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Hydrogenation of heptanal over heterogeneous catalysts

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Among the series of heterogeneous catalysts tested in hydrogenation of heptanal, Ni–Cr–O composition possessed excellent stability and showed the best performance with the heptanol selectivity approaching 100%.

Hydrogenation of aldehydes, which are the products of olefin hydroformylation, is one of the important industrial processes for producing a diversity of aliphatic alcohols. There is a great number of relevant publications, but only a few of them describing the hydrogenation of individual aldehydes demonstrate the aldehyde conversion over 95% and the selectivity to the alcohol over 98%. Raney nickel[1–3] exhibits good activity at temperatures about 20 °C. Nickel supported on alumina, silica and kieselguhr is also used for this purpose. Additives of 4–12% MgO and 1–5% Na_2O keep the selectivity of the nickel catalyst at temperatures above 100 °C[2] (~100% aldehyde conversion and selectivity >98%), however, these figures were valid for gas-phase hydrogenation of butanal. The $Ni/SiO_2–Al_2O_3$ catalyst modified with Mn, Cr, V, or Cu was tested in the hydrogenation of C_{10} aldehydes as well as unsaturated 2-ethyl-2-hexenal.[3] In the latter case, the selectivity was as high as 99.7%; however, complete conversion of the aldehyde was attained only at temperatures over 120 °C, and the space velocity had to be decreased to 0.2 h^{-1}.

The catalysts based on the Ni/kieselguhr system were applied for the manufacture of C_9 alcohol in the hydrogenation of C_9 aldehyde in the batch reactor.[4] When CaO, Ce_2O_3 or MgO was added as a promoter to the Ni/kieselguhr catalyst, the BET and Ni surface areas were increased. The Ni–MgO/kieselguhr catalyst showed the highest activity, the highest yield of C_9 alcohol was 91.5 wt% at 130 °C, 400 psi and WHSV = 3 h^{-1}. Nickel–chromium catalysts[5–8] with ~50% of nickel were found to be the best catalysts for hydrogenation of the products of olefin hydroformylation, in particular, of lower aldehydes (C_3–C_5) since they are highly selective and can be used in a wide range of pressures at moderate temperatures. However, in their cases side hydrogenolysis occurs giving water, carbon monoxide, and other hydrocarbons. Aldehyde condensation followed by the formation of dimeric and trimeric products (ethers, hydroxy aldehydes, acetals, *etc.*) can be another side process. Chromite catalysts,[9,10] like copper–chromium, zinc–chromium, and mixed Zn–Cu–Cr catalysts are suitable for industrial hydrogenation of oxo-synthesis products. They provide alcohol yields close to theoretical values; however, the operating temperature exceeds 150 °C, and the pressure should be as high as 20–30 MPa. Noble metal-based catalysts, in particular, Pt/Al_2O_3 (0.15–0.55% Pt)[11] operating at 160–250 °C and 30 MPa provide hydrogenation of C_6–C_9 aldehydes with 95% selectivity. In recent years, the modified platinum catalysts attracted attention in connection with the selective hydrogenation of α,β-enals.[12–15] Of particular interest is the Pt–Fe–C system, when addition of 20% Fe increased the rate of the cinnamaldehyde carbonyl group hydrogenation by a factor of ~100. However, to sum up these data, none of the described catalysts is capable of providing the higher aldehyde C_{6+} conversion and selectivity to alcohol formation >95% at temperatures below 100 °C at the liquid space velocity higher than 1 h^{-1}.

The aim of our work was to develop the catalyst for the hydrogenation of heptanal operating under mild conditions and providing high selectivity and producibility towards heptanol. Fifteen catalyst samples, both commercial and laboratory ones, were examined in our experiments (Tables 1 and 2).[†] The catalysts were tested both under atmospheric[‡] and elevated[§] pressures.

