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Doping effects of cerium oxide on Ni/Al_2O_3 catalysts for methanation

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Abstract

Ni/Al_2O_3 catalysts doped with cerium oxide were evaluated for activity and metal dispersion to investigate the promoter effects. Enhancement in methanation activity and metal dispersion was observed with all the catalysts on CeO_2 doping. Metal dispersion and activity were found to decrease with increased metal loading. An attempt to optimize the dopant concentration indicated that enhancement in activity is maximum at around 1.5% CeO_2 doping. Temperature programmed reduction and temperature programmed methanation studies reveal that the reducibility is improved and the reaction temperature is lowered on CeO_2 doping. The promoter effect could be attributed to the electronic interactions imparted by the dopant on the active sites under reducing conditions.

Keywords: Cerium oxide; Temperature programmed reduction; Temperature programmed methanation; Ni/Al_2O_3

1. Introduction

Methanation has received considerable attention as an efficient method of producing natural gas substitute which involves the partial oxidation of coal to CO and H_2 followed by the recombination of these gases to form methane. Methanation reaction is also commonly applicable in ammonia plants to remove oxides of carbon from inlet streams which otherwise poison the synthesis catalyst.

A number of reports have been published on the synthesis and characterization of Ni based methanation catalysts. Reduction and reaction are often carried out in ammonia plants in the temperature range 300–350°C for Ni/Al_2O_3 catalysts. Modification of such catalysts are desirable to achieve reduction and reaction at relatively lower temperatures than the conventional design. Incorporation of suitable promoters is believed to improve the metal dispersion and reducibility of the catalyst. It is believed that the rare earth oxide will impart adequate basicity to the methanation catalysts, thus improving the activity. Among the rare earth oxides, CeO_2 and La_2O_3 are commonly used as promoters for hydrogenation catalysts. Effects of La_2O_3 as promoter and CeO_2 as support have been reported earlier [1,2]. In this paper, we report the effect of CeO_2 doping on methanation activity and nickel dispersion. Temperature programmed reduction and temperature programmed methanation of the promoted and unpromoted catalysts are also investigated.

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2. Experimental

2.1. Preparation of promoted catalysts

In the present study, Ni/Al_2O_3 catalysts of UCIL R&D (Ni content varying from 10% to 20%) were doped with varying amounts of CeO_2 (0.5–2.0 wt%) by incipient wetness technique using cerous nitrate solution followed by drying at 120°C and calcination at 450°C.

2.2. Chemical analysis

The nickel percentage in the catalysts was estimated gravimetrically as nickel dimethylglyoximate complex [3]. The dopant (CeO_2) concentrations were determined by volumetric method [3].

2.3. Surface area and pore volume

The surface area of catalysts was determined by BET method using Micromeritics – 2100E Surface Area Analyzer. Pore volume of the catalysts was measured by mercury penetration method on a Carlo Erba – 4000 Model Porosimeter.

2.4. Activity evaluation

Methanation activities of various catalysts were evaluated in a high pressure catalytic reactor (Chemito Series) (cf. Table 1). It consists of a stainless steel reactor of 25 mm diameter and 180 mm length which is mounted vertically inside a furnace. The furnace is provided with adequate temperature control devices and temperature of the reactor could be measured with the help of a thermocouple which can move across the catalyst bed from top to bottom. The reactant gases were purified by passing through a deoxo unit to remove the traces of oxygen and then through a reactor packed with silica gel to remove the traces of moisture. The flow of gases was regulated with appropriate rotameters and system pressure was controlled with needle valves and gauges at the exit. The gas hourly space velocity was measured using a wet gas flow meter.

Table 1
Test conditions for methanation activity evaluation

Loaded catalyst	
Volume and size	8 ml (6 mm diameter spheres)
Reduction	
Temperature	350°C
Duration	16 h
Space velocity (H_2)	2000 h^{-1}
Reaction	
Temperature	270°C
Pressure	1 atm
Space velocity	15 000 h^{-1}
CO:H_2	1:99

The carbon monoxide analyses of the inlet and outlet gas streams were carried out with the help of gas sampling valves connected to the GC (Chemito-3865) with a microcatalytic reactor attachment. The products carbon monoxide and methane were separated over a spherocarb column and then passed through a microcatalytic methanator at 270°C, where CO was converted to methane. Finally, gases were analyzed in a Flame ionization detector (FID).

2.5. Nickel dispersion by oxygen chemisorption

About 0.5 g of the catalyst (9×12 mesh) was reduced in a current of hydrogen using a mircocatalytic reactor which can be heated at a controlled rate with a linear temperature programmer. The chemisorbed hydrogen was purged with helium at an elevated temperature, cooled to ambient temperature and pulses of oxygen were injected for chemisorption measurements. The unadsorbed oxygen in the exit was sensed by thermal conductivity detector. The oxygen pulses were given repeatedly until no adsorption of oxygen takes place as indicated by the peak areas equivalent to the calibration area of the oxygen pulse. Nickel dispersion was calculated assuming a 1:1 stoichiometry for nickel to oxygen (cf. Table 2).

