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The impact of the porous structure on the efficiency of PdIn methanol synthesis catalysts

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Experimental

Catalyst preparation

For the preparation of intermetallic PdIn catalysts, as well as monometallic Pd and In reference samples, air precalcined at a temperature of 550°C commercial SiO_2 (S_{BET}=56 m^2/g, 120 m^2/g and 290 m^2/g, (Khromlab, Russia) were used as a supports. The catalysts were synthesized by the method of incipient wetness impregnation of the support with solutions of $Pd(NO_3)_2$ (Alfa Aesar, 14.86% Pd, Germany) and $In(NO_3)_2$ (Fluka, Germany). The atomic ratios of the metals were optimized for a stoichiometric ratio of 1:1. After impregnation, the samples were dried at room temperature and calcined in a stream of air for 4 hours at a temperature of 550°C. Finally, the calcined catalysts were reduced in a stream of 5% H_2/Ar (Linde Gas Rus, Balashikha, Russia) at 550°C for 3 hours and cooled to 200°C in a stream of 5% H_2/Ar. The catalysts were then cooled to room temperature in a flow of N_2 (Linde Gas Rus, Balashikha, Russia). The composition and designations of the samples used in this work are given in Table 1.

An additional $Cu/ZnO/Al_2O_3$ sample was also synthesized using the co-precipitation method, the composition of which corresponds to the commercial catalyst for methanol synthesis (molar ratio Cu: Zn: Al = 6: 3: 1). The co-precipitation was carried out at a temperature of 60°C with stirring and the pH of the solution was measured by simultaneously dropping the salts $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ into distilled water, as well as sodium carbonate used as a precipitant. The resulting mixture was kept under stirring at a given temperature for 2 hours, after which the precipitate was filtered, washed, dried at 120°C for 12 hours and calcined in an air stream at 350°C for 3 hours.

Before the catalytic experiment, the resulting powder was shaped into granules of 0.3–0.5 mm.

DRIFT-CO

The method of IR spectroscopy of adsorbed CO was used to study the surface structure of catalyst samples. The experiment was carried out using a Bruker Tensor 27 DRIFT spectrometer (Leipzig, Germany) equipped with a Harrick Diffuse Reflectance Kit (Pleasantville, New York, USA) and a liquid nitrogen-cooled detector. A sample of the crushed catalyst (0.02 g) was placed in the cell of the attachment, purged with a stream of pure Ar, and reduced in situ at 500°C in a stream of 5 vol.%H_2/Ar (30 ml/min, Linde Gas Rus, purity 6.0) for 1 hour. After this, the sample was subjected to high-temperature (350°C) oxidative treatment in a flow of 20% O_2/N_2 (Linde Gas Rus, 30 ml/min) for 1 hour, followed by in situ reduction. After this, the cell was cooled to 150°C in a flow of 5 vol.%H_2/Ar and to 50°C in a flow of Ar. CO adsorption spectra were recorded in a flow of 0.5 vol.% CO/N_2 at 50°C after a 10-minute hold. The spectrum obtained in an Ar atmosphere before CO chemisorption was used as a background. Processing of the received data was carried out using the Opus 7.2.139.1294.

Low temperature nitrogen adsorption

The textural characteristics of the samples were studied using the method of low-temperature nitrogen adsorption at 77 K on an Autosorb iQ gas sorption analyzer (Quantachrome inst., USA). Previously, the samples were subjected to degassing in a vacuum environment at 50 Torr for 3 hours at a temperature of 300°C. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The total pore volume was calculated from the amount of nitrogen gas adsorbed at a relative pressure close to unity. The average pore size was determined from the ratio of the pore volume and their surface area. The porous structure of the samples was assessed by the DeBoer method (t-plot). Pore size distribution was calculated using the BJH method (Barrett-Joyner-Halenda).

XRD

The phase composition of the synthesized catalysts was studied by X-ray diffraction analysis (XRD). Diffraction patterns of the catalysts and starting supports were obtained on a DRON-4 diffractometer (NPP Burevestnik, Russia) using Cu-Kα radiation (Ni filter, wavelength $\lambda = 1.54059$ nm). The samples were studied in the angle range of 15 – 75 ° (2θ) with a step of 0.02° (2θ) and holding at a point for 2 seconds. Crystallographic data were calculated using the Rietan-FT software, which uses the Rietveld method. The average size of the resulting nanoparticles was calculated using the Scherrer equation (1):

$$D = \frac{0{,}9\lambda}{\beta \cos\theta}, \quad (1)$$

where 0.9 is the shape factor (Scherrer constant), λ is the x-ray wavelength, β is the width of the diffraction reflection at half maximum, θ is the diffraction angle.

