ISSN 0023-1584, Kinetics and Catalysis, 2011, Vol. 52, No. 2, pp. 273–276. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © A.L. Tarasov, L.M. Kustov, V.I. Isaeva, A.N. Kalenchuk, I.V. Mishin, G.I. Kapustin, V.I. Bogdan, 2011, published in Kinetika i Kataliz, 2011, Vol. 52, No. 2, pp. 282–285.

Platinum-Containing Catalyst Supported on a Metal-Organic Framework Structure in the Selective Oxidation of Benzyl Alcohol Derivatives into Aldehydes

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Received October 16, 2009

Abstract—The platinum catalyst supported on the metal-organic framework structure MOF-5 is usable in the selective oxidation of vanillyl and piperonyl alcohols into the corresponding aldehydes.

DOI: 10.1134/S0023158411020212

The catalytic activity of supported metals depends considerably on the nature of the support [1]. The method of preparing heterogeneous catalysts supported on metal-organic framework structures (MOFs) was suggested by Opelt et al. [2].

The unique feature of the MOFs is that they have no space inaccessible to an adsorbate ("dead" space) [3]. In addition, due to the open architecture of the MOFs, the diffusion coefficients of reactant molecules in these materials are somewhat smaller than in the solvent bulk; that is, mass transfer is not hampered in this case [3].

There is only scarce information concerning the use of MOF-supported heterogeneous catalysts in the aerobic oxidation of alcohols. It was demonstrated that the palladium-containing MOF with the molecular formula $[Pd(2\text{-pymo})_2]_n$ (2-pymo = 2-hydroxypyrimidinolate) is catalytically active in the aerobic oxidation of 3-phenylprop-2-en-1-ol (cinnamic alcohol) into cinnamic aldehyde. The selectivity of this hybrid catalyst toward the target product is as high as 74% (20 h, ~100% conversion).

Here, we report the preparation of an MOF-5–supported Pt-containing system and demonstrate that this system is usable as a catalyst in the aerobic oxidation of piperonyl and vanillyl alcohols into the corresponding aldehydes. MOF-5, which is the best studied representative of the new family of porous materials, is built of Zn_4O clusters and terephthalate (benzene-1,4-dicarboxylate) bridging ligands and has the molecular formula $[Zn_4O(BDC)_3]$ (BDC = benzene-1,4-dicarboxylate).

The catalytic oxidation of benzyl alcohol derivatives into aldehydes is an industrially important process, providing the basis for producing vanillin from guaiacol, heliotropine (piperonal) from pyrocatechol, anisaldehyde, etc. [5]. This reaction is interesting in the context of the strong dependence of the oxidation route on the nature of the catalyst [6]. The conventional foreign technology based on this process [7] produces large amounts of liquid waste, is very energy-intensive, and consumes large amounts of noble metals. There have been examples of use of cadmium, cerium, indium, lanthanum, copper, yttrium, magnesium, and zinc ions as promoters in the oxidation of benzyl alcohol derivatives on conventional catalysts, such as Pt/C [8]. However, in spite of the high consumption of the promoter, no significant reduction of the necessary platinum-group metal content of the catalyst has been attained.

EXPERIMENTAL

Catalyst Preparation

The support for the Pt-containing catalysts was the synthesized metal-organic framework MOF-5 and activated carbon SKT-4A. The textural characteristics of the supports are presented in Table 1.

5% Pt/MOF-5. MOF-5 was synthesized by direct mixing of terephthalic acid and $Zn(NO_3)_2\ 6H_2O$ [9]. An MOF-5 sample was examined by X-ray diffraction on a DRON-3M diffractometer using CuK_α radiation (λ = 1.54 Å). The specific surface area (S_{BET}) was determined from nitrogen adsorption data (–196°C) using a volumetric technique and was calculated using the BET equation [10].

The Pt-containing catalyst was prepared by the same procedure as was developed for the Pd/MOF-5 system (incipient-wetness impregnation) [11]. A solution of $[Pt(NH_3)_4]Cl_2$ (0.04 g, 0.11 mmol) in 0.58 ml of water was gradually added to prepumped MOF-5

Table 1. Textural characteristics of the supports used in the preparation of the Pt-containing catalysts

Support	S_{BET}, m^2/g	Total pore volume, cm^3/g	Micropore volume, cm^3/g	Mesopore volume, cm^3/g
Carbon support SKT-4A	1269	0.66	0.54	0.12
MOF-5	1000	0.52	–	–

Table 2. Catalyst testing data for piperonyl alcohol oxidation at 80°C

Catalyst	Alcohol/catalyst weight ratio	Time, min	Conversion, %	Selectivity, %
9% Pt/SKT-4A*	20	30	62.0	100
		60	100	99.6
5%Pt /MOF-5	5	30	50.8	100
		60	96.1	100

* Data from [8].

