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Enhancing Catalytic Activity and Stability for CO\textsubscript{2} Methanation on Ni-Ru/γ-Al\textsubscript{2}O\textsubscript{3} via Modulating Impregnation Sequence and Controlling Surface Active Species

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Bimetallic Ni-Ru NPs loaded onto γ-Al\textsubscript{2}O\textsubscript{3} were prepared by co-impregnation and sequential impregnation methods and were investigated for CO\textsubscript{2} methanation in the temperature range of 250–500°C under atmospheric pressure to uncover the dependence of activities on surface species. It was found that the activities of CO\textsubscript{2} methanation were dependent on preparation sequence very significantly. Compared activity results dependence with the characterization results of XRD, H\textsubscript{2}-TPR, BET, TEM-EDX and XPS techniques, it was indicated that the dispersion of Ru and Ni was controlled by preparation steps, and the tendency of Ru segregation on the catalyst surface was identified. This tendency led to the high activity of 10Ni-1.0Ru catalyst. Such surface segregation phenomenon of Ru in co-impregnation process controlled the chemical state of surface Ru species, made it to be easily reduced to metallic state. In addition, the 10Ni-1.0Ru catalyst performed with high stability and showed almost no deactivation up to 100h long term stability test. The possible reaction mechanism was proposed, in which CO\textsubscript{2} was dissociation and was activated on Ru species surface to form carbon species (CO\textsubscript{ad}), and then was reacted with activated H on Ni centre to form methane.

Introduction

It is well known that the increase of carbon dioxide concentration in the atmosphere has resulted in remarkable climate change.\textsuperscript{1,4} At present, CO\textsubscript{2} capture and storage (CCS) is considered as a main large scale method to solve CO\textsubscript{2} problem.\textsuperscript{5–8} For its chemical utilization, CO\textsubscript{2} can be converted into many chemicals, such as synthesized urea, salicylic acid, methanol, DME and DMC, aliphatic polycarbonate, CH\textsubscript{4}, low carbon hydrocarbon. One main handicap in CO\textsubscript{2} chemical conversion is its high stability and inertness properties. Previous papers indicated that CO\textsubscript{2} can be converted into CH\textsubscript{4} in the presence of an adequate catalyst.\textsuperscript{9–13}

\[
\text{CO}_2(g) + 4\text{H}_2(g) \rightarrow \text{CH}_4(g) + 2\text{H}_2\text{O}(g), \Delta G^{\circ}_{298K} = -27 \text{ kcal mol}^{-1}
\]

This reaction is called the Sabatier reaction, operating temperatures at 400°C.\textsuperscript{14}

A number of catalysts were reported to be active for Sabatier reaction, such as supported VIII metals and noble metals (e.g., Ru, Rh) on oxide supports. Among those catalysts, Ni-based catalyst was the most extensively studied, for example, Ni/MCM-41, Ni-La/γ-Al\textsubscript{2}O\textsubscript{3}, Ni/RHA-γ-Al\textsubscript{2}O\textsubscript{3}, Ni/ZrO\textsubscript{2}-γ-Al\textsubscript{2}O\textsubscript{3} catalysts exhibited high activities at low temperature.\textsuperscript{15–21} Small Ni crystals in highly dispersed state on the catalyst surface might play an important role. One problem of Ni-based catalysts is its deactivation due to the interaction of the metal particles with carbon monoxide and formation of mobile nickel sub carbonyls.\textsuperscript{22}

Noble metals such as Ru or Rh exhibited good resistant properties to sintering and carbon deposition than Ni,\textsuperscript{23–25} and showed high activity and stability.\textsuperscript{7, 10, 22, 26–30} Therefore, Ni-Ru bi-metal catalyst has attracted extensive attention.\textsuperscript{31–32} The Ni-Ru bimetallic clusters on silica caused a strong improvement in the activity and stability of this bimetallic system.\textsuperscript{33} It is known that the Ru dispersion and its chemical state on the support may play a key role in its catalytic performance,\textsuperscript{34–35} which means the control of surface species in catalyst preparation is needed for further understanding.

