О. Конопліцька, канд. хім. наук
КНУ імені Тараса Шевченка, Київ,
Г. Зайцева, канд. хім. наук
Національний медичний університет імені О.О. Богомольця, Київ,
Н. Кобилінська, канд. хім. наук
КНУ імені Тараса Шевченка, Київ,
О. Кроніковський, доц.
Національний університет харчових технологій, Київ,
В. Зайцев, д-р хім. наук
КНУ імені Тараса Шевченка, Київ

ВПЛИВ МЕТОДУ СИНТЕЗА НА ПРОТОЛІТИЧНІ ТА АДСОРБЦІЙНІ ВЛАСТИВОСТІ КРЕМНЕЗЕМУ, МОДИФІКОВАНОГО ПРОПІЛТІОЕТИЛАМІНОМ

В роботі були отримані адсорбенти із ковалентно іммобілізованими N,S-органічними фрагментами: по реакції силанізаціїї (SiO_2–$SN_{(гом)}$) та методом збирання на поверхні(SiO_2–$SN_{(гет)}$).Дані адсорбенти досліджені методами ІЧ-спектроскопії та електронної спектроскопії дифузного відбиття. Методами pH-метричного та кондуктометричного титрування визначені концентрації закріплених груп пропілтіоетиламіну. Встановлено, що дані адсорбенти не містять груп кислотної природи та стійкі при зберіганні. Вивчені протолітичні та адсорбційні властивості адсорбентів. Показано, що адсорбційні властивості адсорбенту отриманого методом одностадійного модифікування значно вищі, ніж адсорбенту, отриманого двохстадійно.

Ключові слова: N,S-вмісні кремнеземи, кондуктометрія, pH-метрія, адсорбція, срібло, паладій.

O.Konoplitska, PhD
Taras Shevchenko National University of Kyiv, Kyiv,
G.Zaitseva, PhD
Bogomolets National Medical University, Kyiv,
N.Kobylinskaya, PhD
Taras Shevchenko National University of Kyiv, Kyiv,
O. Kronikovskyi, PhD
National University of Food Technologies, Kyiv,
V. Zaitsev, Professor,
Taras Shevchenko National University of Kyiv, Kyiv

EFFECT OF SYNTHESIS CONDITIONS ON THE PROTOLITIC AND ADSORPTION PROPERTIES OF SILICA MODIFIED WITH PROPYLTHIOETHYLEAMINE

Silica chemically modified by propylthioethyleamine was synthesized, their protolytic properties and application as an adsorbent for the removal of ions Pd(II) has been investigated. This ligand was grafted to the silica surface with two different routes: (1) as one-step reaction of silanization(homogeneous procedure, SiO_2-$SN_{(homo)}$); (2) as multistep chemical modification of silica, usingmercaptopropyltriethoxysilane, followed by aminoagent to convert the grafted surface SH-group to aminomoieties (heterogeneous procedure,SiO_2–$SN_{(het)}$). The new solids were characterized by FTIR and diffuse reflectanceUV-visspectroscopy. It was shown that a combination of pH-metric and conductometricmethods can generally picture of the grafted groups presence in the surface of SiO_2.The amount of propylthioethyleaminegroups grafted on the SiO_2-$SN_{(homo)}$ and SiO_2–$SN_{(het)}$is found 1.05 mmol/g and 0.61 mmol/g, respectively. In addition these adsorbentsare not containedfree SH-groups and chemically stable a longperiod oftime.TheN,S-containing silica sampleprepared by homogeneous procedure had 2 times higher adsorption capacity to ions Pd(II) than the sample by heterogeneous procedure.The results suggest that the prepared SiO_2-$SN_{(homo)}$adsorbent is potentially useful material for high effectively adsorption of metal ions from aqueous solution.

Key words: N,S-containing silicas, conductometric titration, pH-metric titration, adsorption, silver, palladium.

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K. Nifantiev, PhD student,
O. Byeda, PhD, E. Ischenko, Professor,
A. Mischanchuk, Engineer
Taras Shevchenko National University of Kyiv, Kyiv

THE METHANATION OF CO_2 OVER CO-NI/AL_2O_3 CATALYSTS AT ATMOSPHERIC PRESSURE

The methanation of carbon dioxide under atmospheric pressure over 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 examined catalysts falls into range 320–450°C at conditions of SV 100 ml/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%.

Key words: methanation, carbon dioxide, supported catalysts, cobalt-nickel catalysts.

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.

Catalysts with different Co:Ni ratio were synthesized by impregnation method. Calculated amount of metals was 5 wt.%. Catalysts impregnated with metal nitrates solution were pretreated with 50% H_2/He in a flow of 50 ml/min at 500°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 = 55:43:2 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. The specific surface area was 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. Scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) (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. Surface state of adsorbed particles was studied by thermally programmed desorption mass-spectrometry (TPD MS) for all samples been studied. 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 quadrupole mass spectrometer MX7304A.

