Co-Ni/Al_2O_3 catalysts for CO_2 methanation at atmospheric pressure

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The methanation of carbon dioxide under atmospheric pressure on a Co-Ni/Al_2O_3 catalyst containing 5 wt% of metals prepared by the impregnation method was studied. Temperature of 95% conversion CO_2 for all catalysts been studied falls into range 320-450°C at conditions of SV 100ml/min, 0.1 MPa pressure, and composition of feeding gas mixture CO_2 – 2%, H_2 – 55%, He – 43%. Methane selectivity was sufficiently high – up to 98%.

Introduction

Reducing CO_2 emissions is an extensive and long-term task. In principle, there are three possible strategies with this regard — reduction of the amount of CO_2 produced storage of CO_2, and usage of CO_2. It is impossible to decrease the CO_2 emissions by suppression of the economic activity. Global CO_2 recycling can solve this problem.

As a renewable and environmentally friendly source of carbon, catalytic approaches for CO_2 fixation in the synthesis of chemicals offer the way to mitigate the increasing CO_2 buildup. From the practical point of view, CO_2 is a cheap source of carbon for synthesis of value-added organic compounds like methanol and formaldehyde.

Low pressure process is more preferable for industrial use due to simplicity and safeness of set-up. First-row transition metals are advantageous as the catalyst because of low cost in comparison with platinum metals.

In recent years scientists focus their attention on high-pressure CO_2 hydrogenation process. Fe-Co and Fe-Ni catalytic systems has also been studied carefully, however low-pressure process and Ni-Co catalytic system are still in its research infancy. Therefore, actual work could shed some light on the problem mentioned.

Results and discussion

In the present study Co-Ni catalysts with different Co:Ni ratio were synthesized by impregnation method. Calculated amount of metals was 5 wt.%. The impregnated with metal nitrates solution catalysts were reduced in 50% hydrogen-helium flow at 500 ^oC, SV = 100ml/min for 2 h.

Table 1 shows the composition, the temperature of 95% conversion of CO_2 to CH_4 and CO (100% conversion is unreachable due to thermodynamical restrictions) and selectivity towards CH_4 synthesis at $T^{95\%}$ for the catalysts been studied.

Sample	Composition by	$T^{95\%}$,	S_{CH4},

numbe r	metals (atomic %)		°C	%
	Ni	Co		
1	100	0	340	98
2	75	25	420	96
3	50	50	430	97
4	25	75	370	96
5	20	80	320	98
6	15	85	335	97
7	10	90	360	97
8	0	100	450	95

Table 1. The composition of catalyst's active mass towards Ni and Co; the temperatures of 95% conversion CO_2 to methane; the selectivity towards CO_2 methanation under operating conditions.

Fig. 1 represents the temperature dependences of the conversion CO_2 to methane for samples been studied.

The most active catalysts are the samples #5 and #6 with 20 wt.% and 15 wt.% Co in active mass of catalyst (total Co and Ni – 5wt.% of bulk catalyst mass). The selectivity toward methane of all catalysts at operating temperature is high – about 95-98%. Pure Ni catalyst (Ni-5wt%/Al_2O_3) has moderate activity in CO_2 methanation and high selectivity towards methane in contrast with low activity of pure Co catalyst (Co-5wt%/Al_2O_3).

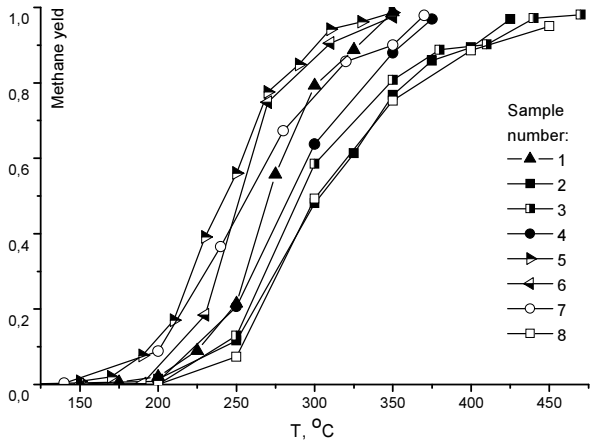

Fig. 1 The temperature dependences of the conversion of CO_2 into CH_4 over studied samples.