In this work, two methods, co-impregnation and sequential impregnation, were used to prepare a series of Ni-Ru/γ-Al\textsubscript{2}O\textsubscript{3} catalysts. By comparison the structure, surface species and catalytic performances of different catalyst, we uncovered the surface species segregation of Ru in Ni-Ru catalysts.\textsuperscript{36} This effect of segregation on catalytic properties was also discussed, and the possible reaction mechanism for CO\textsubscript{2} methanation was proposed.

Experimental

Preparation of the catalysts

A series of Ni-Ru bimetallic catalysts were prepared by co-impregnation and sequential impregnation methods using Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (AR, Shanghai NO.2 Reagent Co. Ltd.) and RuCl\textsubscript{3}·xH\textsubscript{2}O (AR, Shanghai Shapu Chem. Corp., Ltd.) as a precursor. The nickel loading was 10wt% and ruthenium loading is 0.5, 1.0, 2.5, and 5.0% on γ-Al\textsubscript{2}O\textsubscript{3} (40 mesh, Shanghai Meryer Chemical Technology Co., Ltd.). Before impregnation, the support γ-Al\textsubscript{2}O\textsubscript{3} was stabilized in air at 600°C for 6h. After impregnation, the catalyst precursor was dried at room temperature at 110°C for 12h, then it was dried at 400°C in a vacuum furnace for 3h.

To uncover the dependence of activities on surface species, a modified CO\textsubscript{2} methanation was proposed. In which CO\textsubscript{2} was dissociation and was activated on Ru species surface to form carbon species (CO\textsubscript{ad}), and then was reacted with activated H on Ni centre to form methane.
temperature for 24h and at 110°C for another 24h. Finally, the precursor was calcined at 450°C for 5h. Here, the 10Ni-xRu/γ-Al₂O₃ catalysts were prepared by co-impregnation method, which was denoted as 10Ni-xRu. In sequential impregnation process, the catalyst that the first step impregnated Ni and the final step impregnated Ru was denoted as 10Ni-1.0Ru(F), otherwise, it was denoted as 10Ni(F)-1.0Ru.

Catalytic activity

A reductive pre-treatment was performed before test. The catalyst was loaded in each run and diluted with equal amount of quartz. The calcined catalysts were pre-reduced in-situ in a 60% H₂/N₂ stream for 2h with a total gas flow of 70mL·min⁻¹ at 450°C with a heating ramp of 10°C·min⁻¹. Catalytic performances tests were conducted at atmospheric pressure in a fixed-bed continuous flow quartz reactor in the temperature range from 250 to 500°C. A K-type thermocouple was inserted in the furnace to measure the pre-treatment and reaction temperature. The reactor was heated in a tube furnace equipped with a temperature controller. All gases were monitored by calibrated mass flow controllers.

The H₂ and CO₂ reactants were mixed at a H₂:CO₂ ratio of 4:1 and N₂ was added as a carrier gas and internal standard for gas analysis. They were introduced into the reactor at a molar ratio of H₂:CO₂:N₂=4:1:4 and the total flow rate were set to 90 mL·min⁻¹. The gas hourly space velocity (GHSV) was varied between 3000 and 15000h⁻¹. GHSV was varied by changing the catalyst mass while keeping the reactant flows constant. The gas phase products were analyzed on two on-line chromatographs equipped with thermal-conductivity detectors (TCD). Hydrocarbons as well as oxygenated products were separated with a GC112A (SDPTOP, Shanghai in China; column: HPX5, 30m) and analyzed by means of a flame ionization detector (FID). The detection limit for the products was 1×10⁻⁷mol. % at the given conditions. CO₂ conversion, CH₄ yield, CH₄ and CO selectivity were defined as follows:

\[
X_{CO_2}(%) = \frac{CO_2 \times (N_2)_m}{N_2 \times (CO_2)_m} \times 100
\]

\[
S_{CH_4}(%) = \frac{CH_4}{CO_2 + CH_4 + CO + 2C_2H_6} \times 100
\]

\[
S_{CO}(%) = \frac{CO}{CO_2 + CH_4 + CO + 2C_2H_6} \times 100
\]

Where X is the conversion, S is the selectivity, P and (P)ₐ are the reactant/product molar quantities at the exit and at the entrance of the reactor, respectively.

Characterization of the catalysts

Temperature-programmed reduction analysis (H₂-TPR) was carried out by heating a sample (50mg) from 25 to 700°C at 10°C min⁻¹ in a flow of 5 vol% H₂/Ar mixture (40 mL min⁻¹). The amount of H₂ consumed was measured by a TCD.

