³⁺ are also observed [7,13]. On the contrary, in the presence of Zr a shift to higher reduction temperatures can be observed, due to further stabilization and stronger interaction between the mixed Mg-Al oxides and Ni-species. H₂-TPR experiments were repeated after reduction of the catalysts at 900°C for 2 h under 5% vol. H₂/Ar. Two small reduction peaks at much lower temperatures are now shown, i.e. at 172 and 250-300°C, pointing to Ni or NiO segregation from the Mg-Al mixed oxide structure upon the reduction treatment [14] and further oxidized when storing the materials under ambient conditions. Bulk NiO is normally reduced at such low temperatures [15,16].

CO₂-TPD profiles for these reduced materials, Fig. 2, evidence the presence of three types of basic sites on the catalysts surface: (i) weak Brønsted OH-groups (ca. 120-130°C), (ii) medium strength Lewis metal-oxygen pairs (175-235°C), and (iii) strong Lewis-base oxygen anions (300-390°C) [7,17,18]. The total basicity (Table 1) is remarkably influenced by the presence of Ce and/or Zr. The highest basicity corresponds to the CeZr-promoted catalyst, HTNi-CeZr. In general, the addition of both Ce and Zr results in an increased presence of medium-strength and strong basic sites, i.e. strong basic sites account for 50-51% of total basicity in HTNi-Ce and HTNi-Zr whereas they correspond to 85% of total basicity in HTNi-CeZr. Weak and medium strength basic sites contribute to more than 75% of the total basicity in HTNi.

3.2. Activity towards methanation in the absence of plasma (off-plasma experiments)

The results of the off-plasma methanation experiments are shown in Fig. 3, in the presence of the four different catalysts and at temperatures from 130 to 430°C. In the absence of the DBD plasma, CO₂ conversion only becomes significant at temperatures higher than 320°C. It increases rapidly with increasing temperature, tending towards the thermodynamically forecasted values [19,20]. The non-promoted catalyst, HTNi, shows the highest off-plasma activity within this series of catalysts. The addition of Ce results in much lower activity and selectivity towards the production of methane, with CO yields reaching almost 7% (Fig. not shown). Off-plasma activity seems to be directly related to the size and availability of Ni⁰ particles on the catalyst's surface. The 15 nm-size Ni⁰ particles in HTNi seem to be more active towards off-plasma methanation than far too small (8.1 nm in HTNi-CeZr) or incompletely reduced NiO-particles (see TPR profiles for the reduced catalysts in Fig. 1). The influence of basicity on catalytic activity remains unclear, since the off-plasma CO₂ conversion and methane selectivity are not directly related to the total basicity measured for these catalysts. The increased presence of low-strength basic sites in HTNi may, however, enhance a weak-type adsorption of CO₂, resulting in easier CH₄ desorption upon its hydrogenation by the H₂ adsorbed on nearby Ni⁰ sites.

3.3. Hybrid plasma-catalytic methanation (on-plasma experiments)

Fig. 4 presents the results obtained during the on-plasma catalytic methanation experiments. Whereas in the absence of a DBD plasma almost zero CO₂ conversion was measured at temperatures below 270°C, the on-plasma experiments evidence that it is possible to convert CO₂ into methane even at very low temperatures, in the range of 110-420°C, and, at temperatures between 110 and 270°C, even without external heating, i.e. under adiabatic conditions (note that the methanation reaction is exothermic,

$\Delta H_{reaction}^{298K} = -165$ kJ/mol). In the presence of the DBD plasma, the Zr –promoted catalysts show higher activity at lower temperatures than those measured during the off-plasma methanation experiments, i.e. around 70% CO₂ conversion was measured at 240-250°C for both HTNi-Zr and HTNi-ZrCe whereas these catalysts evidenced zero or almost zero CO₂ conversion in the absence of plasma. Ce-promoted catalysts only show interestingly high activities at relatively high temperatures. In any case, the non-doped HTNi catalyst maintains its activity (around 80% conversion with almost 100% selectivity to methane) within the entire temperature window. Even in presence of a DBD plasma, the highest availability of zero-valent Ni⁰ sites of intermediate crystal size might be responsible for the enhanced activity evidenced for this HTNi catalyst. The influence of basicity remains unclear. Though discussed before in the existing literature, there is no general agreement about the type of basic sites leading to enhanced catalytic activity [21,22]. At the sight of the results obtained in the presence of plasma, it seems that low or medium-strength basic sites are still needed in order to boost the methanation reaction. On the contrary, the presence of too strong basic sites introduced by means of Ce and Zr doping does not seem to be beneficial for the overall reaction mechanism. Let us note here that the spent catalysts were characterized by means of transition electron microscopy (TEM) and X-ray diffraction. The micrographs, histograms and diffraction patterns obtained do not evidence any important change in the morphology and structure of the catalyst upon plasma methanation. Crystal sizes remained practically unchanged.

