PHYSICOCHEMICAL STUDIES
OF SYSTEMS AND PROCESSES

Cobalt-containing Catalytic Systems Alloyed with Rare and Rare-Earth Metals as Catalysts for Synthesis of Hydrocarbons from CO and H$_2$

A. S. Seleznev[a], L. A. Petrov[a], O. N. Chupakhin[a], V. I. Kononenko[b],
I. A. Chupova[b], and A. V. Ryabina[b]

[a]*Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia*
[b]*Institute of Solid State Chemistry, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia*

Received December 29, 2008

Abstract—To improve cobalt-containing catalytic systems for synthesis of hydrocarbons from carbon monoxide and hydrogen (Fischer–Tropsch synthesis), supports based on ultradispersed alloys of aluminum with rare and rare-earth metals (G, Ce, Sm) were obtained and studied. The catalytic activity parameters of the new catalysts were determined.

To improve cobalt-containing catalytic systems for synthesis of hydrocarbons from carbon monoxide and hydrogen (Fischer–Tropsch synthesis), supports based on ultradispersed alloys of aluminum with rare and rare-earth metals (G, Ce, Sm) were obtained and studied. The catalytic activity parameters of the new catalysts were determined.

In the present-day situation in oil markets, researchers' interest in improvement of catalysts for Fischer–Tropsch synthesis (FTS) of liquid hydrocarbons, which contain cobalt as the active component, is steadily increasing [1]. Despite that cobalt catalysts are widely used in the industry, there is a necessity for a more in-depth analysis of the relationship between the composition and physicochemical properties of the catalysts (texture, capacity for reduction, acid properties, and specific features of CO and H$_2$ adsorption), on the one hand, and their catalytic behavior in the FTS, on the other. The main criteria for choice of Co-containing catalytic systems is their selectivity and mild hydrocarbon synthesis conditions: low pressure and temperature [2]. Also, it should be mentioned that the existing Co-containing catalytic systems have a shortcoming: the narrow temperature range of synthesis of liquid hydrocarbons. This is manifested in that the fraction of undesirable

products grows and the selectivity for the gasoline–diesel fraction decreases as the FTS temperature is raised (in order to improve the activity of, in particular, methane and CO$_2$) [3].

Extensive studies have been carried out to achieve the maximum activity and selectivity of catalysts by introduction promoters of catalytic centers [4–8]. As promoters have been used platinum metals [9], alkali metals [10], and rare-earth metals [11]. The modification of catalyst supports has been studied to a considerably lesser extent. At the same time, studies of the Co/Al$_2$O$_3$ system have shown that there is a strong metal–support interaction [12–16]. It has been found [17] that the electronic structure of the metallic component of the system is strongly affected by interactions with the support: metal–surface hydroxy groups, metal–basic centers, and metal–Lewis centers. It becomes apparent that the support properties largely determine the behavior of the whole cobalt-containing catalytic system in the FTS process.

As a rule, a support is alloyed by deposition of a salt of an element onto the matrix surface, followed by calcination of the sample. With this method used, the homogeneity of the coating is impaired, especially in the case of a multilayer deposition of several elements.

The reproducibility of this method is not always satisfactory.

In this context, it seemed appropriate to develop unconventional approaches to fabrication of a complex-composition aluminum oxide support from an ultradispersed powder of aluminum alloys alloyed with rare and rare-earth metals. The structure of a powder particle is constituted by a metal core, composed of alloyed aluminum, covered with a film of alloy oxidation products. A distinctive feature of this approach is that the knowledge of the liquid state of a substance is applied to synthesis of heterogeneous metallic catalysts, aluminum alloy powders with a prescribed concentration of components in the bulk and on the oxidized surface of a particle. An alloyed aluminum alloy is regarded as a precursor of an ultradispersed powder, the catalyst support. In this case, our goal is to determine the structure and properties of a support by selecting support synthesis conditions with consideration of data on the most important parameters of the starting aluminum alloys: viscosity ν, electrical resistivity ρ, and surface tension σ.

With our goal formulated in this way, it is appropriate to use the "physical" or structural aspect in studies of the liquid state of the substance [18]. Particularly important are the results of previous experimental and theoretical studies of specific features of interparticle interactions in liquid aluminum alloys with alloying additions of rare and rare-earth metals [19], which differently affect the solvent (aluminum) properties. These specific features can be evaluated by the response of such structurally sensitive and surface properties as ν, ρ, and σ. In the case in question, we take into account the response of the properties to changes in chemical bonding and atomic arrangement, which are manifested as various anomalies in isotherms and polytherms of these physicochemical properties.