The X-ray diffraction patterns (XRD) of the samples were recorded on a Rigaku B/Max-RB X-ray diffractometer with a nickel-filtraled Cu Kα radiation over a 2θ range of 15-85° and a position sensitive detector using a step size of 0.017° and a step time of 15s at 40 mA and 40 kV.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG Scientific ESCALAB 250Xi-XPS photoelectron spectrometer with an Al Kα X-ray resource. The binding energies were calibrated by the C1s binding energy of 284.7 eV. The specific surface areas (SSA) of the catalysts were determined by N₂ adsorption-desorption measurements at 77 K by employing the Brunauer-Emmet-Teller (BET) method (Micromeritics apparatus ASAP 2020M). Transmission electron microscopy (TEM) and HRTEM images were taken with a Tecnai-G2-F30 field emission transmission electron microscope operating at accelerating voltage of 300 kV.

Results and discussion

Effect of temperature and preparation method on catalytic activity

![Fig. 1](image)

Fig. 1 Effect of temperature on the CO₂ conversion (a) and the CH₄ and CO selectivity (b) at the methanation of CO₂ over the 10Ni-1.0Ru, 10Ni-1.0Ru(F), 10Ni(F)-1.0Ru and 10Ni-1.0Ru(used) catalysts; Reaction conditions: 100 mg catalysts, H₂:CO₂=4:1, GHSV=9000h⁻¹, 1atm.

In order to investigate the influence of active species and effective active sites on catalytic performance, the 10Ni-1.0Ru, 10Ni(F)-1.0Ru, 10Ni-1.0Ru(F) and 10Ni-1.0Ru(used, after long-term reaction) catalysts were selected as the representatives and results were exhibited in Fig. 1. Fig. 1a showed that the CO₂ conversion increased with the reaction temperature increase (from 250 to 400°C), and followed by the gradual decrease (above 400°C) over all the samples. Fig. 1b showed the selectivity of CH₄ and by-product (CO) at the different reaction temperatures over all the samples. It was found that CH₄ selectivity was 100% below 400°C. CO was produced only above 400°C. Among 10Ni-1.0Ru, 10Ni-1.0Ru(F) and 10Ni(F)-1.0Ru, the 10Ni-1.0Ru
catalytic activity was higher (CO₂ conversion was 82.7%, the CH₄ selectivity was 100%) at 400°C, suggesting that more effective Ni and Ru species could located on the surface of 10Ni-1.0Ru catalyst. The surface free energy of Ru was 3.05 J·m⁻², Ni was 2.45 J·m⁻², therefore, part of Ru atoms had been moved onto surface layer during co-impregnation, which led to surface segregation. As a result, more effective Ni and Ru species could be located on the surface of 10Ni-1.0Ru catalyst. For 10Ni-1.0Ru(used), the catalytic activity was lower than other samples.

This was possibly due to the change of active species on the surface of 10Ni-1.0Ru(used) during the long-term reaction.

**XRD analysis**

The crystal structures of the fresh and used catalysts were characterized by XRD method, the results were given in Fig. 2. The diffraction patterns of the 10Ni-1.0Ru, 10Ni(F)-1.0Ru, 10Ni-1.0Ru (F) and 10Ni-1.0Ru (used) catalysts showed similar typical peaks. The peaks at 44.5, 51.7, and 76.3° were the characteristic peaks of metallic Ni with a face-centered cubic structure (JCPDS# 87-0712). The peaks at 39.2, 42.3, and 44.0° could be assigned to the diffraction peaks of Ru with a hexagonal close-packed structure (JCPDS# 70-0274), while the peaks at 37 and 67° were assigned to the diffraction of γ-Al₂O₃ phase. The other weak diffraction peaks at 32° and 61° were also detected, which were the characteristic peaks of NiAl₂O₄.