4. Conclusion

Ni-containing hydrotalcite-derived catalysts were prepared using Ce and/or Zr as promoters. Their activity in the methanation of CO₂ was assayed both in the absence and in the presence of a DBD plasma. Off-plasma CO₂ methanation sets off at temperatures higher than 320°C. However, CO₂ conversions as high as 80% were measured in the presence of the

DBD plasma, even at very low reaction temperatures, i.e. 110°C under adiabatic conditions. The on-plasma catalytic methanation was found to be almost completely selective to methane, corresponding to CO yields lower than 2%. The addition of either Ce or Zr did not improve the catalytic activity of the hydrotalcite-derived materials. Zr-containing catalysts showed anyway higher activity than those promoted only with Ce, especially in the presence of the plasma. The presence of medium size zero-valent Ni-crystallites, more readily available in the non-promoted catalyst, was found to enhance the methanation reaction, whereas the influence of the basicity of this series of catalysts on their activity remains relatively unclear.

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Table 1. Basicity (CO₂-TPD), Ni-crystal size (XRD), and textural properties for the HT-derived catalysts.

Catalyst	Total basicity [mmol/g][*]	Ni crystallite size [nm]^{**}	S_{BET} [m²/g]	V_{total} [cm³/g]
HTNi	0.060	15.2	115	0.41
HTNi-Ce	0.094	20.7	102	0.33
HTNi-Zr	0.064	10.5	229	0.62
HTNi-ZrCe	0.119	8.1	158	0.56