When determining the reasons for the appearance of the anomalies, we used Kurnakov's method of physicochemical analysis [20], in which the property–composition chemical diagram is compared with the phase diagram of the system. Previously obtained theoretical and experimental results show that rare and rare-earth metals having a lower, compared with the solvent (aluminum), surface energy are concentrated at the surface and act as surfactants with respect to the solvent [21].

It should also be noted that results of a metallographic analysis with replicas of polished surface of diluted aluminum solutions yielded the following pattern: matrix, a solid solution of metal additives in aluminum or pure aluminum, and small islands, groups of atoms. The composition of these islands depends on the type to which belongs the system under study. For solutions of systems of the eutectic L-type, a uniform and chaotic distribution of atoms is observed. Alloys of E-systems (systems with a component stratification region) are coexisting large regions of like atoms within the stratification dome. In melts of V-systems, larger formations with a short-range order of the type of a compound are observed, with their presence and size determined by the Gibbs potential. These conclusions are confirmed by calculations of complex sizes by Einstein–Smoluchowski, Ziman–Kharkov, and Zhukhovitskii (for the surface).

Thus, our analysis of the results of previous studies [22] enabled us to determine, with a satisfactory degree of confidence, the range of potentially useful additives that can strongly change the surface composition and properties of an ultradispersed alloyed support of a Co-containing catalyst for the Fischer–Tropsch synthesis of hydrocarbons. We chose as additives of this kind rare and rare-earth metals (Ga, Ce, Sm) at their optimal concentrations in aluminum.

The aim of our study was to obtain ultradispersed powders (UDPs) of aluminum, alloyed with rare and rare-earth metals (Ga, Ce, Sm) by special methods, to examine the possibility of using these powders as an oxide support for a Co-containing catalytic system, and to analyze the effect of the phase state and texture of ultradispersed powders of aluminum alloys on the adsorption of CO on their surface and on their catalytic properties in the Fischer–Tropsch synthesis of hydrocarbons.

EXPERIMENTAL

We synthesized alloys and alloying compositions used to obtain powders in alundum crucibles. Depending on the melting points and vapor pressures of the components, the alloys were synthesized in a vacuum or in an inert gas (helium of high-purity grade). The components were fused together in an SShVL industrial vacuum furnace, which provided temperatures of up to 1837 K in the working zone and a vacuum with a residual pressure not exceeding 1×10^{-5} mm Hg or an inert atmosphere at excess pressures of up to 0.3 atm.

We found in preliminary experiments that the stock components start to interact immediately after the melting of aluminum, with the process occurring with
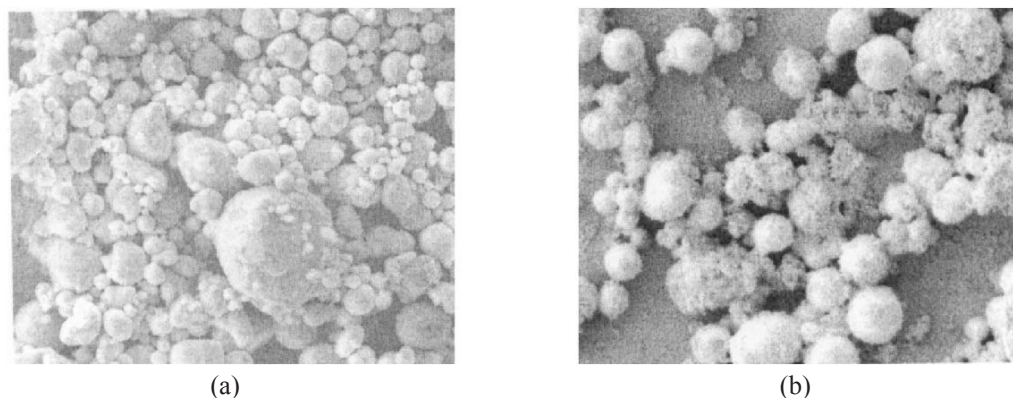
SELEZNEV et al.