Non-linear dependency of the activity of studied catalysts against composition has been observed. To provide a clue to this fact, a methane yield has been plotted against composition of catalysts at temperatures 275°C and 325°C with part of Ni-Co phase diagram (fig.2).

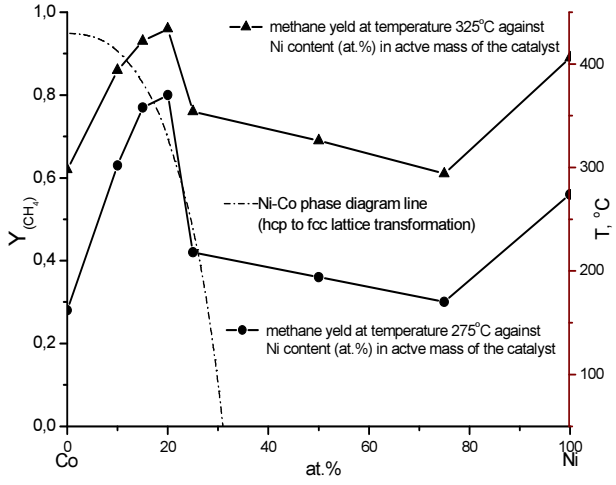

Fig. 2 Methane yield at temperatures temperatures 275°C and 325°C plotted against the catalyst composition; Ni-Co phase diagrame line.

Therefore it could be suggested that low-temperature hcp phase is more active than high-temperature fcc phase. Also increment of Ni

content in active phase leads to enhance performance of the catalyst, provided that the hcp lattice will be saved.

To justify these suggestion SEM photographs of catalyst surface and XRD patterns have been performed.

Due to low metal load there are no structural changes on catalysts surface in comparison with pure support (fig.3).

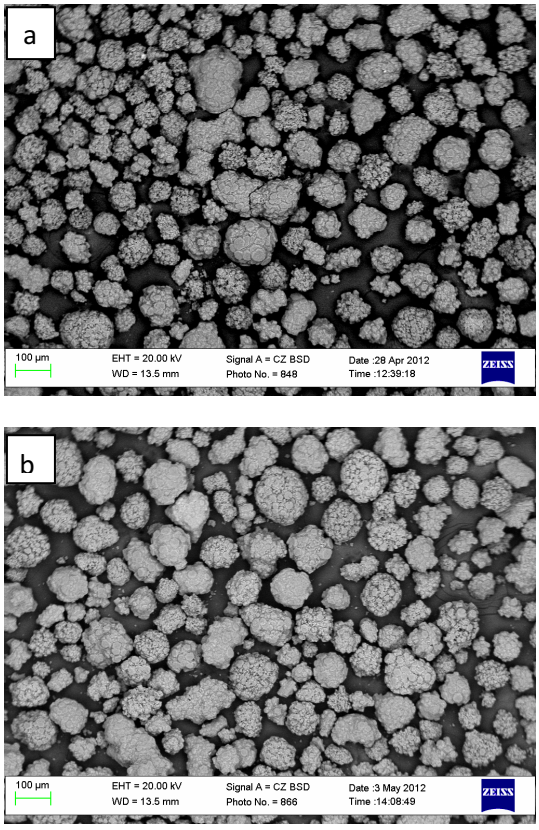

Fig. 3. SEM photographs of pure support (a) and sample #3 (b)

Metal distribution on the catalyst surface is even according to EDS analysis. Therefore XRD pattern (fig. 4) is not informative due to absence of relevant to Ni and Co peaks.