[†] The 1% Ir/SiO_2 catalyst was prepared by impregnation of KSK silica gel (Ryazan refinery production, 450 $m^2 g^{-1}$, particle size of 2–3 mm) with an aqueous solution of $[Ir(NH_3)_5Cl]Cl_2$. Prior to supporting, silica gel was calcined in an air flow at 500 °C for 2 h. The supported ammonia complex was decomposed in an air flow in a tube reactor according to the following procedure: initial heating from 20 °C to 350 °C at the rate of 5 K min^{-1}; a 30-min exposure at 350 °C; further heating to 450 °C at the rate of 1.5 K min^{-1}; and an exposure at this temperature for 5 h. After cooling to room temperature, the catalyst was treated with hydrogen initially at 300 °C for 40 min and then at 400 °C for 2 h.

The 1% Ir/C catalyst was prepared using a special carbon-based Sibunit 1 support (product of Institute of Catalysis, Russia, 350 $m^2 g^{-1}$, particle size of 0.5–2 mm). Prior to supporting, Sibunit 1 was heated at 70 °C in a vacuum for 120 min and was then impregnated with an aqueous solution of $[Ir(NH_3)_5Cl]Cl_2$. Further treatment of the catalyst was performed as above.

1% Ir/Al_2O_3 was prepared by impregnating γ-Al_2O_3 (product of Ryazan refinery, 170 $m^2 g^{-1}$, particle size of 2–3 mm) with an aqueous solution of $[Ir(NH_3)_5Cl]Cl_2$. Alumina was preliminarily dried at 200 °C for 2 h. To suppress its acid sites, it was additionally treated with hexamethyldisilazane followed by heating in a vacuum (100 °C, 12 h). The complex was decomposed and the catalyst was reduced in a manner similar to that used for the 1% Ir/SiO_2.

1% Ru/Al_2O_3 and 1% Ru/C (Sibunit 1) were prepared by impregnating γ-Al_2O_3 or Sibunit 1 with an aqueous solution of $[Ru(NH_3)_6]Cl_2$. Preparation of the support and subsequent treatment of the catalyst were analogous to those for the 1% Ir/SiO_2.

(5% Pt, 0.4% Fe)/C (Sibunit 1) was prepared by incipient wetness impregnation with alcoholic H_2PtCl_6 and $FeCl_2$ solutions containing Pt and Fe in required amounts. The catalyst was dried at room temperature and then reduced in an H_2 flow at 200–220 °C for 1 h and at 400 °C for 1 h.

(8.4% Ni, 1.2% Mg)/Al_2O_3 was prepared by triple incipient wetness impregnation of the support with a magnesium oxalate 0.02 N solution in oxalic acid with intermediate drying at 110–130 °C for 2 h followed by single impregnation with a nickel chloride solution. The reduction was performed in an H_2 flow at 320–350 °C for 1 h.

(9% Ni, 2.4% Mg)/Al_2O_3 was prepared by hot incipient wetness impregnation of the support with an oxalic acid solution followed by drying and repeated impregnation with a Mg and Ni chloride solution. The reduction was performed in an H_2 flow (35 ml min^{-1}) at 320–350 °C for 1 h.

Ni–Cr–O (52% Ni, 20% Cr) was prepared from nickel and chromium nitrate solution by co-precipitation of mixed nickel–chromium hydroxide carbonate with a sodium carbonate solution followed by drying, calcination, reduction, and passivation by a treatment of the catalyst by the argon–oxygen (1%) gas mixture at room temperature for 1 h.

Table 1 Testing of the catalysts at the atmospheric pressure of hydrogen (heptanal space velocity, 1 h^{-1}).

