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Preparation of a mesoporous sorption complex catalyst and its evaluation in reactive sorption enhanced reforming*

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Abstract: A mesoporous sorption complex catalyst was prepared by pore-forming modification and evaluated by the CO_2 reactive sorption enhanced reforming (ReSER) process, which is used to produce hydrogen from methane. Three samples of polyethylene glycol (PEG) with molecular weights between 2000 and 20 000 were added as templates into a mixed slurry to create catalysts with different pore properties by further formation and calcination. The pore characteristics determined by Brunauer-Emmett-Teller (BET) analysis showed that one of the mesoporous catalysts, named M-NiAlCa-6000, had a pore size of 9.2 nm and a surface area of 70.52 m^2/g and the CO_2 sorption capacity of this catalyst was 44% higher than that of the catalyst without the PEG 6000 modification. The catalyst was evaluated in the ReSER process in a fixed-bed reactor system at 0.1 MPa and 600 °C with an H_2O/CH_4 molar ratio of 4. An H_2 concentration of 94.2% and a CH_4 conversion of 86.0% were obtained at a carbon space velocity of 1700 h^{-1}, while CO_2 was hardly detected.

Key words: Hydrogen, Ni catalyst, Mesoporous, Steam methane reforming, CO_2 sorption
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1 Introduction

The process of adding CO_2 sorbent during steam methane reforming (SMR) is a potential way of reducing emission of the greenhouse gas CO_2 and enhancing the reforming process for hydrogen production (Han and Harrison, 1994; Carvill *et al.*, 1996; Balasubramanian *et al.*, 1999; Ding and Alpay, 2000; Xiu *et al.*, 2003; Harrison, 2008; Chanburanasiri *et al.*, 2011; Wang *et al.*, 2011). He and Wu (2007) developed a ReSER process that uses nano-CaO as the CO_2 reactive adsorbent in a sorption complex catalyst to produce high-purity hydrogen with control of CO_2 emissions. The sorption complex catalyst contains nano-CaO as the CO_2 reactive adsorbent and NiO as the reforming catalyst in one microsphere particle. The exothermic reaction of CaO with CO_2 enhances the endothermic reaction of steam reforming in each particle (Wu *et al.*, 2008; 2010).

As a new catalyst, the sorption complex catalyst can be further improved in activity and stability. Wu and Wang (2010) and Feng *et al.* (2012) focused on a method of adding assistant catalysts such as ZrO_2 or La_2O_3. Although both studies reported some degree of improvement in stability, the catalysts were all evaluated at a very low carbon space velocity of 340 h^{-1}, which is far from the industrial requirement of at least 1000 h^{-1}. Based on the features of the sorption complex catalyst, the reaction between CaO and CO_2 is the most important reaction. Additionally, the available pore structure will affect the gas-solid reactivity of CaO with CO_2, thus affecting the SMR reaction in terms of both heat and mass transmission.

Previous studies (Inoue *et al.*, 1988; 1991; Oyekunle and Ikpekri, 2004; Gong *et al.*, 2005) have

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shown that a larger pore size and a greater number of pores promote the reactions by facilitating the transmission of heat and mass into and out of the catalyst. Moreover, it is well known that high porosity implies high surface area, which provides a large number of reactive sites. Seo *et al*. (2009) increased the pore size of a Ni-based catalyst from 4.2 nm to 9.6 nm, and obtained an 8%–15% increase in the CH_4 conversion rate. Sun *et al*. (2010) studied the pore structure of a Ni catalyst for the CO_2 reforming of CH_4 and found that catalysts with large pore volumes showed very high catalytic activity. The catalyst developed in previous study (Wu and Wang, 2010; Feng *et al*., 2012) for the ReSER process exhibits a pore size smaller than 5 nm and pore volume less than 0.2 cm^3/g. Therefore, it is necessary and interesting to study the effect of pore expansion on the catalytic performance of the sorption complex in the ReSER process.