2.6. Temperature programmed reduction (TPR)

About 1 g of the catalyst sample (9×12 mesh) was loaded in a microcatalytic reactor of 6 mm diameter and 300 mm length coupled with a thermal conductivity detector (TCD). About 2 ml glass beads were packed at the top and bottom of the catalyst. The catalyst is preheated in a current of nitrogen at 420°C for 30 min and cooled to room temperature.

Table 2
Test conditions for oxygen chemisorption

Loaded catalyst	
Weight and size	0.5 g, 8×12 mesh
Reduction	
Temperature	400°C
Duration	1 h
Hydrogen flow	30 ml min^{-1}
Purging with He	
Temperature	420°C
Duration/He flow	30 ml min^{-1}
Chemisorption	
Pulse volume	0.4 ml
Temperature	Ambient
He flow	30 ml min^{-1}

Temperature programmed reduction was carried out in the range ambient to 500°C in a stream of nitrogen/hydrogen gas mixture (95:5) flowing at a rate of 40 ml min^{-1}. Using a linear temperature programmer, heating rate was maintained at 10°C min^{-1}. Hydrogen consumption was monitored using TCD.

2.7. Temperature programmed methanation (TPM)

The catalyst sample (1 g, 9×12 mesh) was reduced in a flow of hydrogen (40 ml min^{-1}) at 400°C for 2 h. The reactor was cooled to room temperature and 10 pulses of CO (1 ml each) were injected. Temperature was raised to 500°C at a heating rate of 20°C min^{-1}. Methane formation was monitored by gas chromatograph with a thermal conductivity detector attachment.

3. Results and discussion

The results of physico-chemical analysis and activity of both doped and undoped catalysts are given in Tables 3 and 4, respectively.

Surface area and pore volume of the doped as well as undoped catalysts are in the range 125–135 $m^2 g^{-1}$ and 0.3–0.4 ml g^{-1}, respectively. From the data it is evident that the texture of the catalysts does not appreciably change on doping.

3.1. Activity

Catalysts were evaluated for methanation activity in a continuous flow test reactor. It is observed that the catalyst doped with 1.5 wt% CeO_2 exhibited highest increase in turn over frequency (TOF) as indicated in Fig. 1. Therefore, the optimum concentration is taken as 1.5% CeO_2 for further studies with Ni/Al_2O_3 catalysts containing varying amounts of nickel. From Table 2, it is obvious that the catalyst with lower nickel content showed higher increase in activity. Increase in nickel dispersion and metal surface area

Table 4
Methanation activity, metal dispersion and surface area of Ni/Al_2O_3 catalysts

Ni/Al_2O_3 catalyst	TOF[a]	Ni Dispersion	Metal surface area ($m^2 g^{-1}$)
20% Ni	1.69	6.80	22.02
20% Ni–D	1.87	10.70	38.96
15% Ni	2.066	11.64	30.01
15% Ni–D	2.395	17.20	52.40
10% Ni	2.882	13.80	46.42
10% Ni–D	3.674	21.20	70.74

[a]Turn over frequency (number of molecules of CO reacted/nickel atom/s), D=CeO_2 doped catalyst.

Table 3
Physico-chemical data of the catalysts

Ni/Al_2O_3 Catalyst	Surface area ($m^2 g^{-1}$	Pore volume (ml g^{-1})	CeO_2 (wt%)	Na_2O (wt%)	Cl (wt%)	S (wt%)
20% Ni	125	0.41		0.03	0.03	0.03
15% Ni	135	0.31		0.01	0.01	0.02
10% Ni	133	0.28		0.02	0.01	0.02
20% Ni–D	123	0.38	1.48	0.03	0.03	0.03
15% Ni–D	132	0.30	1.51	0.01	0.01	0.02
10% Ni–D	132	0.30	1.47	0.02	0.01	0.02

D=CeO_2 doped catalyst.

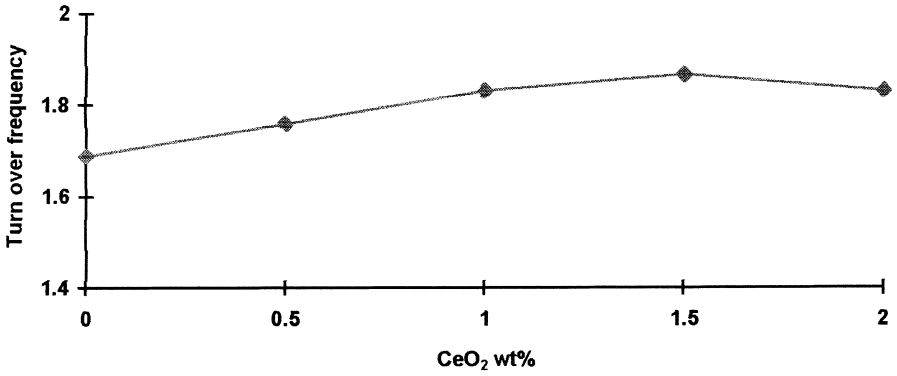

Fig. 1. Variation of turnover frequency with dopant concentration

was also found to be higher at lower nickel loading. It is believed that there is a back donation of electron from metal to antibonding orbitals of chemisorbed CO molecule [4]. The back donation is enhanced by the electron donating promoters, and therefore, results in increased dissociative chemisorption of CO which is the rate determining step of methanation reaction. The enhancement in activity can be explained in terms of hard and soft acid–base concept also [5]. Ce^{3+} sites are hard acid type and have stronger interactions with oxygen atom (strong base) of the chemisorbed CO molecule. These interactions weaken the C–O bond and thus facilitates surface carbon formation which can easily get hydrogenated to form methane.