(0.38 g) under continuous stirring. The solvent was evaporated at room temperature for 2 h. Next, the system was pumped while raising the temperature to 300°C (5 h).

9% Pt/C (reference catalyst). Activated carbon SKT-4A (10 g, 0.05–0.1 mm size fraction) was loaded with platinum by incipient-wetness impregnation with an aqueous H_2PtCl_6 solution (10 ml). Paraformaldehyde (10 wt %) as the reductant was added to the aqueous solution. After the supporting of platinum, the sample was placed on a filter and was washed with distilled water until free of Cl^- ions. Thereafter, the catalyst was dried at 90°C for 2 h, calcined in flowing air in a flow reactor (300°C, 2 h), cooled in flowing nitrogen to room temperature, reduced in flowing H_2 (30 ml/min) while raising the temperature to 300°C at a rate of 100 K/h, and cooled to room temperature in flowing nitrogen.

Conducting the Oxidation Reaction in a Batch Reactor

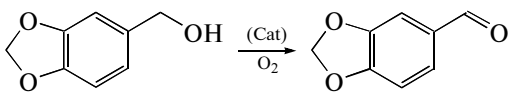
The reactor (20-ml glass test tube) was charged successively with 2 g of piperonyl alcohol (2,4-methylenedioxyphenylmethanol) or vanillyl (3-methoxysalicylic) alcohol, 10 ml of 0.25–1.25 N NaOH, 0.1 ml of 0.05 M lead acetate ($Pb(OAc)_2$) as the catalyst activator, and 0.1–0.5 g of the catalyst (substrate/catalyst = 5–20 by weight). The reactor was purged with air, and the stock was heated to 60–80°C. The catalyst and alcohol in the alkaline solution were agitated by intensive air bubbling (50 ml/min). Thirty (sixty) minutes after the initiation of the reaction, the reaction mixture was sampled for a GLC analysis. After the completion of the reaction, samples of the reaction mixture were transferred into separatory funnels and were acidified there with hydrochloric acid to pH 7. The heterogeneous catalyst was filtered out, and the initial alcohol and the resulting aldehyde were multiply extracted with chloroform with separation of the organic and aqueous phases.

The alcohols and the corresponding aldehydes in the organic phase were identified by GLC on a Model 3700 chromatograph (capillary column SE-54, 25 m) in a temperature-programmed mode (temperature rise to 100°C over 4 min and then to 280°C at a rate of 20 K/min).

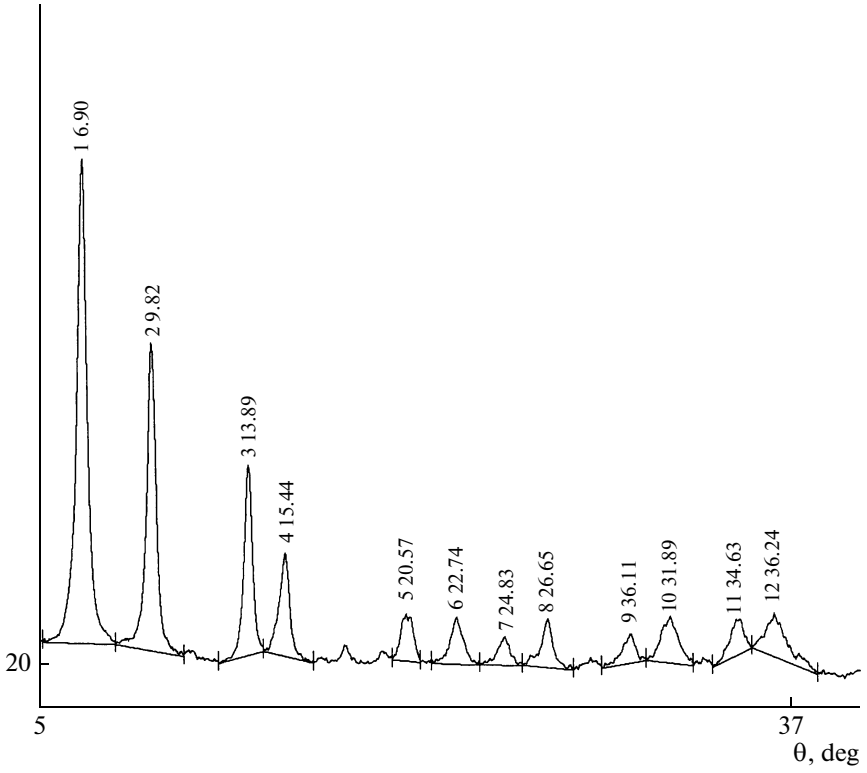
RESULTS AND DISCUSSION

The MOF-5 sample that was synthesized to be platinized had a high degree of crystallinity, which persisted up to 330°C, and a large specific surface area (Table 1). The X-ray diffraction pattern of this MOF structure (figure) coincided with the diffraction pattern calculated for MOF-5 [12]. The metal-organic framework retained its crystallinity after the introduction of platinum. The catalytic activity of the 5% Pt/MOF-5 system was studied in the aerobic oxidations of piperonyl alcohol into piperonal and of vanillyl alcohol into vanillin.