(a)   (b)

Fig. 1. Surface micrographs of ultradispersed powders of cerium-alloyed aluminum alloys, produced by (a) atomization of a melt with inert gas and (b) plasma recondensation of powder as.

a considerable warming-up. Weighed portions of the components, preliminarily mechanically cleaned to remove the oxide film, were placed in a conical alundum crucible mounted within a large-diameter crucible to preclude ejections. From the above, a cover with an appropriate diameter and height was put on the protruding part of the main crucible. The thus prepared weighed portions were mounted on the stand of the vacuum furnace and fixed with upper screens with a cover. The furnace was sealed and evacuated to a required residual pressure or filled with the inert gas. Then the temperature in the furnace was gradually raised to the melting point of aluminum. The furnace was kept at this temperature for 30–40 min and then was heated to a temperature exceeding by approximately 50°C the melting point of the alloy and kept at this temperature for no more than 1 h. Then the heater was switched off and the furnace was cooled to room temperature in the sealed state.

The alloying compositions further served for preparing alloys with a prescribed concentration and for obtaining powdered alloys by the ASD-4 method by melt atomization with nitrogen. This technique yields powders with spherical particles and a rather narrow particle size distribution. To advantages of this technique belongs the uniform distribution of rare and rare-earth metals in the melt, which is preserved in particles produced by atomization.

The resulting samples were then subjected to plasma recondensation to obtain powders with a more developed surface.

Figure 1b clearly shows the voids formed and the loose surface of ultradispersed particles. The voids are produced upon discharge of the pure metal from a particle, which occurs because the thermal expansion coefficients of the

metal and oxides strongly differ and a very high pressure builds-up within a particle. The oxide film formed on the particle surface cracks as temperature increases and the particle permanently loses a part of pure metal converted into the oxide. In this way, we obtained highly dispersed powders of aluminum alloys, which contain up to 0.1 wt % Sm, Ce, and Ga and have an average particle size of about 100–300 nm.

Such a material seems to be promising for catalysis in the following respects: two-phase ultradispersed particles have a developed surface with a complex texture; the composition of the surface oxide phase is in equilibrium with the metallic core and is corrected by the core in an operating catalyst [23], which can serve as a guarantee of its stability.

The catalysts were fabricated by the conventional method of impregnation of powdered ultradispersed aluminum alloys with rare and rare-earth metals with a cobalt(II) nitrate solution with a prescribed concentration providing 10 wt % cobalt. After the impregnation, the catalysts were dried on a water bath and calcined in a flow of air at 400°C for 1 h.

The catalysts were studied by the temperature-programmed desorption (TPD) method on a BI-SORBchemo2 installation (developed at Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences) of the gas-chromatographic type with a U-shaped quartz reactor. A catharometer served as a detector. The reactor was heated with an electronic temperature-programming unit. The signal from the catharometer was delivered via an analog-to-digital converter to a computer and processed using the Chemosorb software. Simultaneously, the signal from the thermocouple measuring the temperature in the reactor

was recorded via the second analog-to-digital converter channel.

A weighed portion of the catalyst was placed in the reactor and reduced with hydrogen in the course of 1 h at a temperature of 400°C and volumetric flow rate of H_2 of 3000 h^{-1}. Then, hydrogen was replaced with helium and the sample was blown with helium at 400°C for 1 h. The reactor was cooled to room temperature and carbon monoxide was introduced pulsewise into the carrier-gas flow until the absorption of CO by the sample terminated.

After the catalyst was saturated, the reactor was heated from room temperature to 450°C at a rate of 15–20 deg min^{-1} and a TPD spectrum was recorded. The desorption peaks areas were calculated after resolving the experimental TPD curve into separate peaks by the Microcal Origin software.

Hydrocarbons were synthesized from CO and H_2 in a flow-through catalytic installation under atmospheric pressure in the temperature range 160–250°C. A 20-ml portion of the catalyst was charged into a quartz reactor with an inner diameter of 20 mm, equipped with a pocket for a thermocouple. Before introduction into the reactor, the catalyst was mixed with quartz in a catalyst : quartz volume ratio of 1 : 3. The heating was provided by an electric furnace equipped with a KVP-1 temperature controller with an accuracy of 1–2°.