T/°C	H_2 : heptanal molar ratio	Conversion (%)	S (%)	By-products (%)	Time on stream
		(5% Pt, 0.4% Fe)/C			
90	15:1	20	65	7.0	
120	15:1	25	72	7.0	
		(8.4% Ni, 1.2% Mg)/Al_2O_3			
90	15:1	10	60	4.0	
120	15:1	15	73	4.1	
		(9% Ni, 2.4% Mg)/Al_2O_3			
90	10:1	5	60	2.0	
		Ni–Cr–O			
130	10:1	64	96	2.5	60 min
130	10:1	48	98	1.0	90 min
165	15:1	95	88	11.3	60 min
165	15:1	99	96	3.9	90 min
165	15:1	99	97	3.0	120 min
		1% Pt/Ni–Cr–O			
100	10:1	45	88	5.4	
120	10:1	50	90	5.0	
120	10:1	67	90	6.7	60 min
120	10:1	50	98	1.0	90 min
120	10:1	40	97	1.0	120 min
150	15:1	99	95	5.0	
165	10:1	99	93	6.9	
		1% Pd/Ni–Cr–O			
120	15:1	70	71	20.3	
150	15:1	84	90	8.4	
		NCO-2-1 commercial catalyst			
90	15:1	5	60	2.0	
100	15:1	50	90	5.0	
150	15:1	62	87	8.1	
		Ni/kieselguhr commercial catalyst GM-3			
100	15:1	30	73	8.1	
150	15:1	75	86	10.5	

Table 2 Testing of the catalysts in heptanal hydrogenation at elevated pressures of hydrogen.

Catalyst	P/MPa	T/°C	LHSV/h^{-1}	Conversion (%)
1% Ir/SiO_2	0.6	100	1	12
1% Ir/C	0.9	115	0.8	21
1% Ir/Al_2O_3	0.6	120	1	10
1% Ru/Al_2O_3	0.6	100	1	8
	1.0	140	1	32
1% Ru/C	0.6	120	1	57
	0.6	130	1	51
Ni/kieselguhr	0.6	95	1	98
Ni–Cr–O	0.9	90	1	96
	0.9	120	1	97
Ni–Cr–O (Si) Silanized	0.6	110	1	93
	0.6	95	1	91
	1.1	100	1	95
1% Pt/Ni–Cr–O	0.6	100	1	98

The runs were carried out at 90–165 °C and the H_2 : aldehyde molar ratios varied from 5 : 1 to 15 : 1. Table 1 presents the results of testing the samples at an atmospheric pressure and demonstrates that the catalysts tested noticeably differ in the activity. The iron-modified platinum catalyst and supported Ni–Mg catalysts exhibit a poor activity. Nickel–copper and nickel catalysts are more active, and nickel–chromium catalysts, particularly, a platinum-modified catalyst, show the maximum activity.

Almost complete aldehyde conversion at a selectivity >95% is attained on nickel–chromium catalysts under optimum condi-

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The 1% Pt/Ni–Cr–O and 1% Pd/Ni–Cr–O catalysts were prepared by incipient wetness impregnation of the nickel–chromium catalyst with a chloroplatinic acid or $PdCl_2$ solution followed by drying at 120 °C and reduction at 200 °C for 3 h.

Prior to hydrogenation, the catalysts were crushed, and a fraction of 1–1.2 mm was taken and loaded in the reactor. The system was pressurized, purged with an inert gas flow and then with hydrogen, and the catalyst was reduced at 200 °C.

For comparison, following three commercial catalysts were employed: a nickel–copper catalyst (NCO-2-1) prepared from Ni and Cu hydroxide carbonates and an Al_2O_3–CaO cement support (25% Ni, 11.3% CuO, 17.8% CaO, 41.8% Al_2O_3); a catalyst GM-3 which is kieselguhr supported nickel, 40%. The commercial catalysts were reduced with hydrogen at 400 °C for 2 h.

The catalysts with a high nickel content were reduced by the following program. (1) Gradual heating at a rate of 50 K h^{-1} to temperature of 200 or 300 °C in an inert gas flow. (2) Gradual replacement of the inert gas with a hydrogen flow, starting from 1% H_2. (3) Reduction in a hydrogen flow for 2 h. (4) Lowering the temperature at a rate of ~50 K h^{-1} to a chosen reaction temperature.