**TEM analysis**

In order to better understand the role of Ni and Ru in the catalyst, the TEM and HRTEM images of Ni and Ru impregnated γ-Al₂O₃ were taken (Fig. 3a-f). The particle sizes distribution was shown in the Fig. 3a-c. It could be noticed that nickel and ruthenium particles were small and uniformly dispersed in the 10Ni-1.0Ru and 10Ni-1.0Ru(F) samples. However, the agglomerative phenomenon occurred on 10Ni(F)-1.0Ru catalyst. This reflected the difference of preparation and calcination process. The average size of Ni and Ru particles on 10Ni-1.0Ru was about 7–9nm (Fig. 3a). The d-spacing of adjacent fringe for Ni nanocrystals was 0.204 nm, that could be indexed to the (111) crystalline plane of face-centered cubic Ni lattice. The d-spacings of 0.209nm and 0.234nm could be indexed to as the (101) and (100) crystalline plane of hexagonal close-packed Ru lattice, respectively. For 10Ni-1.0Ru(F) and 10Ni(F)-1.0Ru, the average particle sizes were 5–8 and 6–10 nm, respectively (Fig. 3b-c). The d-spacings of Ni(111) and Ru(101) were also given in Fig. 3e-f, which suggested that crystalline features of Ni and Ru particles on 10Ni-1.0Ru(F) and 10Ni(F)-1.0Ru were similar to that on 10Ni-1.0Ru. This result was in accordance with those results of XRD characterization.

**H₂-TPR analysis**

H₂-TPR measurements were carried out to investigate the reducibility of the 10Ni-1.0Ru, 10Ni(F)-1.0Ru and 10Ni-1.0Ru(F) catalysts and the interaction between impregnated metal particles and supports. Fig. 4 showed TPR profiles of 10Ni-1.0Ru, 10Ni(F)-1.0Ru and 10Ni-1.0Ru(F) calcined at 450°C for 5h. All the catalysts showed two main reduction regions at 225 and 400°C. The reduction peaks of surface Ni species and Ru species were at 400 and 225°C, respectively. The shapes of Ru species reduction peak of 10Ni-1.0Ru and 10Ni-1.0Ru(F) catalysts were similar, suggesting that those Ru species were same. The results were in good agreement with the results of XRD characterization. The Ru species of 10Ni(F)-1.0Ru was different from those of 10Ni-1.0Ru and 10Ni-1.0Ru(F). The
difference in the Ru species was one of the main influencing factors on the different catalytic activities. The shapes or intensities of Ni species reduction peak were very similar for the three catalysts mentioned above, implying that the surface Ni species of all the catalysts was almost same. Compared 10Ni-1.0Ru(used) with 10Ni-1.0Ru, it was found that the Ru species changed during the long-time reaction.

**BET**

As shown in Fig. 5a, the nitrogen adsorption-desorption isotherms of all samples exhibited the IV type with H3 type hysteresis loop. The corresponding pore size distributions were very narrow at 10.0 nm (Fig. 5b), indicating the presence of mesopore structure in all the catalysts.

![Fig. 5](image-url)

**Table 1** Structural parameters obtained from N\(_2\) adsorption isotherms analysis

<table>
<thead>
<tr>
<th>Samples</th>
<th>(S_{\text{BET}}) (m(^2) g(^{-1}))</th>
<th>Pore volume (cm(^3) g(^{-1}))</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma)-Al(_2)O(_3)</td>
<td>169.6</td>
<td>0.4876</td>
<td>11.50</td>
</tr>
<tr>
<td>10Ni-1.0Ru(used)</td>
<td>149.0</td>
<td>0.4049</td>
<td>11.45</td>
</tr>
<tr>
<td>10Ni-1.0Ru</td>
<td>149.5</td>
<td>0.4736</td>
<td>12.67</td>
</tr>
<tr>
<td>10Ni(F)-1.0Ru</td>
<td>144.3</td>
<td>0.3759</td>
<td>9.941</td>
</tr>
<tr>
<td>10Ni-1.0Ru(F)</td>
<td>148.5</td>
<td>0.3699</td>
<td>10.27</td>
</tr>
</tbody>
</table>

\(a\) Obtained from BET method  
\(b\) Total pore volume taken from the nitrogen adsorption volume at a relative pressure (P/P\(_0\)) of 0.99.  
\(c\) Average pore diameter determined from the adsorption data of the isotherms using BJH method.

