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Nickel/Alumina Catalyst for Carbon Oxides Methanation. Flash Calcination of the Catalyst Precursor

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Calcination of the catalyst precursor is an important step in manufacturing of many catalysts. Flash calcination, performed at high temperature for a very short time, may influence advantageously the properties of the catalytic systems, *i.e.* their activity in chemical reactions, surface area, porosity and crushing strength, when compared with the properties resulting from the conventional, low-temperature, long-time calcination. The effect of the flash calcination on the properties of aluminas used as supports and catalysts was described in [1–4]. Unfortunately, there is a lack of data illustrating the effect of flash calcination of the NiO/Al_2O_3 precursor on the catalytic properties of the resultant catalyst, used in industrially important reactions of carbon oxides methanation.

This work compares the activities of the carbon oxides methanation catalysts, obtained from a NiO/Al_2O_3 precursor by the flash calcination with the activity of the catalyst obtained from the same precursor by a fluid-bed calcination performed under industrial conditions. The studies show clearly that the flash calcination leads to high activities in both CO and CO_2 methanation reactions, significantly higher than those after the conventional fluid-bed process, thus, making the novel procedure a valuable alternative for the traditional one.

The precursor of NiO/Al_2O_3 was prepared by the co-precipitation method, followed by drying in a spray drier. The powder obtained (grain size 15 μm) contained 43 wt.% Ni and 5.3 wt.% Al, thus giving the $NiO:Al_2O_3$ wt. ratio of 5.5:1 in the residue after ignition; the loss due to ignition was 35 wt.%.

The flash calcination was performed in a stream of air between 400°C to 1000°C with a residence time lower than 0.1 s. A small stream of the precursor was dosed continuously to the stream of heated air. The temperature differences in the calcination zone did not exceed 5–15°C. After calcination, the material was quickly cooled to room temperature and collected in a filter. The calcination of the precursor in an industrial fluid-bed reactor was run at 400°C–420°C for 4 hours. The calcined precursors were pelleted (6 mm×6 mm) and crashed into small grains (0.1–0.2 mm). Each

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sample was subjected to further studies, *i.e.* the calcination degree and catalytic activities in the carbon oxides methanation reactions were determined. Chemisorption measurements were also performed for selected samples. The calcination degree was determined from the mass balance for the calcined specimen: a mass loss resulting from overheating (calcining) was referred to that resulting from the full conversion of the precursor to oxides, NiO and Al_2O_3.

Catalytic studies were carried out under atmospheric pressure, in the 200°C–270°C temperature range, using a gradientless microreactor [5]. Separate experiments were performed for each of the methanation reactions. Prior to the measurements, the samples were *in situ* reduced with a hydrogen stream during the heating of the reactor to 400°C, and then reduced at 400°C for 4 h in a H_2 stream. Afterwards, the temperature was lowered, and the feeding with the reaction mixture (H_2 + 5000 ppm CO or H_2 + 5000 ppm CO_2) was started. The reaction products concentrations were monitored by gas chromatograph Pu 4500. The kinetic data obtained were used for the calculation of the reaction rates and, subsequently, for the calculation of rate constants k_{CO} and k_{CO2} in empirical equations: $r_{CO} = k_{CO} \cdot C_{CO}^{a}$, $r_{CO2} = k_{CO2} \cdot C_{CO_2}^{b}$ [6], that characterize the catalyst activities. Chemisorption experiments were performed in a separate setup [5,7,8]. Both hydrogen and carbon monoxide uptakes were measured. The sample was prereduced in a hydrogen stream of 1 cm^3/s at 500°C for 2.5 h, followed by flushing with a helium stream of 0.5 cm^3/s for 0.5 h. Adsorption of hydrogen was performed at atmospheric pressure in three stages: 1 – initially at 150°C for 0.25 h, 2 – at gradually decreasing temperature from the initial value to 20°C and 3 – at constant temperature of 20°C for 0.25 h. Subsequently, the sample was flushed with argon. Then the temperature was linearly increased and the hydrogen concentration in the outlet Ar stream was monitored. Consequently, the amount of hydrogen preadsorbed on the Ni surface could be determined. The CO chemisorption measurements were carried out by a pulse method, dosing 4.5 μmol CO portions into a stream of helium at 20°C. Both Ni dispersion (D) and the mean size of the nickel crystallites (d) were determined from the obtained data, the latter being calculated from the generalized formulas proposed in [9]. As expected, the conversion of the NiO/Al_2O_3 precursor to oxide species-achieved in the flash calcination, proved to be strongly dependent on temperature. The calcination degree was varied from 0.4 at 400°C to about 0.9 at 1000°C. Over the range of 600°C–1000°C, the relationship was found to be roughly linear. The calcination degree for the conventionally pretreated material (fluid-bed process) was equal to 0.9. The catalytic activity studies performed with samples calcined according to the "flash procedure" revealed the rates of CO and CO_2 methanation to be highest when the precursor was calcined between 500°C–650°C. Fig. 1 gives the comparison between the most active catalyst obtained by the flash calcination (sample A) and that calcined conventionally (sample B). The rate constants of the carbon monoxide (k_{CO}) and carbon dioxide (k_{CO_2}) methanation reactions for the A catalyst are higher by 40% and 25%, respectively, than those for sample B, thus showing the former procedure to be more advantageous. The difference in the activities observed (see Fig. 1) might be attributed to the difference in the nickel disper-