Piperonyl Alcohol Oxidation



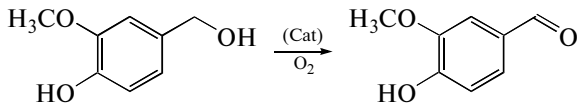
In piperonyl alcohol oxidation with air, the activity and selectivity of the MOF-5–supported catalyst was compared to those of the conventional Pt/C catalyst. It is clear from the experimental data listed in Table 2 that the activity of the 5% Pt/MOF-5 catalyst is com-



X-ray diffraction pattern of synthesized MOF-5.

parable with the activity of the 9% Pt/SKT-4A catalyst, which has a higher platinum content. Both catalysts show ~100% selectivity toward the target product.

Vanillyl Alcohol Oxidation



Vanillin synthesis is an industrial-scale process, so it is of interest to compare the catalytic performances of the catalytic systems in this reaction.

It is clear from the data presented in Table 3 that the MOF-5–based system is much less active than the conventional 9% Pt/SKT-4A catalyst. Note, however, that the Pt content of the MOF-supported catalyst is almost two times lower (5 wt %) and the target product selectivity of this catalyst is several times higher. In addition, only 0.2% resinous products were observed in the catalysate obtained with the MOF-supported catalyst.

Note also that the Pt/MOF-5 system retains its catalytic activity in vanillyl alcohol oxidation under static conditions over 10 reaction cycles, without platinum being washed out into the solution.

Thus, it was demonstrated that the Pt/MOF-5 is an efficient catalyst for obtaining vanillin and piperonal via the aerobic oxidation of benzyl alcohol derivatives. The activity and selectivity of Pt/MOF-5 is comparable with those of the conventional heterogeneous catalyst Pt/C.

Table 3. Catalyst testing data for vanillyl alcohol oxidation at 80°C and an alcohol/catalyst ratio of 20 (on-stream time of 1 h)

Catalyst	Reaction mixture composition, wt %		Resins, wt %	Conversion, %	Selectivity, %
	vanillin	alcohol			
9% Pt/SKT-4	90.0	5.2	4.8	94.8	94.9
5% Pt /MOF-5	24.3	75.5	0.2	24.5	99.2

REFERENCES

1. Freidlin, L.Kh. and Litvin, E.F., *Problemy kinetiki i kataliza* (Topics in Kinetics and Catalysis), vol. 11: *Nauchnye osnovy podbora katalizatorov* (Principles of Catalyst Selection), Moscow: Nauka, 1966, p. 162.
2. Opelt, S., Turk, S., Dietzsch, E., Henschel, A., Kaskel, S., and Klemm, E., *Catal. Commun.*, 2008, vol. 9, p. 1286.
3. Czaja, A.U., Trukhan, N., and Mueller, U., *Chem. Soc. Rev.*, 2009, vol. 38, p. 1284.
4. Llabres i Xamena, F.X., Abad, A., Corma, A., and Garcia, H., *J. Catal.*, 2007, vol. 250, no. 2, p. 294.
5. (a) Beletskaya, I.P. and Cheprakov, A.V., *Chem. Rev.*, 2000, vol. 100, no. 8, p. 3009; (b) Kustov, L.M. and Beletskaya, I.P., *Ross. Khim. Zh.*, 2004, vol. 48, no. 6, p. 3.
6. Tkachenko, O.P., Kustov, L.M., Tarasov, A.L., Klementiev, K.V., Kumar, N., and Murzin, D.Yu., *Appl. Catal., A*, 2009, vol. 359, p. 144.
7. US Patent 6184421, 2001.
8. US Patent 3673257, 1970.
9. Isaeva, V.I., Tkachenko, O.P., Mishin, I.V., Kapustin, G.I., Kostin, A.A., Klementiev, K.V., and Kustov, L.M., *Stud. Surf. Sci. Catal.*, 2008, vol. 174, p. 463.
10. Klyachko-Gurvich, A.L., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1961, p. 1884.
11. Sabo, M., Henschel, A., Frode, H., Klemm, E., and Kaskel, S., *J. Mater. Chem.*, 2007, vol. 17, p. 3827.
12. Huang, L., Wang, H., Chen, J., Wang, Z., Sun, J., Zhao, D., and Yan, Y., *Microporous Mesoporous Mater.*, 2003, vol. 58, p. 105.