[‡] *Hydrogenation of heptanal under atmospheric pressure.* The starting aldehyde was purchased from Aldrich, the purity was 98% (GC). The hydrogenation process was performed in a vertical cylinder glass reactor 18 mm in diameter equipped with a thermocouple in the catalyst bed. The catalyst bed height was 20 mm; the volume was 5.0 cm^3. Quartz grains (2 ccm) were loaded over the catalyst bed. The reactor was placed in an electric heater. Hydrogen was supplied to the reactor from the top through a flow regulator, and starting heptanal was supplied using a liquid pump. The reaction products from the reactor were collected in a trap cooled with water, the liquid from the trap was sampled at regular intervals for the chromatographic analysis.

At the beginning of each experiment, aldehyde diluted with heptane was fed (heptane : aldehyde = 10 : 1 by volume). After 20 min, the aldehyde concentration in the initial mixture was raised to 100%.

[§] *Hydrogenation of heptanal at elevated hydrogen pressures.* A laboratory setup was used for the experiments under elevated pressures up to 3 MPa and temperatures up to 250 °C. The reactor was a stainless steel tube 250 mm in length (i.d. 10 mm). The catalyst was loaded on a metal gauze arranged at the center of the reactor. The operating volume of the reactor was 5 cm^3. Starting aldehyde and hydrogen were supplied to a mixer. The hydrogen pressure at the reactor inlet was kept constant using a pressure regulator and measured with a manometer. A gas-liquid mixture of aldehyde with hydrogen was fed from the top of the catalytic reactor. The reactor was placed in an electric heater. The reactor temperature was measured with a thermocouple located in the catalyst bed. The reaction products from the reactor passed a coil condenser and then were trapped in a collector, both the coil condenser and collector were cooled with water. The hydrogen flow rate through the reactor was controlled and measured with a flow meter.

Prior to experiments, a setup was purged with an inert gas and then with hydrogen, and a specified pressure and flow rate of hydrogen at the outlet were adjusted. Next, the temperature was raised to a specified value. The catalyst was kept for 15 min at this temperature, and then aldehyde was fed. In the course of experiments, the reaction products from the collector were sampled at regular intervals. The data on the catalyst activity and selectivity summarized in the tables and figure refer to the periods of stable catalyst operation (after 3–6 h on stream).

The reaction products were analyzed by GC using a packed column (3 m × 3 mm, 5% SE-30 on Inerton AW) and a thermal conductivity detector and a capillary column (OV-1, 25 m × 3 mm; film thickness, 0.26 mm) and a flame ionization detector. Reference samples of 1-heptanal and 1-heptanol were used for identifying chromatographic peaks. The chromatographic procedure using the capillary column allowed us to determine by-products with a high boiling point (up to C_{23} products).

Under conditions of low-temperature hydrogenation (<100 °C), impurities of compounds with low boiling points (cracking products) were formed only at the initial stage when the catalyst activity did not yet reach a stationary level. Under steady-state conditions, the total concentration of these impurities was no higher than 0.5%. Aldehyde condensation products were predominant impurities. These compounds appeared in chromatograms after heptanol as 3–4 peaks. One of these peaks was identified as heptanal diheptyl acetal $C_6H_{13}CH(OC_7H_{15})_2$, whose authentic sample was prepared by acetalization of heptanal with 1-heptanol in the presence of $CaCl_2$. The aldehyde conversion and the selectivity to 1-heptanol were calculated from the GC data.

Table 3 Activity of the catalysts in heptanal hydrogenation at elevated pressures of hydrogen.