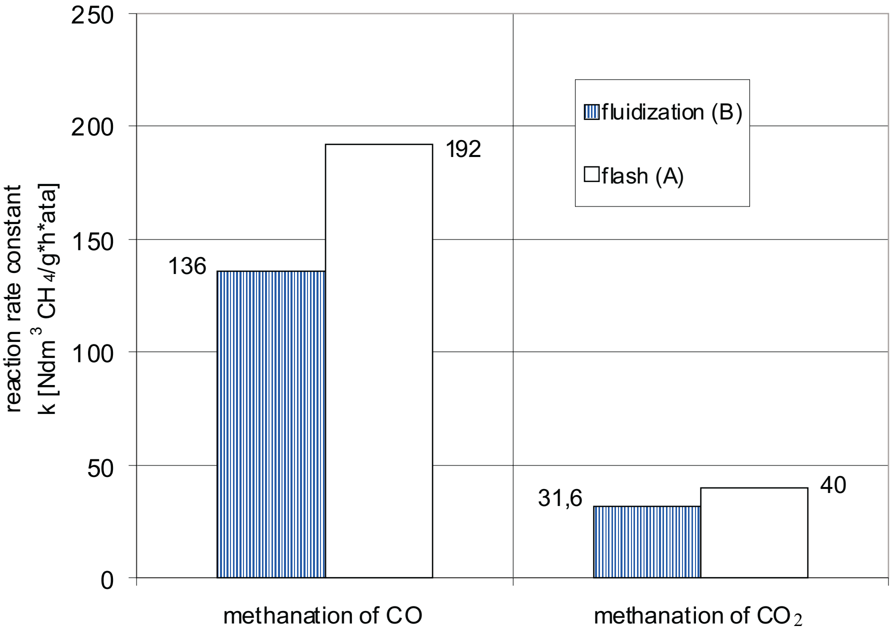

Figure 1. Reaction rate constants at 240°C for the most active catalyst obtained by the flash calcination (sample A) and for the catalyst obtained by fluid-bed calcination (sample B).

sions only: both hydrogen chemisorption and that of carbon monoxide show the mean Ni crystallite size in sample A to be slightly lower than that in sample B (Table 1). Consequently, the active surface area of the A specimen was slightly larger, thus resulting in higher reaction rates based on the catalyst mass and, correspondingly, in higher rate constants (k_{CO}, k_{CO_2}). However, the ratios of k-constants, (1.4:1 for CO methanation and 1.25:1 for CO_2 methanation) are considerably higher than the ratio of corresponding dispersions (about 1.1:1 both for CO and H_2 adsorptions).

Table 1. Nickel dispersion (D) and nickel crystallites mean size (d), as determined by the H_2 and CO chemisorption methods.

Calcination procedure	H_2 chemisorption		CO chemisorption	
	D [%]	d [nm]	D [%]	d [nm]
Flash calcination (A)	18.0	6.9	20.0	6.1
Fluid-bed calcination (B)	16.2	7.7	19.3	6.7

The following adsorption stoichiometry: $H/Ni_s = 1$, $CO/Ni_s = 0.5$, and a mean diameter of nickel atoms = 2.48 Å were assumed.

Possibly, the calcination procedure influences not only the Ni dispersion (active phase area) but, additionally, it influences the catalytic properties of the Ni surfaces in the reactions considered. Further studies that are in progress should give a more decisive answer whether this is the case or not.

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