3.2. Nickel dispersion

Metal dispersion and surface area are calculated [6] from oxygen chemisorption data at room temperature and are given in Table 2. The increase in activity on doping with CeO_2 could be well explained by the observed increase in metal dispersion and surface area. As the metal dispersion increases, the crystallite size decreases, the number of crystallites increases which in turn increases the number of active sites.

Earlier work revealed that the maximum monolayer dispersion of nickel oxide was observed in the rare earth oxide doped catalysts and was found to have smaller crystallite size than that for a sample without promoter. A small amount of rare earth oxide was believed to be dispersed as a monolayer covering the carrier [1].

3.3. Temperature programmed reduction and temperature programmed methanation

The catalyst with 20% Ni loading was selected to study the effect of CeO_2 on reducibility and reaction initiation temperature by temperature programmed reduction and temperature programmed methanation, respectively.

Temperature programmed reduction and temperature programmed methanation curves are given in Figs. 2 and 3, respectively. The extent of reduction in low temperature region was found to be higher for doped catalyst as indicated by an increase in peak area and decrease in peak maxima temperature in TPR curves. The improved reducibility could be attributed to decreased metal–support interactions on doped catalysts. The high temperature peak corresponds to the reduction of fixed nickel oxide in the form of amorphous nickel aluminate [7]. Turlier and co-workers [8] have studied the influence of nature of support on the reducibility and catalytic properties of nickel. Highest nickel reducibility was observed with CeO_2-support.

Temperature programmed methanation (TPM) curves imply that the reaction initiation temperature was found to be lowered for CeO_2 doped catalyst. The low temperature peak corresponds to the adsorption site where the interaction between the active metal phase and its chemical environment are minimum. High temperature methanation peak corresponds to another CO adsorption site where the metal–support interactions are relatively stronger [9].

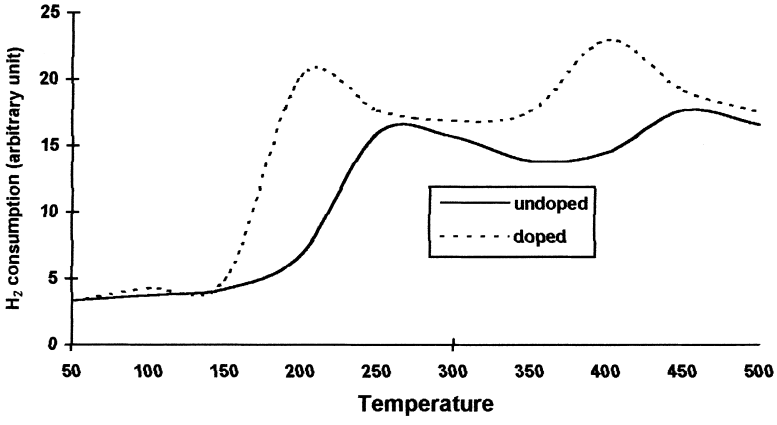

Fig. 2. Temperature programmed reduction.

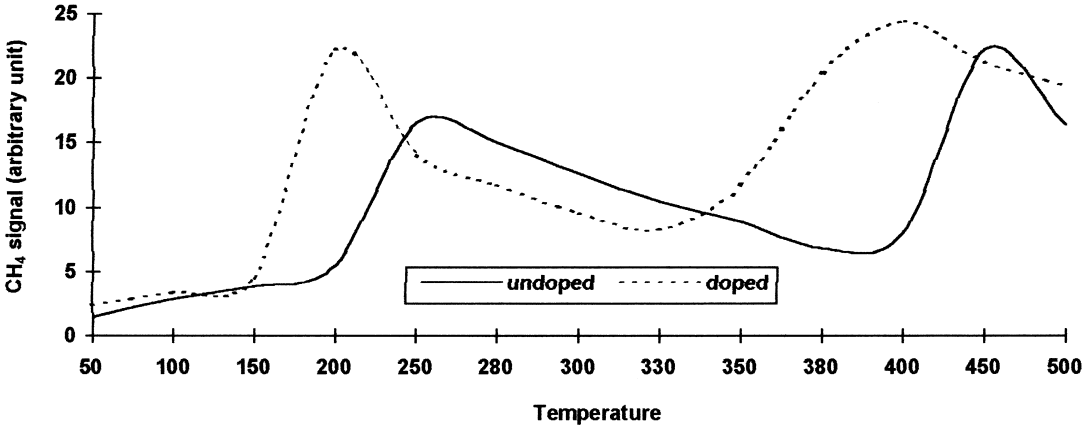

Fig. 3. Temperature programmed methanation.

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