Table 1 shows the composition, the temperature of 95% conversion of CO_2 to CH_4 and CO ($T^{95\%}$) (100% conversion is unreachable due to thermodynamical restrictions) and selectivity (S_{CH_4}) towards CH_4 synthesis at $T^{95\%}$ for the catalysts been studied. Fig. 1 represents the temperature dependences of the conversion CO_2 to methane for samples containing Ni only, Co only and the most active sample (20% Ni). The most active catalysts are the samples № 5 with 20 wt.% Co (S_{CH_4} = 98% at 320°C) and № 6 with 15 wt.% Co (S_{CH_4} = 97% at 335°C) 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 sample № 1 (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 samples № 8 (Co-5wt%/Al_2O_3).

Table

The composition of catalyst active mass towards Ni and Co; the temperatures of 95% conversion CO_2 to methane ($T^{95\%}$); the selectivity towards CO_2 methanation under operating conditions (S_{CH_4})

Sample number	Composition by metals (at. %)		$T^{95\%}$, °C	S_{CH_4} %
	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

The specific surface area of the studied catalysts lies within the range of 35–40 m^2/g.

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 along with part of Ni-Co phase diagram (Fig. 2). 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). Dimensions of the particles of support are *ca.* 100 μm. 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. Only reflexes of two phases: Al_2O_3 and AlO(OH) – are present.

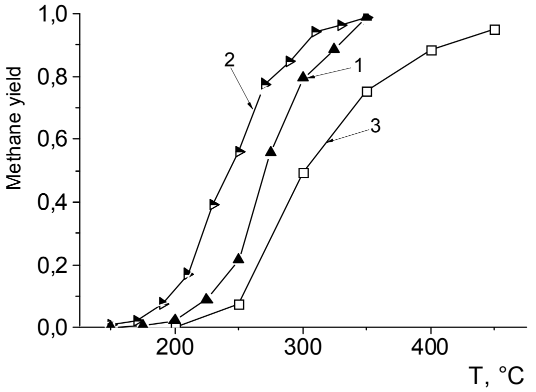


Fig. 1. The temperature dependences of the conversion of CO_2 into CH_4 over studied samples:
1– the sample № 1 (100% Ni); 2 – the sample № 5 (20 % Ni 80% Co); 3 – the sample № 8 (100% Co)

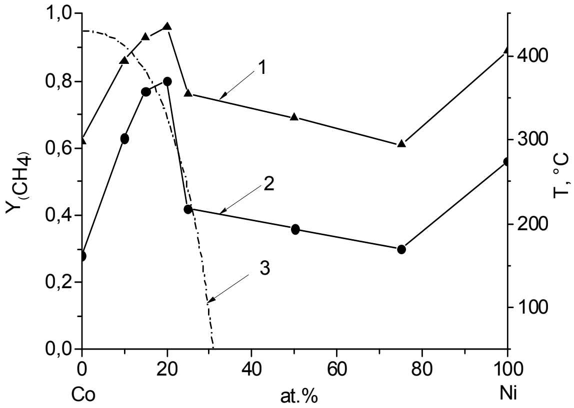
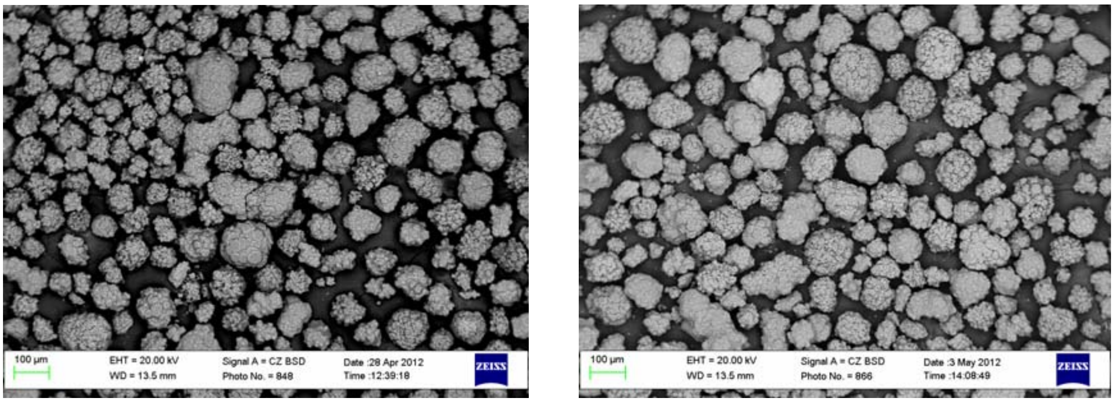


Fig. 2. Methane yield at temperatures 275°C and 325°C plotted against the catalyst composition; Ni-Co phase diagrame line.
1 – methane yeld at temperature 325°C against Ni content (at.%) in active mass of the catalyst;
2 – methane yeld at temperature 275°C against Ni content (at.%) in active mass of the catalyst; 3 – Ni-Co phase diagram line hcp to fcc lattice transformation

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 TPD MS 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). Desorption of water, CO and CO_2 is detected. The low-temperature desorption peaks (100–200°C) refer to physically adsorbed molecules, and high-temperature desorption peak of CO and CO_2 at approximately 400°C refers to the dissociatively adsorbed form of CO_2, presumably the one that is utilized in the catalyzed process. Thermally programmed desorption results allowed to suggest that the formation of CH_x surface carbon species was not a rate-limiting step, due to absence of relevant CH_x species desorption peaks.