Hydrogen or a mixture with carbon(II) oxide and hydrogen (volume ratio 1 : 2) was delivered from cylinders via a reducer, fine adjustment valve, and drying system (columns with solid NaOH) into the reactor at a volumetric flow rate of 100 h^{-1}. The gas flow rate was controlled on the basis of rheometer indications. Liquid reaction products were condensed successively in the receiver at room temperature (cooling with water) and in a trap cooled to –78°C with a mixture of dry ice with acetone. After being passed through the foam separator, the gaseous products and unreacted starting substances were sampled into gas burettes for analysis and then discharged into the atmosphere. Carbon(II) oxide and hydrogen from cylinders were used. Carbon(II) oxide was 99.99% pure. Hydrogen was of the standard purity (99.999%).

Before being used in synthesis, the catalysts prepared by support impregnation with an aqueous solution of cobalt(II) nitride were reduced in a flow of hydrogen (99.999%, volumetric flow rate 3000 h^{-1}) at a temperature of 450°C for 1 h. Experiments on synthesis of hydrocarbons from CO and H_2 on a single catalyst were performed in the course of 5–7 days, with temperature raised from 200 to 250°C in steps of 10°C in a run. The duration of a daily experiment was 5–6 h. Data on the catalytic activity are presented for a temperature of 200°C, at which the optimal yield/selectivity ratios were obtained for C_{5+} hydrocarbons.

The starting substances and gaseous and liquid reaction products were analyzed by the gas-adsorption method on an LKhM-8MD chromatograph.

The composition of liquid paraffins was determined by gas-liquid chromatography on a BIOKhROM-1 chromatograph. The content of olefins in liquid synthesis products was found from the change in the volume of a sample after its treatment with concentrated sulfuric acid.

The probability α of the hydrocarbon chain growth was found from the Schultz–Flory equation

$$\log (m_p/P) = \log (\ln^2\alpha) + P\log \alpha,$$

where m_p is the mass fraction of the product, calculated from the chromatogram, and P is the number of carbon atoms in the molecule of the product.

Experimental data on the molecular-mass distribution were approximated by the least-squares method on a computer.

The results obtained by analysis of the TPD spectra of the cobalt-containing catalysts based on powdered alloys of ultradispersed aluminum, promoted with rare-earth metals, are listed in Table 1.

Previously, a two-center model of a Co-catalyst for FTS has been suggested [13, 14, 24–27]. According to these concepts, metallic cobalt crystallites are centers of the first type. CO is dissociatively adsorbed on these centers and then is hydrogenated to methane. To centers of the first type corresponds the peak with T_{max} in the range 250–350°C; the reaction of CO disproportionation leading to catalyst coking occurs at the same centers. To centers of the second type corresponds the peak with Tmax < 250°C. These centers have the form of the boundary between metallic cobalt and the oxide phase on the catalyst surface and are responsible for the carbon chain growth. The presence of centers of this type on the surface of cobalt catalysts is a necessary condition for synthesis of liquid hydrocarbons from a mixture of CO and H_2. The types of CO adsorption on the surface can be determined on the basis of a TPD spectrum of CO. The ratio between
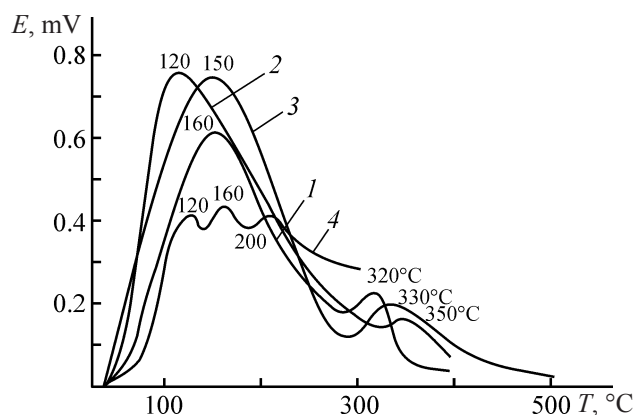
Fig. 2. TPD spectra. (*E*) Thermocouple voltage and (*T*) temperature. (*1*) 10% Co/UDP(Al), (*2*) 10% Co/UDP(Al + 0.1% Ce), (*3*) 10% Co/UDP(Al + 0.1% Sm), and (*4*) 10% Co/UDP[Al + 0.1% (CE + Ga)].