Evaluation of catalytic performance

The catalytic characteristics of the synthesized samples were assessed in the process of hydrogenation of carbon dioxide into methanol on a commercial setup UlKat-1M (Russia), equipped with a flow reactor, a three-zone furnace, thermomass gas flow regulators, and a system for setting and regulating pressure. Experimental conditions: temperature range from 220 to 310 °C, pressure in the reactor 35 bar, gas hourly space velocity (GHSV) 3000 h^{-1}, ratio of initial reagents H_2:CO_2 = 3 : 1. The change in temperature of the catalyst layer was controlled using a chromel-alumel thermocouple. A sample of the catalyst (1 g) was placed in the reactor between layers of quartz wool. For the activation of the sample it was heated to 150°C in a flow of N_2 (high purity, 100 ml/min), after which the temperature was increased to 300°C in a flow of 3% H_2/N_2 (150 ml/min) at a rate of 3°C/min and kept for 40 minutes.

For the $Cu/Zn/Al_2O_3$ reference sample, the holding time was 2 hours. Upon completion of the activation stage, residual nitrogen was removed from the reactor, then in the flow of the reaction mixture H_2:CO_2 = 3:1 (flow 50 ml/min), the pressure in the reactor was increased to 35 bar, upon reaching which the catalyst was stabilized for 3 hours under operating conditions (P=35 bar, T=220 – 310°C, 3000 h^{-1}).

The reaction mixture composition changes were monitored using a Kristall 5000 gas chromatograph (Khromatek, Russia), equipped with a 2-meter-long Porapak Q 80/100 packed chromatographic column, a thermal conductivity detector, and a six-way valve for automatic gas sampling. Hydrogen was used as a carrier gas. The values of CO_2 conversion (X_{CO2}), selectivity (S_{MeOH}) and methanol productivity (STY) were calculated based on the results of three consecutive analyzes at each temperature point according to equations 2 – 4. In order to conduct a more correct comparative study, the methanol productivity value was calculated based on the total content of the metal phase both in the case of intermetallic supported PdIn catalysts (g_{MeOH}/g_{Pd+In}) and in the case of a bulk $Cu/ZnO/Al_2O_3$ reference sample ($g_{MeOH}/g_{Cu+Zn+Al}$).

At the end of the experiment, the pressure and temperature in the reactor were gradually reduced to normal conditions, after which the catalyst was passivated in a stream of air.

$$X_{CO_2} = \frac{a_{CO} + a_{MeOH}}{a_{CO_2} + a_{MeOH} + a_{CO}} \times 100\% \qquad (2)$$

$$S_{MeOH} = \frac{a_{MeOH}}{a_{MeOH} + a_{CO}} \times 100\% \qquad (3)$$

$$STY = \frac{a_{MeOH} \times M_{MeOH} \times (F_{H_2}^0 + F_{CO_2}^0) \times 60 \times 1000}{V_m^0 \times m_{Me}} \qquad (4)$$

where a_{CO}, a_{CO_2}, a_{MeOH} – are the mole fractions of the components; $F_{H_2}^0$ и $F_{CO_2}^0$ – volumetric flows of initial reagents (nml/min); $n_{CO_2}^0$ $n_{CO_2}^i$ - CO2 molar flows; m_{cat} – catalyst weight (g); V_m^0 - molar volume of gas under normal conditions (22.413 l/mol).

Results and discussion

Table S1. Composition and samples porous structure

Catalyst	ω_{Pd}, wt. %[a]	ω_{In}, wt. %[a]	S_{BET}, m^2/g	V_{total}, cm^2/g	D^{Av}_{pore}, nm	D_{av}, nm[b]
SiO_2 (120)	-	-	101	0.94	3.68	-
SiO_2 (290)	-	-	287	0.35	4.88	-
Pd/SiO_2 (120)	2.5	-	89	0.79	3.51	6.4
In/SiO_2 (120)	-	5.4	-	-	-	-
Pd_1In_1/SiO_2 (56)	2.5	2.7	47	0.24	12.6	6.1
Pd_1In_1/SiO_2 (120)	2.5	2.7	93	0.89	38.1	5.8
Pd_1In_1/SiO_2 (290)	2.5	2.7	239	0.27	4.8	4.4
$Cu/ZnO/Al_2O_3$	-	-	76	0.44	2.31	-

[a] Amounted by ICP-MC.

[b] Average size of nanoparticles calculated using the Scherrer equation.