The Brunauer-Emmett-Teller specific surface areas \(S_{\text{BET}}\) were determined by \(N\)_\(_2\) isotherms at 77K (as shown in Table 1). The \(S_{\text{BET}}\) of 10Ni-1.0Ru, 10Ni-1.0Ru (used), 10Ni(F)-1.0Ru and \(\gamma\)-Al\(_2\)O\(_3\) were 149.5, 149.0, 148.5, 144.3 and 169.6, respectively. 10Ni-1.0Ru and 10Ni-1.0Ru(F) had larger \(S_{\text{BET}}\) than that of 10Ni(F)-1.0Ru. Meanwhile, 10Ni-1.0Ru had the biggest pore volume and average pore size among these three samples, which benefited gas molecules diffusing into the holes.

**XPS analysis**

Fig. 6a showed typical XPS survey (wide-scan) spectra of the 10Ni-1.0Ru (fresh and used), 10Ni-1.0Ru(F), and 10Ni(F)-1.0Ru. Obviously, C, O, Al, Ni, and Ru elements with comparable peak intensities were presented on the surfaces of all the samples, which were verified by EDS characterization (Fig. 3g). Here, the XPS spectra of the Ni\(_2p\) and Ru\(_3d\) of the four catalysts were presented in Fig. 6b-e. For the Ni\(_2p\), it was observed that the binding energies at 852.5, 857.9, 869.9, and 876.7eV were assigned to Ni\(_{2p_{3/2}}\) (Ni), Ni\(_{2p_{3/2}}\) (NiAl\(_2\)O\(_4\)), Ni\(_{2p_{1/2}}\) (Ni), and Ni\(_{2p_{1/2}}\) (NiAl\(_2\)O\(_4\)), respectively. It implied that Ni species on surface were Ni\(_0\) (Ni) and Ni\(_{2+}\) (NiAl\(_2\)O\(_4\)), which was strongly verified by the results of XRD.

The Ru\(_3d\) spectra of all the catalysts were shown in Fig. 6b-e. The peaks at 280.1 (Ru\(_{3d_{5/2}}\)) and 284.2eV (Ru\(_{3d_{3/2}}\)) were observed for 10Ni-1.0Ru (fresh), 10Ni-1.0Ru(F), and 10Ni(F)-1.0Ru, suggesting that metallic Ru was present on the surface. The peak at 281.0eV were only present for 10Ni-1.0Ru(F) and 10Ni(F)-1.0Ru, and the intensity was weak, indicating that a small part of Ru species was RuO\(_2\) for 10Ni-1.0Ru(F) and 10Ni(F)-1.0Ru. The RuO\(_2\) originated from the incompletely reduced catalysts after calcined at 450°C for 5h. For the 10Ni-1.0Ru (used) catalyst (Fig. 6e), the peaks assigned to RuO\(_2\) were also observed, which might originate from the partial oxidation of the ruthenium surface. Simultaneously, the C1s peak at 284.7eV indicated there was contaminated carbon on the surface of all samples. These results verified that the active species (Ru\(_0\)) had changed on the surface of 10Ni-1.0Ru (used) after reaction. Combined with the results of catalytic activity experiments, the higher catalytic activity of 10Ni-1.0Ru might result from the Ru species (Ru\(_0\)). The catalyst prepared by the co-precipitation method exhibited...
the good catalytic performance. Therefore, the details of Ru loading, H₂:CO₂ molar ratios, GHSV, and stability were discussed in the subsequent sections.

![Figure 6](image)

**Fig. 6** All the samples XPS survey spectra (a); Ni2p and Ru3d XPS spectra for (b) 10Ni(F)-1.0Ru, (c) 10Ni-1.0Ru(F), (d) 10Ni-1.0Ru, and (e) 10Ni-1.0Ru (used).

**Effect of Ru loading on catalytic activity**

The catalytic activities of various 10Ni-xRu(x=0.5, 1.0, 2.5, and 5.0) catalysts prepared by co-impregnation method, with Ru loadings varying from 0.5 to 5.0wt% were studied at temperatures ranging from 250 to 500°C at a GHSV of 9000 h⁻¹, a H₂:CO₂ molar ratio of 4:1. The CO₂ conversion increased firstly with the reaction temperature increase from 250 to 400°C, then decreased (above 400°C) (Fig. 7a). This might be due to the deactivation of the catalyst at higher temperature (above 400°C). Fig. 7b showed the selectivity of CH₄ and CO. It was noticed that CO was the only by-product, which was produced on the surface of 10Ni-0.5Ru and 10Ni-5.0Ru catalysts above 350°C. The CH₄ selectivity was always 100% from 250 to 350°C for all samples, and was less than 100% for the 10Ni-1.0Ru and 10Ni-2.5Ru catalysts above 400°C. Obviously, the conversion maximum was 82.71% for the 10Ni-1.0Ru at 400°C. It was suggesting that 10Ni-1.0Ru might provide more active sites.