P/MPa	T/°C	LHSV/h^{-1}	Conversion (%)	S (%)	By-products (%)
			Ni–Cr–O		
0.2	95	1	88	96	3.5
0.2	110	1	80	88	10
0.5	95	1	90	95	4.5
0.5	110	1	96	97	3.1
1.0	70	1	80	99	0.8
1.0	80	1	94	97	2.8
1.0	95	1	98	96	3.9
1.0	95	2	99	98	2
			1% Pt/Ni–Cr–O		
1.0	75	1	>99	90	10
1.0	75	2	>99	92	8
1.0	85	1	>99	93	7.5
1.0	85	2	>99	94	6
1.0	95	1	>99	94	6
1.0	95	2	>99	96	4

tions at high temperatures (150–165 °C). The aldehyde conversion also increases with increasing the hydrogen : aldehyde molar ratio. Thus, the highest extent of hydrogenation is observed when aldehyde is in the vapour phase. The reaction is first-order with respect to hydrogen and zero-order with respect to aldehyde.

At a temperature below 120 °C, the major portion of aldehyde is liquid, and hydrogen diffuses through a liquid film that covers catalyst particles. In this case, hydrogen diffusion may be a rate-limiting step. Note that catalysts are rapidly deactivated at low temperatures. Thus, the aldehyde conversion on a nickel–chromium catalyst at 130 °C decreases from 64 to 38% within 2 h, whereas it remains unchanged for 3 h when operating at 160 °C.

It can be seen in Table 2 that low-percentage iridium-, ruthenium-, and palladium-based catalysts exhibit a low activity. The aldehyde conversion usually did not exceed 57% even for the most active ruthenium catalyst from this group.

In agreement with the experiments at an atmospheric pressure of hydrogen, the catalysts with a high nickel content exhibited the highest activity; the aldehyde conversion was 96–98% at 95–100 °C.

Table 3 summarizes the results of testing the catalysts at elevated pressures of hydrogen. The catalyst activity was estimated as the aldehyde conversion at a space velocity of liquid heptanal of 0.8–1.2 h^{-1}, a hydrogen pressure of 0.6–1.1 MPa, and an outlet H_2 flow rate of 500 cm^3 min^{-1}.

The 1% Pt/Ni–Cr–O catalyst was characterized by XRD[¶] analysis (Figure 1). The XRD pattern of the sample in the 2θ range from 20 to 85° has 4 diffraction maxima. The most intense reflections were observed at $2\theta = 37.28$, 43.88, 62.92 and 75.0°. These peaks correspond to the reflections from the different planes of NiO crystallites. No peaks associated with the crystalline phase of Cr_2O_3 were found. It allows one to consider that the Cr_2O_3 oxide in our sample is amorphous and does not form a definite crystallite phase that could produce corresponding XRD peaks. A small peak was found at $2\theta = 39.44$°. It corresponds to Pt in the reduced metallic state.

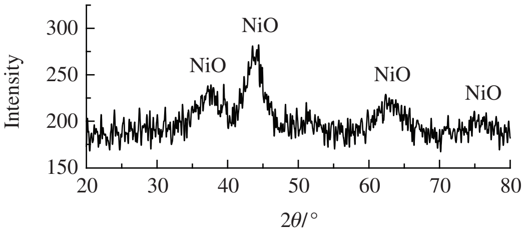

Figure 1 XRD pattern of the 1% Pt/Ni–Cr–O catalyst before and after testing in heptanal hydrogenation.

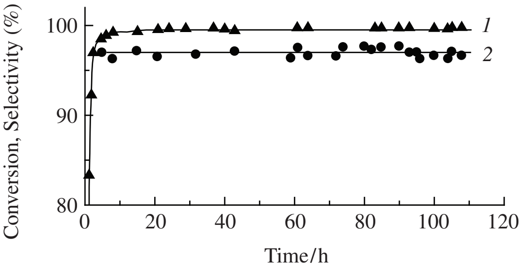

Figure 2 Heptanal (*1*) conversion and (*2*) selectivity to heptanol in the long-term heptanal hydrogenation over the 1% Pt/Ni–Cr–O catalyst.

