The Studies on Catalytic Activity of Nanometer $BaTiO_3$-supported Ni Based Catalyst in the Reaction of CO_2 Reforming CH_4 to Syngas*

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Abstract: Superfine $BaTiO_3$ support was prepared by sol-gel method. The properties of superfine $BaTiO_3$ were investigated by DTA-TG, XRD, TEM and BET. Nanometer $BaTiO_3$ was used as support to prepare Ni/$BaTiO_3$ catalyst by impregnation method. The catalyst is applied to the reaction of CO_2 reforming CH_4 to syngas and shows high activity. The effects of catalytic activity of nanometer $BaTiO_3$-supported Ni based catalyst on calcination temperature, reduction temperature, reaction temperature and the method of preparation of Ni/$BaTiO_3$ catalyst were investigated.

Key words: superfine; nickel catalyst; barium titanate; reforming
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1 Introduction

Compared to conventional solid-state reaction and coprecipitation method[1,2], sol-gel method offers a promising approach for preparing ultrafine, homogeneous, high-purity powders at temperatures far below other required methods. Currently. There is almost no literature report that nanometer $BaTiO_3$ was used as support to prepare catalyst. In this paper, performance of the catalyst with nanometer $BaTiO_3$ as support in the reaction of CO_2 reforming CH_4 to syngas was described. CO_2 reforming of CH_4 is paid general attention due to a low H_2 in its product gas that is desirable Fischer-Tropsch synthesis and its significance in relieving energy crisis and greenhouse effect[3]. Precious metals such as Ru, Rh, Pd and Pt supported catalysts show high activity and stability in CO_2 reforming of CH_4. But resource of the metals is limited. Ni catalyst also possesses high activity, but it is easy to deactivate due to carbon deposition or strong metal-support interaction at high temperature. Some research results indicate that the support has great effect on activity and stability of catalysts.

2 Experimental

2.1 Synthesis procedure

At first, homogeneous and transparent solution was prepared by mixing 0.0147 mol titanate and 10 mL alkanol solvent, after stirring vigorously for 20 min, 10 ml glacial acetic acid was added into the solution at room temperature. Subsequently, certain volume of barium acetate solution was dropped into the prepared solution with the mole ratio of Ba/Ti = 1.0 and followed by continuing stirring for 30 min to promote complete hydrolysis reaction. The pH value is kept 4 ~ 5. At last, the mixture solution was put into water-bath with temperature of 343 K to start the process of formation of sol and transformation of sol into gel. Amorphous barium titanate gel was obtained in a few minutes. Then the gel was dried in vacuum at temperature of 333 K for 24 h, and nanometer $BaTiO_3$ was prepared by calcinating the dry gel at 973 ~ 1073 K for 2 h.

2.2 Characterization

The morphology of $BaTiO_3$ powder was observed with TEM (Japan H-600). Thermal analyses were carried out by using TG/DTA (Shimadzu DT-40). The X-ray diffraction patterns of $BaTiO_3$ was recorded with XRD (D/max-3B diffractometer). Specific surface area was measured with ST-08 Specific surface area apparatus.

2.3 Preparation and test of catalyst

The catalyst sample of Ni/$BaTiO_3$ was prepared by wet impregnation of an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ onto nanometer $BaTiO_3$ obtained by sol-gel method for 24 h. After being dried, the sample was calcinated in air at 923 K for 3 h (the content of Ni in catalyst is 5.0%). The calcinated catalyst was made into particles of 60 ~ 80 mesh. Before the catalyst test, the catalyst was reduced in situ at 773 K for 1 h. The catalytic reaction was conducted in a fix-bed reactor under atmospheric

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pressure, the catalyst bed contains 150 mg $Ni/BaTiO_3$, the catalytic reaction was performed with a feed of 1 : 1 CH_4/CO_2 unless otherwise specified, the flow rate of the feed is GHSV = 1.2×10^4 $mL \cdot h^{-1} \cdot g^{-1}$, product gases were immediately injected into a gas chromatograph for analysis.