The methods (Inoue *et al*., 1994; Liu *et al*., 2009) used to improve catalyst porosity use polyethylene glycol (PEG), a polymer that exhibits good dispersion and solubility, as a template. When PEG is mixed with a catalyst or catalyst support, it decomposes at 200–400 °C and creates many pores of different sizes, depending on its degree of polymerization.

In this study, we used PEG as a template to prepare a mesoporous sorption complex catalyst. The catalyst was then evaluated with respect to its CO_2 sorption properties and hydrogen production performance in the ReSER process.

2 Experimental

2.1 Preparation of mesoporous sorption complex catalyst

Nano-$CaCO_3$ (Huzhou Linghua Co., Ltd., China) was used as a nano-CaO-based adsorbent precursor, and $Ni(NO_3)_2{\cdot}6H_2O$ (98% purity, Shanghai Hengxin Chemical Reagent Co., Ltd., China) was used as the Ni source. PEG (analytical reagent, Sinopharm Chemical Reagent Co., Ltd., China) with molecular weights of 2000, 6000, and 20 000 were chosen as templates to obtain the desired mesoporous structures. The sorption complex catalyst was prepared by the slurry mixing method. PEG was dissolved in hot water before being added to a nano-$CaCO_3$ water-suspended solution, and stirred to make a slurry. Then, an alumina sol (10%, Zibo Longao Co., Ltd., China) and a $Ni(NO_3)_2{\cdot}6H_2O$ solution were added to the slurry. The slurry was then dried, extruded, and calcined at 500–800 °C in a muffle furnace. The catalysts with and without added PEG were denoted as M-NiAlCa-*n* (with added PEG, where *n* represents the molecular weight of the PEG that was used) and N-NiAlCa (without added PEG).

2.2 Characterization of mesoporous sorption complex catalyst

The surface area and pore structures of the catalysts were determined by the Brunauer-Emmett-Teller (BET) method (nitrogen physisorption) using a MiCromeritiCs BELSoRP-mini II device (BEL Japan, Inc.). The crystalline phase of the catalyst was determined by X-ray diffraction (XRD, D/MAX-RAX, Rigaku, Japan). A temperature-programmed reduction (TPR) was carried out to test the interaction between NiO and the support of the catalysts (TP-5000III, Tianjin Xianquan Industry and Trade Development Co., Ltd.); tubes were filled with 50 mg of catalyst, placed under a feed gas of 5% H_2 in N_2 and heated from 373 K to 1073 K at 10 K/min.

2.3 Adsorption properties of mesoporous sorption complex catalysts

Thermal gravimetric analysis (TGA) (type Pyris 1, Perkin Elmer Corporation, America) was used to measure the adsorption properties of mesoporous sorption complex catalysts. First, 1–2 mg of the catalysts was placed on the testing platform. The adsorption stage temperature was set to 600 °C and held for 10 min in 20% CO_2/80% N_2, and the desorption stage temperature was set to 750 °C and held for 10 min in N_2 atmosphere. Before the adsorption-decomposition program, $CaCO_3$ in the catalyst was first decomposed to CaO at 750 °C in TGA. The adsorption capacity (mol/kg) was defined as the molar mass of the actual adsorption of CO_2 per mass of catalyst. The reason why we chose a reaction temperature of 600 °C and the regeneration temperature of 800 °C is that, in our previous studies, He and Wu (2007) determined that 600–640 °C is the optimal temperature for the ReSER process. In this research, we chose 600 °C as our reaction temperature. Also, the decomposition temperature of a sorption complex catalyst completely is 750 °C by TGA testing. Considering the effect of mass and heat transfer, we chose the regeneration temperature as 800 °C to decompose the nano-$CaCO_3$ in the catalyst completely in a fixed-bed.