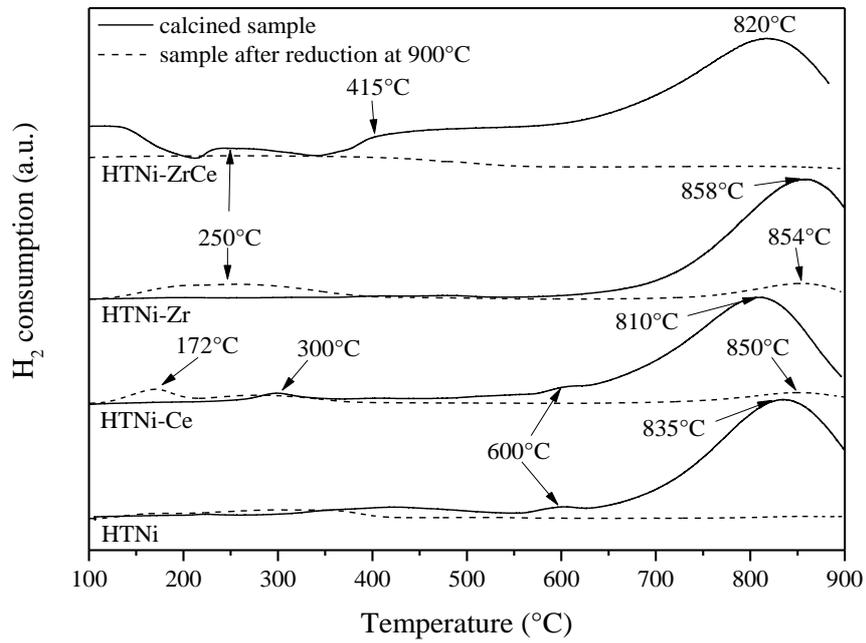


Fig. 1. TPR profiles for both calcined and reduced HT-derived catalysts

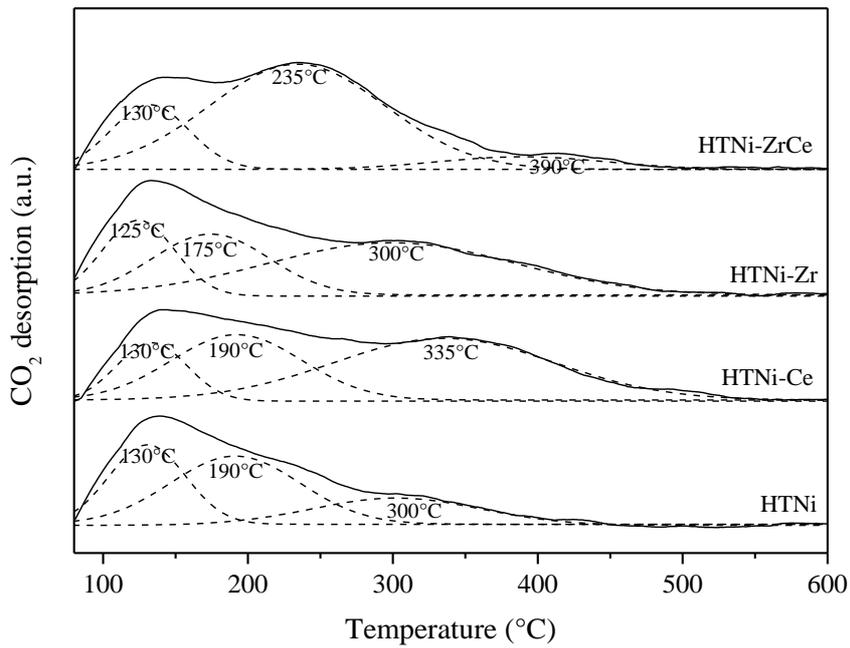
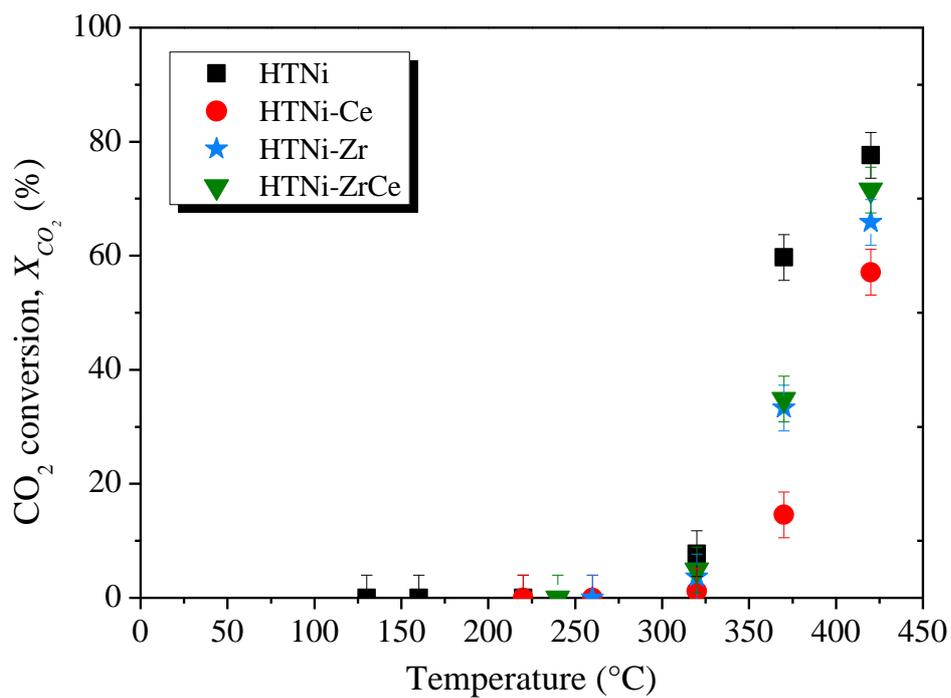


Fig. 2. CO₂-TPD profiles for the reduced HT-derived catalysts.

A)



B)