3 Results and discussion

3.1 Influencing factors of powder quality

3.1.1 Influence of water volume.

The structure of final product prepared by sol-gel method is in shape preliminarily in solution, and following process is relevant to the characteristic of sol directly. So the characteristic of sol is very important. The essential reason for transformation of homogeneous solution into sol is the hydrolysis of alcoholate and the condensation polymerization. Controlling conditions for hydrolysis of alcoholate are the key to the preparation of sol with promising quality.

The research revealed that water volume has great effect on the structure of alcoholate polymer. There are a little alkoxy group formed by hydrolysis under small water volume, and products with low cross-linking level are easy to form by condensation polymerization of molecules related to hydrolysis reaction. On the contrary, when water volume is large, products with high cross-linking level are easy to form. In the experiment, when barium acetate solution is dropped into the solution prepared by dissolvation of $Ti(OR)_x(OAc)_y$ (OR is *n*-butyl alcohol or alcohol, OAc is acetic acid radical) in absolute alcohol, the compound of $Ti(OH)_a(OAc)_b$ can be formed because of faster hydrolysis rate of alkoxy group than that of acetic acid radical, and the compound is able to be dissolved in excess water. Sol particles are not formed in the process of hydrolysis of $Ti(OR)_x(OAc)_y$ to $Ti(OH)_a(OAc)_b$. The formation of sol was next to the rapid transformation of sol into gel. That is to say, there is no apparent boundary between them. The process of transformation carrying out in water-bath includes the formation and the transformation of sol. When different volumes of water used, there is different gel time (the time lasts from starting heating to ending gel formation), that is to say, water volume will affect greatly the formation of final sol particles and the transformation of sol into gel, and influence powder quality. Relationship between water volume and powder quality is shown in Tab.1.

It is known from Tab.1 that gel time increases with the increase of water volume for hydrolysis. Transparent gel body can be obtained under 10 mL or 20 mL of water, whereas it becomes opaque and shows light white when water volume increases to 40 mL. The structure of gel body becoming loosen and a little solution will bleed under the following drying, and gel can not be formed when water volume rises up to 50 mL. White precipitate is obtained under continuing heating in water-bath at 343 K, which may be due to the less concentration of compound of $Ti(OH)_a(OAc)_b$ under more water volume and the result of weak interaction force among compound molecules which causes the formation of sol body and transformation of sol into gel to slow down. When water volume increases to 50 mL, the interaction force among sol nucleus weakens to the degree that they can't aggregate, which makes the gel not be formed. The compound of $Ti(OH)_a(OAc)_b$ continues to hydrolyse and $TiO_2 \cdot 2H_2O$ is formed in the end.

Tab.1 Relationship between water volume of hydrolysis and powder quality

Sample	V_w / mL	Gel time / min	d / nm	A / ($m^2 \cdot g^{-1}$)
A	50	Without gel		
B	40	Loosen gel		
C	30	33	85	8.78
D	20	25	70	9.04
E	10	17	25 ~ 60	10.76
F	4	10	100	8.18

Particle size rises with the increase of water volume, specific surface area reaches its maximum and particle size is minimum when water volume is 10 ml. Samples prepared under minimum water volume feels bad, and there are much hard conglobation and soft conglobation.

3.1.2 Selection of solvent

Solvent is important for preparation of sol. —OR group in alcoholate is easy to exchange with —OR' group in solvent, which results in the variation of activity of hydrolysis of alcoholate. If the same alcoholate chooses different solvent, its hydrolysis rate and gel time will follow to be different. In the experiment, three kinds of solvent are selected: alcohol, *iso*-panol and *n*-butyl alcohol. The research result reveals that sol will be formed in all occasions, but gel time was greatly different. Particle size and specific surface area also vary slightly. That is because that polarity, pole moment, and achievement ability to active proton result in different effects on the exchange reaction in sol.