![Figure 7](image)

**Fig. 7** Effect of temperature and Ru loading on the CO₂ conversion (a) and the selectivity (b) over 10Ni-xRu(x=0.5, 1.0, 2.5, 5.0) catalysts; Reaction conditions: 100 mg catalysts, H₂:CO₂=4:1, GHSV=9000h⁻¹, 1atm.

**Effects of H₂:CO₂ molar ratio**

Different H₂:CO₂ molar ratios were studied at a temperature ranging from 250 to 500°C, GHSV was 9000 h⁻¹ over the 10Ni-1.0Ru catalyst. CO₂ conversion and CH₄ selectivity over 10Ni-1.0Ru at different H₂:CO₂ molar ratios and temperatures were shown in Fig. 8.

CO₂ conversion and CH₄ selectivity increased when H₂:CO₂ molar ratios were increased from 2:1 to 6:1 at the same reaction temperature, but corresponding CO selectivity decreased. Fig. 8 showed that CO₂ conversion was 94.75% and CH₄ selectivity was 100% (at 400°C, H₂:CO₂ molar ratio was 6:1). According to the results, it could be found that increasing H₂:CO₂ molar ratio was beneficial to CO₂ methanation.
Fig. 8 The CO\textsubscript{2} conversion (a) and the selectivity (b) over 10Ni-1.0Ru catalyst at different H\textsubscript{2}:CO\textsubscript{2} molar ratio (ranging from 2:1 to 6:1); Reaction conditions: 100 mg catalyst, GHSV=9000 h\textsuperscript{-1}, 1 atm.

**Effects of GHSV**

To study the effect of GHSV on the activity, the GHSV was varied between 3000 and 15000 h\textsuperscript{-1}. Fig. 9 showed that the catalytic activity of 10Ni-1.0Ru was tested at different GHSV, H\textsubscript{2}:CO\textsubscript{2} molar ratio was 4:1 and temperatures ranging from 250 to 500°C.

![Graph showing CO\textsubscript{2} conversion over 10Ni-1.0Ru catalyst at different GHSV (ranging from 3000 to 15 000 h\textsuperscript{-1}); Reaction conditions: 100 mg catalyst, H\textsubscript{2}:CO\textsubscript{2}=4:1, 1 atm.](image)

It was found that the temperature curves could be divided into two domains. First, CO\textsubscript{2} conversion decreased at GHSV between 3000 and 6000 h\textsuperscript{-1}. As the GHSV increased, the velocity for the reactants through the catalyst bed became larger; therefore, the contact time on the surface of the catalyst bed became shorter. Thus, the thermodynamic equilibrium conversions for the reactants were not achieved due to insufficient contact time. In addition, the number of the reactants through the catalyst bed became larger with the increase of GHSV; consequently, the catalyst was not able to provide sufficient active sites for redundant reactants. In addition, CO\textsubscript{2} conversion almost remained constant at 400, 450 and 500°C when GHSV varied from 6000 to 15000 h\textsuperscript{-1}, and the other three temperature curves (250, 300 and 350°C) showed a slow upward trend. In addition, regarding the mentioned-temperature curves, the optimum GHSV was 9000 h\textsuperscript{-1}, meaning the entire catalyst works efficiently.

**Long-term stability tests**

Fig. 10 showed the catalytic activity during 100 h on CO\textsubscript{2} methanation over 10Ni-1.0Ru at 400°C and H\textsubscript{2}:CO\textsubscript{2} molar ratio was 4:1, at 9000 h\textsuperscript{-1}. Obviously, CO\textsubscript{2} conversion remained above 82% and CH\textsubscript{4} selectivity was almost 100% during long-term over 10Ni-1.0Ru. The by-product (CO) was only produced on the 10Ni-1.0Ru catalyst after 80 hours. However, CO selectivity was less than 0.5%.