2.4 Evaluation method of ReSER hydrogen production

Fig. 1 shows the laboratory-scale fixed-bed reactor that was used to evaluate the activity of the mesoporous sorption complex catalysts during the ReSER process. The catalyst powder was placed in the flat-temperature zone in the fixed-bed reactor. The temperature of the reactor was controlled by a temperature-control device. CH_4, H_2, and N_2 were supplied from steel cylinders, and three mass flow controllers were used in front of the reactor to control their flow rates. Steam came from water vaporization and the flow of water was controlled by a high-precision water pump. The product gas after reaction was piped in gas chromatography (GC) to be analyzed, and the test results are the percentage concentrations of CH_4, CO_2, and CO. The reaction conditions were: a temperature of 600 °C, a pressure of 0.1 MPa, and an H_2O/CH_4 molar ratio of 4. Before the reaction, the catalyst was first regenerated to decompose $CaCO_3$ to form CaO at the regeneration temperature of 800 °C in a N_2 atmosphere. Then NiO was reduced to form Ni by diluting H_2 with N_2.

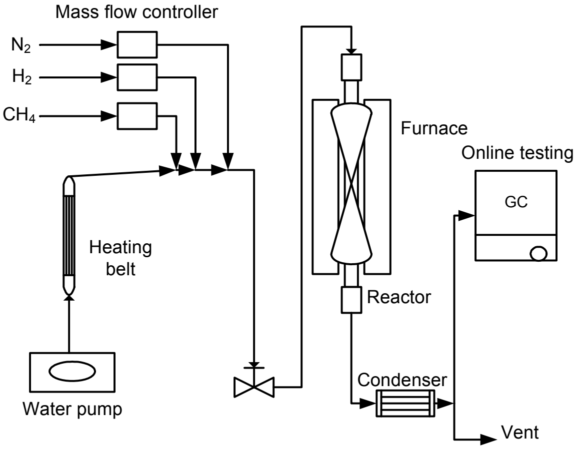

Fig. 1 Reaction system of the ReSER process for hydrogen production

3 Results and discussion

3.1 Pore properties with PEG modification

The pore properties and surface areas of the catalysts modified with PEG with different molecular weights were tested by the BET method. Fig. 2 shows

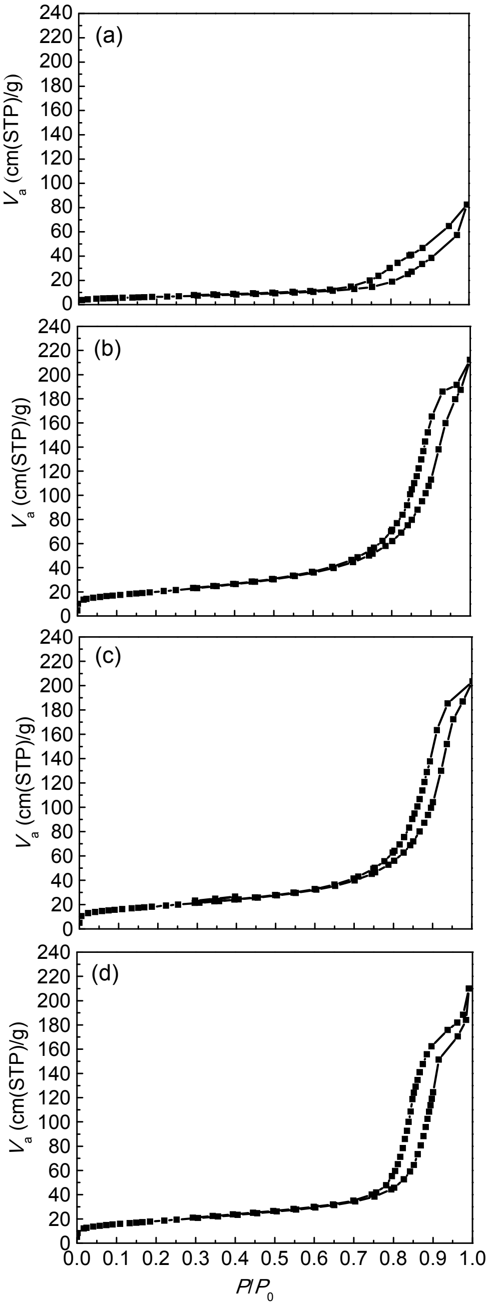

Fig. 2 N_2 adsorption/desorption curves of different catalysts

(a) N-NiAlCa; (b) M-NiAlCa-2000; (c) M-NiAlCa-6000; (d) M-NiAlCa-20000. V_a presents the adsorption volume per gram adsorbent, and P/P_0 presents the partial pressure the N_2 adsorption/desorption curves of the catalysts. A typical type-IV hysteresis loop is observed in Figs. 2b–2d, indicating that by using PEG as the template, a mesoporous framework is formed and stabilized in the reflux stage. However, N-NiAlCa, prepared by the same procedure without the addition of PEG, does not show a distinct mesoporous framework, as shown in Fig. 2a.