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°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.



a b

Fig. 3. SEM photographs of pure support (a) and sample № 3 (b)

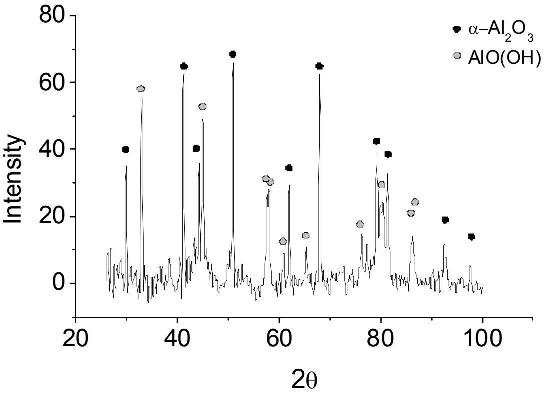


Fig. 4. XRD pattern of sample № 3

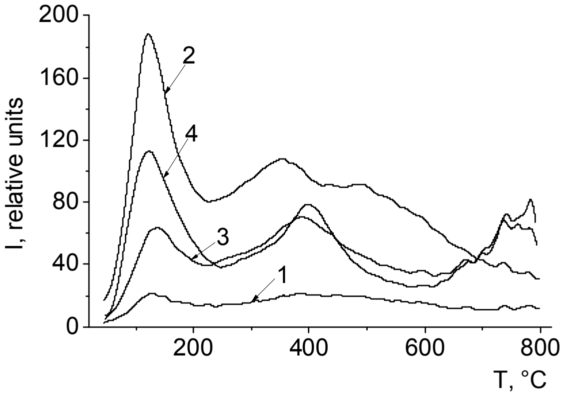


Fig. 5. TPD-MS pattern of sample № 6:
1 – m/z 15 (x10); 2 – m/z 18 (x0.3); 3 – m/z 28; 4 – m/z 44

Conclusions. The present study shows that mixed Ni-Co supported catalysts with 15–20 % Ni show higher activity and selectivity towards CO_2 methanation than single-metal Ni or Co catalysts.

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**К. Ніфантьєв, аспірант, О. Бєда, канд. хім. наук,
О. Іщенко, д-р хім. наук, О. Місчанчук, інженер,
КНУ імені Тараса Шевченка, Київ**

МЕТАНУВАННЯ CO_2 НА Co-Ni/Al_2O_3 КАТАЛІЗАТОРАХ ПРИ АТМОСФЕРНОМУ ТИСКУ

Досліджено метанування діоксиду вуглецю за атмосферного тиску на Ni-Co/Al_2O_3 каталізаторах, що містять 5 % металу, приготованих методом просочування з наступним відновленням. Температура 95 %-ї конверсії CO_2 для всіх досліджених каталізаторів знаходиться в межах 320–450°С за наступних умов: об'ємна швидкість газового потоку – 100 мл/хв., тиск – 0,1 МПа, склад реакційної суміші – 2 % CO_2, 55 % H_2, 43 % He. Селективність за метаном складає близько 98%.

Ключові слова: метанування, діоксид вуглецю, нанесені каталізатори, кобальт-нікелеві каталізатори.

**К. Нифантьев, аспирант, А. Беда, канд. хим. наук,
Е. Ищенко, д-р хим. наук, А. Мисчанчук инженер,
КНУ имени Тараса Шевченко, Киев**

МЕТАНИРОВАНИЕ CO_2 НА Co-Ni/Al_2O_3 КАТАЛИЗАТОРАХ ПРИ АТМОСФЕРНОМ ДАВЛЕНИИ

Исследован процесс метанирования диоксида углерода при атмосферном давлении на Ni-Co/Al_2O_3 катализаторах с содержанием металла 5 %, которые были получены методом пропитки с последующим восстановлением. Температуры 95%-ой конверсии для всех исследованных катализаторов находятся в интервале 320–450°С при следующих условиях: объемная скорость газового потока – 100 мл/мин., давление – 0,1 МПа, состав реакционной смеси – 2% CO_2, 55% H_2, 43% He. Селективность по метану составляет 98%.

Ключевые слова: метанирование, диоксид углерода, нанесенные катализаторы, кобальт-никелевые катализаторы.