Table 1. CO TPD data for catalysts composed of 10% Co/UDP(Al + alloying additive)

Alloying additive (0.1 wt %)	T_{max} of indicated peak, °C (relative area, %)		
	peak I	peak II	peak III
–	160 (81.9)	320 (14.2)	200 (43.8)
Ce	120 (85.8)	350 (14.2)	
Sm	150 (78.8)	330 (21.2)	
(Ce + Ga)	120 (20.5)	160 (35.7)	

the peak areas can be used to judge about the share of each type of centers and, accordingly, to prognosticate the catalytic activity of a catalyst [28].

It can be seen from Table 1 that, compared with a pure aluminum UDP, introduction of an alloying addition of cerium into the aluminum alloy shifts the T_{max} of the first desorption peak to lower temperatures, and the second, to higher temperatures. The ratio between the peak areas under the TPD curve (Fig. 2) suggests that the associative adsorption of CO both on metallic cobalt and on the oxide part of the catalyst predominates on the surface of a cobalt-containing catalyst alloyed with Ce. Upon addition of gallium to cerium, the TPD curve divides into three peaks with maxima at different temperatures. This indicates that there are three different catalytic centers on the catalyst surface. In addition, the fraction of centers with weak CO adsorption decreases upon addition of gallium by nearly a factor of 4, which means that the catalytic activity of this sample decreases as compared with the catalyst alloyed with cerium.

According to the peak temperatures and to the ratio of areas under the TPD curve, the catalyst with an alloying addition of Sm contains a large fraction of weakly bound centers of CO adsorption. Hence follows a conclusion that this catalyst has the same properties as the catalyst alloyed with Ce.

The catalytic data obtained for the 10% Co/UDP(Al) catalyst alloyed with Ce, Sm, and Ga are listed in Table 2. Introduction of an alloying addition of Ce and Sm leads to an increase in the yield of C_{5+} hydrocarbons, whereas in the presence of Ga, the yield of the C_{5+} fraction noticeably decreases. In addition, joint introduction of Ce and Ga markedly diminishes the selectivity with respect to C_{5+} hydrocarbons to 36%. For the catalyst alloyed with Sm, the content of the C_5–C_{10} fraction noticeably increases as compared with the unalloyed sample, whereas upon addition of Ce and Ga, this content decreases. At the same time, the content of the diesel fraction C_{11}–C_{18} increases upon addition of Ce and Ga and somewhat decreases upon alloying with Sm.

CONCLUSIONS

(1) It is advisable to search for effective alloying

Table 2. Catalytic activity of samples composed of 10% Co/UDP(Al + alloying additive) P = 0.1 MPa, T = 220°C, degree of CO conversion ~60%

Alloying additive (0.1 wt %)	Yield, g m^{-3}			Selectivity, %		Fractional composition of liquid hydrocarbons, %			α
	CH_4	C_{5+}	CO_2	CH_4	C_{5+}	C_5~C_{10}	$C1_1$–C_{18}	C_{19+}	
–	21.5	79	14	18.1	66.5	47.5	43.2	9.3	0.8
Ce	20.2	79.2	11.2	17.0	68.2	41.7	45.1	13.2	0.82
Sm	27.5	81.9	13.8	20.0	59.3	61.6	31.9	6.5	0.77
(Ce + Ga)	26.5	48	59.2	17.0	36.0	33.1	54.9	12.0	0.83

additives to aluminum melts among elements exhibiting a pronounced surface activity toward the matrix and having a distribution of like atoms in the melt, characteristic of systems of the V-type.

(2) Among the three alloying additives studied (Ce, Ga, Sm), cerium was found to be the most effective.

(3) The method of temperature programmed desorption was used to demonstrate the presence of two types of carbon monoxide adsorption centers on the surface of new cobalt-containing catalytic systems.

(4) New cobalt-containing catalytic systems including nano- and ultradispersed alloyed aluminum alloys prepared on the basis of the selected parameters of the starting aluminum alloys (v, ρ, σ) exhibited a high catalytic activity in the Fischer–Tropsch synthesis of hydrocarbons. The high carbon chain growth probability α was noted, in the range from 0.77 to 0.83.

ACKNOWLEDGMENTS

REFERENCES

1. Krylov, O.V. and Kiselev, V.F., *Adsorbtsiya i kataliz na perekhodnykh metallakh i ikh oksidakh* (Adsorption and Catalysis on Transition Metals and Their Oxides), Moscow: Khimiya, 1981.