Fig. 3 shows the pore size (r_p) distribution curves of the catalysts. M-NiAlCa-2000, M-NiAlCa-6000, and M-NiAlCa-20000 show increasing peak values ranging from 7.0 nm to 10.8 nm.

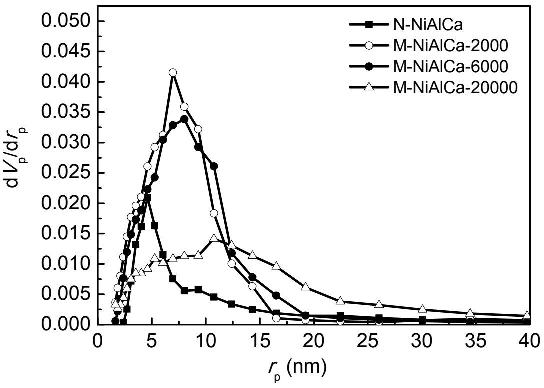

Fig. 3 Pore size distribution curves of the catalysts

Table 1 shows the surface area, pore size, and pore volume of sorption complex catalysts. As the molecular weight of the added PEG increases from 2000 to 20000, the average pore size increases from 8.0 nm to 11.8 nm. The surface area and pore volume of the sorption complex catalysts increase by 2–3 times with added PEG. However, with the increase in molecular weight of PEG, the surface area decreases gradually. This is because, for the same mass of added PEG, the higher-molecular-weight sample contains fewer but larger molecules and thus produces fewer pores and a smaller surface area but a larger pore size. Combining the results shown in Table 1 and Figs. 2 and 3, we conclude that the catalysts modified with PEG2000 and PEG6000 show good average pore sizes and surface areas. The pore analysis above indicates successful pore formation.

Table 1 Pore properties of sorption complex catalysts

Sample	Average pore size (nm)	Surface area (m^2/g)	Pore volume (cm^3/g)
N-NiAlCa	7.2	22.56	0.13
M-NiAlCa-2000	8.0	67.52	0.30
M-NiAlCa-6000	9.2	65.79	0.31
M-NiAlCa-20000	11.8	46.98	0.28

3.2 Adsorption properties by PEG modification

The sorption complex catalyst is a combination of a CO_2 adsorbent and a reforming catalyst. The sorption properties constitute one of the key factors that affect the kinetics of the reforming reaction. The sorption properties of the catalysts N-NiAlCa, M-NiAlCa-2000, and M-NiAlCa-6000 were tested by TGA, and the results are shown in Figs. 4–6.

Fig. 4 shows that M-NiAlCa-6000 has the largest sorption capacity. Fig. 5 shows the sorption rate calculated from the data of Fig. 4 by a differential method, and it is clear that the sorption rate of M-NiAlCa-6000 is the highest. Based on ion migration mechanism, CO_2 molecules are adsorbed on the catalyst surface and react with O^{2-} ions to form CO_3^{2-} ions. At the beginning of the adsorption reaction, the number of CO_3^{2-} ions in the reaction system is few, and thus the initial reaction rate is slow. As the reaction progresses, the number of CO_3^{2-} ions in the reaction system increases, and thus the reaction rate increases. That stage is the so-called fast adsorption stage, when CO_2 molecules react with external CaO, and the process is reaction-controlled. After that, the reaction moves to a slow-adsorption stage, because the CO_2 molecules must penetrate the product $CaCO_3$ layer to react with the internal CaO, so the reaction rate is slower, and the process is diffusion-controlled.

Fig. 6 illustrates the durability of the sorption capacity of the catalysts. It is clear that M-NiAlCa-6000 exhibits the best durability and is more stable than M-NiAlCa-2000.