The platinum-modified nickel–chromium catalyst showing a somewhat more stable activity at lower temperatures was chosen for long-term stability tests. The experiment was performed at 95 °C, 0.8 MPa, the aldehyde space velocity of 1 h^{-1}, and the H_2 : aldehyde molar ratio of 2 : 1. The data obtained are presented in Figure 2.

After 5–6 h, the process attained steady-state conditions under which the selectivity for heptanol was higher than 95%. It can be seen in Figure 2 that the aldehyde conversion remained almost unaffected (⩾ 99%) during the entire 100 h experiment, making thus the process selective.

To conclude, we have discovered a promising nickel–chromium–platinum catalytic system for selective flow hydrogenation of heptanal into 1-heptanol.

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References

1 L. L. Klinova, M. I. Silich, D. B. Kazarnovskaya, A. I. Patsukova, N. M. Malygin, D. I. Kal'nitsky and V. F. Smovzh, *Khim. Prom.*, 1975, **5**, 341 (in Russian).

2 G. Deckers, G. Diekhaus, D. Bernd, C. D. Frohning, G. Horn and B. Horrig, *DE Patent, 4310053*, 1994 (*Chem. Abstr.*, 1994, **121**, 255247v).

3 H. Corr, F. Haarer, H. Hoffmann and S. Winderl, *US Patent 3 991 127*, 1967 (*Chem. Abstr.*, 1968, **69**, 105882s).

4 J.-K. Jeon, J.-H. Yim and Y.-K. Park, *Chem. Eng. J.*, 2008, **140**, 555.

5 G. S. Gurevich, A. L. Shapiro, R. A. Shmelev and V. M. Kazantsev, *SU Patent 1172917*, 1985 (*Chem. Abstr.*, 1986, **104**, 88114q).

6 V. Grosser, A. Cirova, E. Antkowicz, M. Huml, I. Kopecky and V. Macek, *CS Patent 247969*, 1987 (*Chem. Abstr.*, 1988, **108**, 188927h).

7 V. Grosser, M. Huml, I. Kopecky, V. Macek, A. Cirova and E. Antkowicz, *CS Patent 248317*, 1988 (*Chem. Abstr.*, 1989, **110**, 233636s).

8 Z. Tang, Y. Zhou and Y. Feng, *Appl. Catal. A: Gen.*, 2004, **273**, 171.

9 A. N. Bashkirov, G. A. Kliger, L. S. Glebov, O. A. Lesik and E. V. Marchevskaya, *SU Patent 789477*, 1980 (*Chem. Abstr.*, 1981, **94**, 139213f).

10 J. Jenck and J. E. Germain, *J. Catal.*, 1980, **65**, 141.

11 G. S. Gurevich and S. Z. Levin, *US Patent 150110*, 1962 (*Chem. Abstr.*, 1963, **58**, 12438f).

12 Z. Poltarzewski, S. Galvagno, R. Pietropaolo and P. Staiti, *J. Catal.*, 1986, **102**, 190.

13 S. Galvagno, Z. Poltarzewski, A. Donatoi, G. Neri and R. Pietropaolo, *J. Mol. Catal.*, 1986, **35**, 365.

14 M. Shirai, T. Tanaka and M. Arai, *J. Mol. Catal. A: Chem.*, 2001, **168**, 99.

15 G. Neri, G. Rizzo, L. De Luca, F. Corigliano, I. Arrigo, A.S. Aricò and A. Donato, *Appl. Catal A: Gen.*, 2008, **350**, 169.

16 D. Goupil, P. Fouilloux and R. Maurel, *React. Kinet. Catal. Lett.*, 1987, **35**, 185.

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[¶] Powder X-ray diffraction (XRD) was performed on a DRON-2 X-ray diffractometer using CuKα radiation with a 2° step size at room temperature and the spectra were recorded over the 2θ range of 5–85°.