Tab.2 Relationship between solvent and powder quality

Solvent	Gel time / min	d / nm	A / ($m^2 \cdot g^{-1}$)
Alcohol	17	25 ~ 60	10.76
Iso-panol	20	85	10.43
n-butyl alcohol	44	145	8.25

3.1.3 Influence of pH value on gel time

Experiment result reveals that pH value has great effect on gel time. It can be seen that gel time increases with the fall of pH value. When pH value is equal or down to 3, it is not gel body but white precipitate that is obtained when mixing solution is heated in water-bath at 343 K for 8 h. When pH value is 4 ~ 5, transparent gel can be obtained. The solubility and stability in mixing solution of $Ti(OH)_a(OAc)_b$ vary with surrounding temperature. Temperature has great effect on the formation and transformation of sol. The gel time increased with the fall of gel temperature and it is more difficult to form gel under lower temperature.

4 Activity of the $Ni/BaTiO_3$ catalyst

Investigation result of the catalyst is listed in Tab.3, and it can be seen that nanometer $BaTiO_3$ (~ 30 nm) supported Ni based catalyst has high activity in CO_2 reforming of CH_4 and may not deactivate under high reactive temperature. The conversion of both CH_4 and CO_2 increases with the rise of reactive temperature. Whereas many Ni based catalysts such as $Ni/\gamma\text{-}Al_2O_3$ also show high activity, they often deactivate rapidly due to carbon deposition or crystal structure transformation of the support occurring at high reactive temperature.

Tab.3 Catalytic activity of $Ni/BaTiO_3$ catalyst

T/K	x/%		Content of dry product/%			
	CH_4	CO_2	CH_4	CO_2	CO	H_2
973	80.1	82.3	8.0	8.5	43.7	39.8
1073	94.4	93.3	3.5	2.7	48.3	45.5
1123	99.2	98.9	0.4	0.5	50.6	48.5

5 Factors of influencing the activity of $Ni/BaTiO_3$ catalyst

5.1 Influence of calcination temperature

To investigate the effect of calcination temperature on performance of the catalyst, $Ni/BaTiO_3$ catalyst precursors were calcinated at 973 K, 1073 K and 1173 K, respectively and catalyst samples A_1, A_2 and A_3 were attained. Their performances were shown in Tab.4.

Tab.4 Catalytic activity of $Ni/BaTiO_3$ catalyst calcinated at different temperature

Sample	T/K	x/%		Content of dry product/%			
		CH_4	CO_2	CH_4	CO_2	CO	H_2
A_1	973	91.9	92.6	4.2	3.5	50.2	42.1
A_2	1073	94.5	94.8	3.9	3.7	48.2	44.2
A_3	1123	92.7	93.7	4.0	3.8	48.1	44.1

From these data, it can be seen that conversions of CH_4 and CO_2 showed no great variation which the rise of calcination temperature compared to that of the catalyst calcinated at 973 K. With the rise of calcination temperature, particle size of $BaTiO_3$ crystallites may grow a little, specific surface area may decrease and pore structure may be destroyed. Meantime, interaction between NiO and $BaTiO_3$ support may be strengthened, the amount of Ni cation incorporated in crystal lattice may increase, which results in the decrease of reduction degree of the catalyst and the descent of the amount of active nickel species. Based on electric balance theory, more oxygen vacancy will occur, these oxygen vacancy can promote the conversion of CO_2 to CO and hinder the deep oxidation of CO and H_2.

So, as far as chemical effect is only concerned, the rise of calcination temperature will promote the improvement of the activity, but high calcination temperature would reduce specific surface area and further reduce activity of the catalyst from the view point of physical effect. It is by influencing the comprehensive chemical and physical effect that calcination temperature affects catalytic activity of the catalyst. Much low temperature was harmful to chemical effect, much high temperature was harmful to physical effect, which is helpful to chemical effect.

5.2 Influence of reduction temperature

To investigate the influence of reduction temperature on the activity of the catalyst, two $Ni/BaTiO_3$ catalysts B_1 and B_2 were attained at the reduction temperature of 873 K and 973 K respectively. Their performances were shown in Tab.5. It can be seen from Tab.5 that the conversions of CH_4 and CO_2 at low temperature over these catalysts showed no clear difference.