The above results show that the sorption complex catalyst M-NiAlCa-6000 with a larger pore size of 9.2 nm and a higher surface area of 65.79 m^2/g yields a better sorption capacity and sorption rate.

The experimental results discussed above suggest that, first, a larger surface area provides more reactive CaO sites for CO_2 adsorption reaction, thus increasing the sorption capacity and sorption rate. This has also been shown in (Wu and Wang, 2010), in which a catalyst with a surface area of 69.5 m^2/g has a higher sorption capacity than a catalyst with a surface

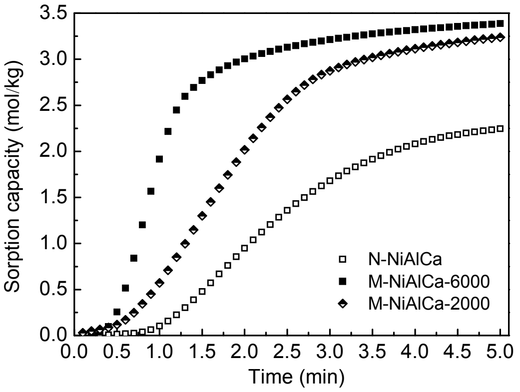

Fig. 4 Sorption capacity of the catalysts

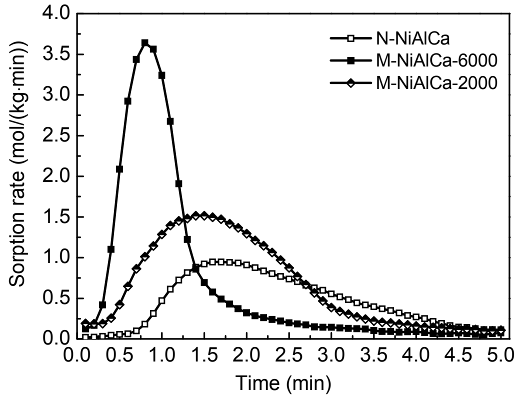

Fig. 5 Sorption rate of the catalysts

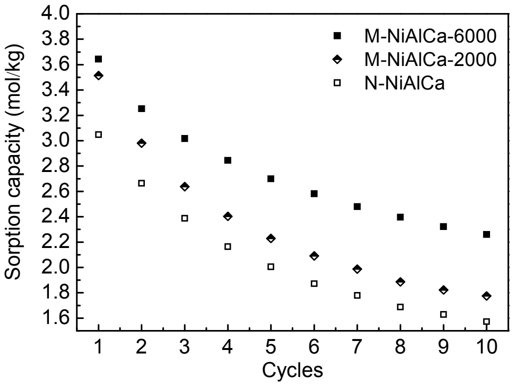

Fig. 6 Durability of the catalysts' sorption capacity

area of 30.8 m^2/g; second, the larger pore size facilitates the transmission of heat and mass, enhancing the reaction of CO_2 with CaO and increasing the sorption capacity and reaction rate. Therefore, by carefully considering the BET and TGA results, we chose the mesoporous catalyst M-NiAlCa-6000 as the subject of our study on hydrogen production in the ReSER process. The catalyst N-NiAlCa was also evaluated in the ReSER process for comparison.

3.3 Performance of hydrogen production in ReSER process

The performances of the sorption complex catalysts N-NiAlCa and M-NiAlCa-6000 with respect to the ReSER hydrogen production process were evaluated on a laboratory-scale fixed-bed reactor. The highest H_2 concentration and CH_4 conversion rate in the sorption-enhanced segment were obtained under different carbon space velocities (Table 2). Both catalysts yielded similar H_2 concentrations above 95% and CH_4 conversion rates of approximately 90% in the sorption-enhanced segment when the carbon space velocity was only 340 h^{-1}. However, when the carbon space velocity increased to 1020 h^{-1}, the catalyst N-NiAlCa produced a lower H_2 concentration, 81.1%, and exhibited a reduced CH_4 conversion rate, 53.1%. By comparison, for the mesoporous catalyst M-NiAlCa-6000, when the carbon space velocity increased to 1020 h^{-1}, the H_2 concentration and CH_4 conversion rate were still 96.8% and 94%, respectively. When the carbon space velocity increased to 1700 h^{-1}, the H_2 concentration and CH_4 conversion were still 94.2% and 86%, respectively. Both the CH_4 conversion rate and H_2 concentration of M-NiAlCa-6000 were higher than those of N-NiAlCa with the increase of the carbon space velocity. The high concentration of hydrogen also indicated low CO_2 emission.