Fig. 10 Long-term (100h) stability tests over 10Ni-1.0Ru catalyst; Reaction conditions: 100 mg catalyst, H\textsubscript{2}:CO\textsubscript{2}=4:1, GHSV=9000 h\textsuperscript{-1}, 1 atm, 400°C

There were two reasons for the decrease of CH\textsubscript{4} selectivity after 80 hours. First of all, although the atmosphere was rather reductive in carbon dioxide methanation, the metallic nickel (Ni) of catalyst surface could be gradually re-oxidized to nickel oxide (NiO) by CO\textsubscript{2} or by water produced, deactivating the catalyst during the long-term reaction. The nickel species (Ni\textsuperscript{0} or Ni\textsuperscript{2+}) located at the cationic deficient sites of γ-Al\textsubscript{2}O\textsubscript{3} phase strongly interacted with the carrier, resulting in the formation of solid solution of nickel oxide (NiO) and nickel aluminate spinel phase (NiAl\textsubscript{2}O\textsubscript{4}) at 400°C\textsuperscript{39, 45-46}. The second reason was that the noble metal Ru was also oxidized to RuO\textsubscript{2}. Noble metals (Ru, Pt, Rh, etc.) had better resistance to carbon deposition than Ni\textsuperscript{2+}, and enhanced the high activity and stability of the catalysts and achieved high CO\textsubscript{2} conversions with low carbon formation\textsuperscript{7, 10, 26-28}. The decrease of CH\textsubscript{4} selectivity was due to RuO\textsubscript{2} located on the surface of the catalyst. Therefore, all the phenomena mentioned above indicated that 10Ni-1.0Ru catalyst performed the excellent catalytic activity and stability.

**Possible reaction mechanism of CO\textsubscript{2} methanation on 10Ni-1.0Ru**

Scheme 1 gave a possible reaction mechanism of CO\textsubscript{2}...
methanation on 10Ni-1.0Ru. The methanation of CO$_2$ involved the conversion of CO$_2$ to CO prior to methanation, and the subsequent reaction followed the same mechanism as CO methanation.

The first step of the methanation reaction could be the chemisorption of CO$_2$ on the catalyst and the dissociation of CO$_2$ into carbon species (CO$_{ads}$) and oxygen species (O$_{ads}$) on the surface. At the same time, H$_2$ is dissociated into H on Ni. Crisafulli et al. studied H$_2$ adsorption on metallic Ni. Their work had emerged a picture of relatively facile H chemisorption of CO$_2$ on the surface of the catalysts. C could react with H to produce CH$_4$ on metallic Ru, and H and O atoms formed H$_2$O.

Conclusion

A series of bimetal Ni-Ru catalysts had been successfully prepared by co-impregnation and sequential impregnation methods. The obtained catalysts performed high catalytic activities, selectivities, and excellent stabilities for CO$_2$ methanation. Besides, it was also found that the segregation phenomenon of Ru occurred on the catalyst surface in the co-impregnation preparation process, by which more active Ni and Ru species (metallic Ru) could be provided on the surface of 10Ni-1.0Ru catalyst. The high catalytic activity was obtained at Ru loading of 1.0%, GHSV 9000h$^{-1}$ and higher H$_2$:CO$_2$ molar ratio. The 10Ni-1.0Ru showed more stable and highly active properties during the long-term reaction. Based on the characteristics, it was proposed that CO$_2$ was dissociated and activated to form carbon species (CO$_{ads}$) on Ru species surface, then reacted with activated H on Ni species to form methane.

Acknowledgment

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Scheme 1: The proposed possible reaction mechanism of CO$_2$ methanation over 10Ni-1.0Ru catalyst.
Enhancing Catalytic Activity and Stability for CO$_2$ Methanation on Ni-Ru/$\gamma$-Al$_2$O$_3$ via Modulating Impregnation Sequence and Controlling Surface Active Species

In this work, two methods, co-impregnation and sequential impregnation, were used to prepare a series of Ni-Ru/$\gamma$-Al$_2$O$_3$ catalysts. By comparison the structure, surface species and catalytic performances of different catalyst, we uncovered the surface species segregation of Ru in Ni-Ru catalysts. The effect of this segregation on catalytic properties was also discussed, and the possible reaction mechanism for CO$_2$ methanation was proposed.