Tab.5 Catalytic activity of $Ni/BaTiO_3$ catalyst reduced at different temperature

Sample	T/K	x/%		Content of dry product/%			
		CH_4	CO_2	CH_4	CO_2	CO	H_2
B_1	873	93.4	94.1	3.1	3.1	47.3	46.5
B_2	973	94.9	94.7	2.9	3.3	48.2	45.6

5.3 Influence of preparation

The catalyst prepared by impregnation method must be calcinated again after impregnating, which causes specific surface area to decrease and destroy pore structure of the catalyst. We prefer sol-gel method to prepare ultrafine catalyst. In the process of preparing ultrafine $BaTiO_3$ precursors, stoichiometric $Ni(CH_3COO)_2$ solution ($w(Ni) = 5.0\%$) was added into the mixed solution before the sol was formed, then the precursors were

calcinated at 1173 K. The activities of the catalyst were demonstrated by the data shown in Tab.6.

Tab.6 Catalytic activity of $Ni/BaTiO_3$ catalyst prepared by sol-gel method

T/K	x/%		Content of dry product/%			
	CH_4	CO_2	CH_4	CO_2	CO	H_2
973	85.8	85.5	5.6	5.9	42.5	46.0
1073	96.2	97.1	2.7	2.3	48.4	46.6
1123	98.9	98.7	0.9	0.7	50.0	48.4

It can be seen from the table that conversions of CH_4 and CO_2 were higher than these over catalyst prepared by impregnation method, which may be resulted from physical and chemical effects. The catalyst prepared by sol-gel method had larger surface area and better pore structure because impregnation and calcination process was avoided.

As far as chemical effect is concerned, sol-gel method was easier to result in the interaction between Ni and $BaTiO_3$, and when the interaction occurs, a certain amount of Ni atoms will be incorporated in the Ti sites of $BaTiO_3$ perovskite structure and $BaTi_{1-x}Ni_xO_{3-\delta}$ perovskite mixed oxide was formed, which resulted in a great amount of oxygen vacancy and higher dispersion of nickel particle. The studies on activity of CH_4 and CO_2 and the reforming mechanism were the basis for transforming and utilizing CH_4 and for the theorical research. In recent years, there are many literatures concerned. But under various catalyst systems, reactive conditions and analysis methods, there are different explanations for the activity process of CH_4 and CO_2 and for the speed controlled step. In the $Ni/BaTiO_3$ system, the reaction process of CO_2 reforming of CH_4 to syngas over $Ni/BaTiO_3$ catalyst may be expressed as following on an assumption:

$$CO_2 + * \rightleftharpoons O^* + CO$$

$$CH_4 + * \longrightarrow CH_3^* \longrightarrow CH_2^* \longrightarrow CH^* \longrightarrow C^*$$

$$CH_x^* + O^* \rightleftharpoons CO + x/2\ H_2 + 2^*$$

During the reaction, CO_2 will dissociate to absorbed oxygen and gas CO, and CH_4 will be activated and dissociated to H_2 and CH_x, the latter will further react with absorbed oxygen to form CO. The existence of the absorbed oxygen speeds up the activation and dissociation of CO_2.

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纳米 $BaTiO_3$ 负载 Ni 基催化剂在 CO_2 重整 CH_4 制合成气反应中催化活性的研究

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摘 要:通过溶胶-凝胶法制备的纳米 $Ni/BaTiO_3$,并把浸渍 Ni 所得的 $Ni/BaTiO_3$ 催化剂用于 CO_2 重整 CH_4 制合成气的反应,研究表明,此两种催化剂对反应均具有高活性。通过研究焙烧温度、还原温度、反应温度和制备方法对催化反应活性的影响,发现焙烧温度、还原温度对反应活性影响不大,但用溶胶-凝胶法制备的 $Ni/BaTiO_3$ 催化剂催化活性比浸渍法制备的要高。

关键词:纳米;$BaTiO_3$;CO_2 重整;合成气
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