Table 2 ReSER hydrogen production of N-NiAlCa and M-NiAlCa-6000 catalysts

Space velocity (h^{-1})	M-NiAlCa-6000		N-NiAlCa	
	H_2 concentration (%)	CH_4 conversion (%)	H_2 concentration (%)	CH_4 conversion (%)
340	95.8	89.9	90.6	95.5
680	95.3	85.1	84.4	94.5
1020	96.8	94.0	53.1	81.1
1360	95.0	95.6		
1700	94.2	86.0		

Table 3 shows the activity of catalysts reported by Feng *et al.* (2012). They modified a sorption complex catalyst with La_2O_3 (named LNCA); LNCA exhibited a surface area of 29.18 m^2/g and pore size of 4.6 nm. The performance of LNCA in the ReSER process was then evaluated in a fixed-bed reactor. Compared with Tables 2 and 3, it is clear that the catalyst M-NiAlCa-6000 can be used with a higher carbon space velocity. Moreover, M-NiAlCa-6000 yields a higher CH_4 conversion and H_2 concentration than LNCA.

Table 3 ReSER hydrogen production of catalyst modified by La_2O_3 reported in (Feng *et al.*, 2012)

Space velocity (h^{-1})	H_2 concentration (%)	CH_4 conversion (%)
396	93.1	89.4
792	89.6	87.6
1188	90.2	85.1
1386	85.4	65.4

These results indicate that mesoporous catalysts with a large surface area of 65.79 m^2/g and pore size of 9.2 nm exhibit higher activity and would be more suitable for industrial application.

3.4 Performance of the mesoporous catalyst

The microscopic characteristics of a catalyst can provide an explanation for the catalyst's macroscopic performance. XRD was used to test the phase characteristics of the catalyst, including grain size and metal dispersion (Fig. 7).

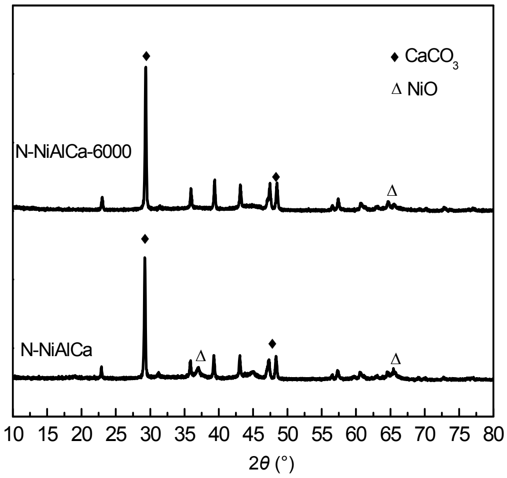

Fig. 7 XRD spectra of catalysts N-NiAlCa and M-NiAlCa-6000

The characteristic peaks of fresh, unreduced complex catalysts N-NiAlCa and M-NiAlCa-6000 mainly belong to $CaCO_3$ and NiO. Al_2O_3 peaks were not detected. No characteristic NiO peak was detected at 35°–40° for M-NiAlCa-6000, and the strength of the characteristic peak at 60°–70° is weaker compared with that observed for N-NiAlCa, which suggests that the dispersion of the active component NiO in M-NiAlCa-6000 is better than in N-NiAlCa. The NiO grain sizes calculated by the Scherrer formula were 20.38 nm and 11.57 nm for fresh N-NiAlCa and M-NiAlCa-6000, respectively. This means that the catalyst with the more porous structure has a smaller NiO grain size. The porous catalyst exhibited a larger surface area, leading to a better dispersion of the active component NiO; and thus more reactive sites are created for the ReSER process, thus improving the activity of the catalyst.