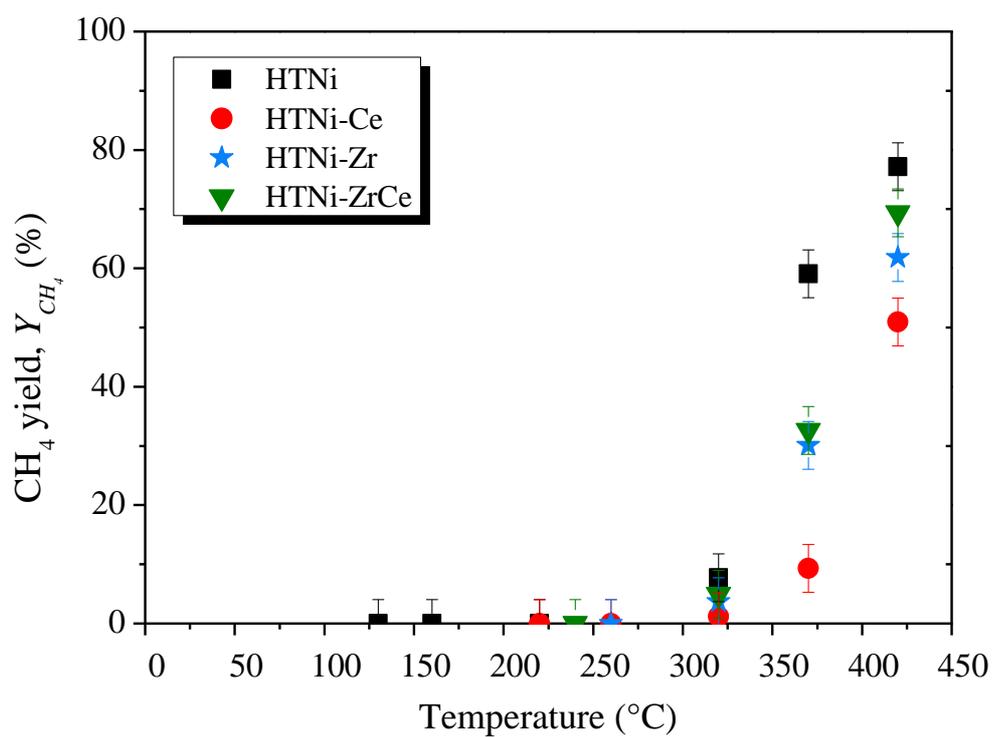


Fig. 3. Off-plasma catalytic methanation experiments: (A) CO₂ conversion, (B) CH₄ yield

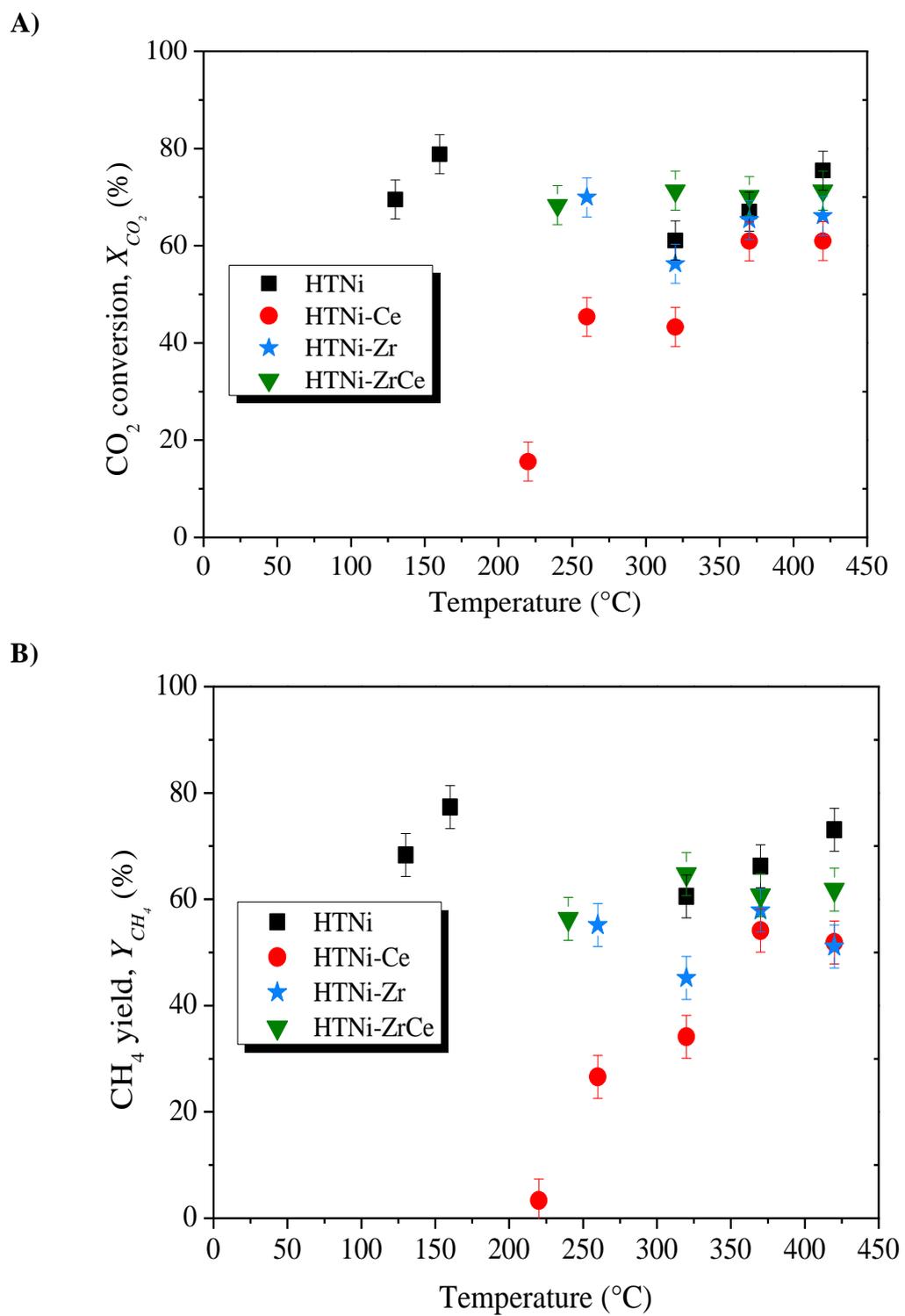


Fig. 4. Hybrid plasma-catalytic methanation experiments: (A) CO₂ conversion, (B) CH₄ yield