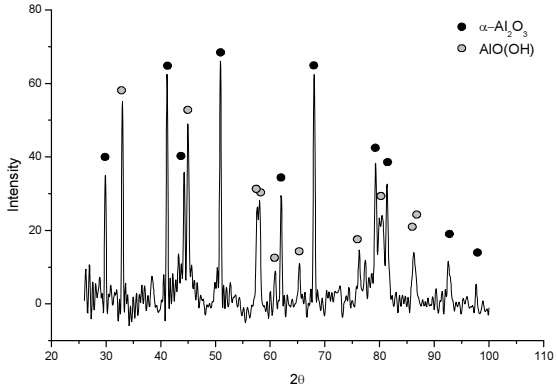

Fig. 4 XRD pattern of sample #3

Assuming mentioned above, influence of hcp-fcc lattice transformation on catalytic activity should be the subject of a separate study.

Surface state of adsorbed particles was studied by thermally programmed desorption for all samples been studied. There are no significant peaks relevant to CH_x species, although weak backgrounds signal of m/z = 15 (CH_3) species is present (fig. 5).

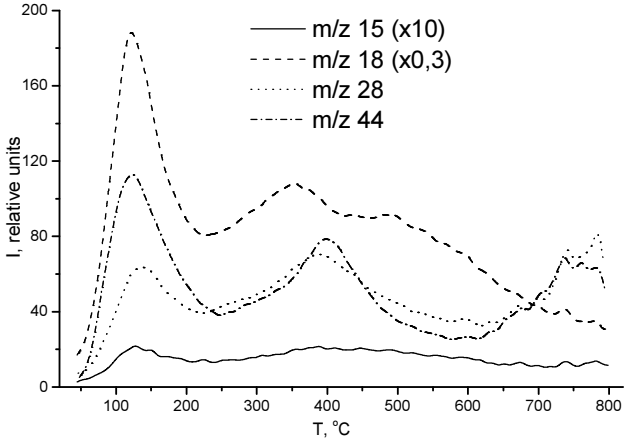

Fig. 5 TPD-MS pattern of sample #6

Conclusions

Gas chromatography of products revealed that the only product of reaction was CH_4, with traces of CO.

The activity for samples with 15-20 % of Co was extremely higher than that for pure Co

or Ni (100 ^{o}C lower conversion temperature). This can be attributed to optimal size of metal clusters and to the phase transition from hexagonal Co (low-temperature, more active) to cubic Co (high-temperature, less active); the temperature of this transition can be shifted in the presence of nickel.

Surface state of adsorbed particles was studied by thermally programmed desorption and allowed to guess that the formation of CH_x was not a rate-limiting step, as no adsorbed CH_x species were detected.

Experimental part

Catalyst Preparation. Catalysts with different Co:Ni ratio were synthesized by impregnation method. Calculated amount of metals was 5 wt.%. The impregnated with metal nitrates solution catalysts were pretreated with 50% H_2/Hein a flow of 50 ml/min at 500 ^{o}C for 2 h prior to the methanation.

The methanation of CO_2 was performed with 1.0 g of catalyst in a 8 mm diameter fixed-bed reactor. The reaction was carried out at 0,1 MPa pressure in the temperature range of 150 to 500^{o}C. The reactants, H_2 and CO_2 mixed with He at a ratio of H_2/He/CO_2 = 43:55:2 were co--fed into the reactor. The gas effluent was analyzed by an online gas chromatograph (Shimadzu GC-2014) equipped with a TCD detector using a molecular sieves 5A packed column for the separation of CO_2, CO, CH_4.

Surface area. Surface areas were measured by low-temperature adsorption of argon. Composition of feeding gas mixture was 90% He, 10% Ar. The gas effluent was analyzed with a TCD detector.

SEM and EDS. Scaning electron microscopy and energy dispersion spectroscopy (Jeol JSM-6490; Zeiss EVO 50 equipped with INCA EDS analyzers) was employed to determine metal distribution on the catalyst surface.

XRD experiments were performed on DRON-4-07 using a filtered Co-Kα X-ray source. Traces were collected from 2θ=20° to 100° with a step size of 0.05.

TPD-MS. The reduced catalyst was exposed under methanation experiment conditions. The catalyst was then cooled to ambient temperature, and than heated linearly in vacuum at 14°C min to 800°C while the effluent stream was analyzed for m/z range from 10 up to 60 by on-line MS MX7304A.

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