A TPR test was conducted to study the effect of the strong metal-support interaction (SMSI effect) of the catalyst (Fig. 8). Xu *et al.* (2001) and Feng *et al.* (2009) showed that the interaction between the active component and the support in catalysis is one of the most important factors affecting catalyst performance. The weak interaction related to the low temperature peak (<450 °C) in the TPR spectrum will result in the migration and clustering of the active Ni, and thus will reduce the activity of the catalyst during the reaction; while the very strong interaction related to the high temperature peak (>750 °C) in the TPR spectrum will lead to the formation of spinel, which has no activity in the reforming reaction. Therefore, both weak and very strong metal-support interactions will lead to bad catalyst performance. The shared reduction peak of N-NiAlCa at 360 °C is attributed to free NiO, but the peak of M-NiAlCa-6000 at the same temperature is not as distinct. That means that NiO with weak interaction with the support in the catalyst M-NiAlCa-6000 is less than that in the catalyst N-NiAlCa. Dueso *et al.* (2010) believed that large grain sizes are easier to reduce for the same type of NiO, which also implies that the NiO grain size in catalyst decreases after adding PEG. The peak at 500–700 °C represents fixed NiO, which indicates a stronger interaction between the active components and the support. The integrated area between 500 °C and 700 °C for the catalyst M-NiAlCa-6000 is larger than that of N-NiAlCa, indicating that the catalyst

M-NiAlCa-6000 has an appropriate metal-support interaction. The reduction peak of N-NiAlCa at approximately 880 °C represents nickel-aluminum spinel $NiAl_2O_4$ (Hao *et al.*, 2009), and does not occur in M-NiAlCa-6000. The SMSI effect of a catalyst can be regulated to be more suitable by modification of the pore-forming characteristics.

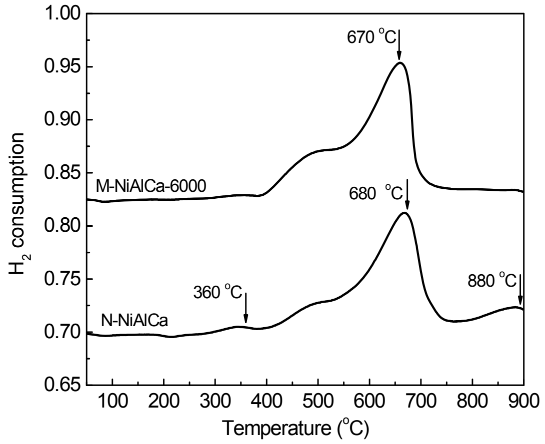

Fig. 8 TPR spectra comparison of catalysts N-NiAlCa and M-NiAlCa-6000

Consequently, the better performance of the catalyst M-NiAlCa-6000 may be attributed to the addition of PEG for pore formation. A mesoporous structure was obtained after PEG was added and then decomposed at the calcination temperature. Larger surface area and pore size were obtained in the mesoporous catalyst, which facilitate the transmission of mass and heat. Moreover, during modification, NiO disperses more evenly on the support surface and the NiO grain size decreases, as determined by XRD. Additionally, the TPR results show that the generation of $NiAl_2O_4$ is inhibited, while more active sites emerge on the support surface.

4 Conclusions

The mesoporous catalyst M-NiAlCa-6000, created using PEG 6000 as a template, showed the best pore properties of all the samples with a surface area of 65.79 m^2/g and an average pore size of 9.2 nm. The CO_2 sorption capacity of the catalyst was 44% higher than that of the unmodified N-NiAlCa catalyst, and the CO_2 sorption rate was accordingly faster. The mesoporous sorption complex catalyst produced an H_2 concentration of 94.2% at a carbon space velocity of 1700 h^{-1} and exhibited a CH_4 conversion rate of 86.0%. XRD results demonstrated that the Ni grain size in the mesoporous catalysts was smaller, while TPR results demonstrated that there were more active sites in the mesoporous catalyst.

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