2. *Kataliz v C₁ khimii* (Catalysis in C_1 Chemistry), Kal'm, V., Ed., Leningrad: Khimiia. 1987

3. RU Patent Appl. 2024297.

4. Iglesia, E., Soled, S.L., Fiato, R.A., and Via, G.H., *J. Catal.*, 1993, vol. 143, pp. 345–368.

5. Iglesia, E., Soled, S.L., and Fiato, R.A., *J. Catal.*, 1992, vol. 137, pp. 212–224.

6. Hillmen, A.M., Schanke, D., and Holmen, A., *Catal. Lett.*, 1996, vol. 38, pp. 143–147.

7. Holmen, A., Schanke, D., Vada, S., et al*., Catal. Lett.,* 1995, vol. 156, pp. 85–95.

8. Oukasi, R., Singleton, A.H., and Goodwin, J.G., *Appl. Catal., A: General*, 1999, vol. 186, pp. 129–144.

9. Tsubaki, N., Sun, Sh., and Fujimoto, K*., J. Catal.,* 2001, vol. 199, pp. 236–246.

10. Raje, F.P., O'Brein, P.J., and Davis, B.H., *J. Catal.,* 1998, vol. 180, pp. 36–43.

11. US Patent 4657885.

12. Lapidus, A., Krylova, A., Kazanskii, V., et al., *Appl. Catal.*, 1991, vol. 73, pp. 65–81.

13. Lapidus, A., Krylova, A., Rathousky, J., et al., *Appl. Catal.*, 1992, vol. 80, pp. 1–11.

14. Rathousky, J., Zulkal, A., Lapidus, A., and Krylova, A., *Appl. Catal.*, 1991, vol. 79, pp. 167–180.

15. Zowtaik, J.M. and Bartholomew, C., *J. Catal.*, 1983, vol. 83, pp. 107–120.

16. Reuel, R.C. and Bartholomew, C., *J. Catal.*, 1984, vol. 85, pp. 63–77.

17. Mikhailov, M.N., Zhidomirov, G.M., and Krylova, A.Yu., *Izv. Akad. Nauk, Ser. Khim.*, 2005, pp. 2194–2199.

18. Vertman, A.A. and Samarin, A.M., *Metody issledovaniya svoistv metallicheskikh rasplavov* (Methods for Studies of Properties of Metallic Melts), Moscow: Nauka, 1969.

19. Ryabina, A.V., Shevchenko, V.G., Kononenko, V.I., et al., *Teplofizicheskie svoistva veshchestv i materialov: Materialy dokladov i soobshchenii* (Thermal Properties of Substances and Materials: Proceedings), St. Petersburg, 2005, pp. 41–42.

20. Kurnakov, N.S., *Vvedenie v fiziko-khimicheskii analiz: Uchebnoe posobie dlya khimicheskikh fakul'tetov gosudarstvennykh universitetov* (Introduction to Physicochemical Analysis: Textbook for Chemical Departments of State Universities), Anosov, V.Ya., and Klochko, M.A., Eds., Moscow: Akad. Nauk SSSR, 1940.

21. Sukhman, A.L., *Doctoral Sci. (Chem.) Dissertation*, Sverdlovsk. 1985.

22. Ryabina, A.V., Kononenko, V.I., Shevchenko, V.G., and Torokin, V.V., Abstracts of Papers, *VI Vserossiiskaya konferentsiya "Fizikokhimiya ul'tradispersnykh (nano)-sistem"* (VI All-Russia Conf. "Physical Chemistry of Ultradispersed (Nano)systems"), Tomsk, 2000. pp. 81–28.

23. Ryabina, A.V., Shevchenko, V.G., Kononenko, V.I., et al., *Metally*, 2005., no. 3, pp. 20–25.

24. Lapidus, A.L., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, no. 12, pp. 2681–2698.

25. Lapidus, A.L. and Krylova, A.Yu., *Usp. Khim.,* 1998, pp. 1032–1043.

26. Krylova, A.Yu., Lapidus, A.L., Yakerson, V.I., et al*., Izv. Akad. Nauk.*, Khimiya, 1992, no. 1, pp. 55–59.

27. Krylova, A.Yu., Malykh, O.A., Emel'yanova, G.I., and Lapidus, A.L., *Kinet. Kataliz*, 1989, no. 30(6), pp. 1495–1499.

28. Dry, M.E., *Appl.Catal., A: General*, 1996, vol. 138, pp. 319–344.