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1,3-Cyclohexadiene Hydrogenation in the Presence of a Palladium-Containing Catalytic System Based on an MOF-5/Calixarene Composite

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Abstract—A palladium-containing material based on the new metal-organic framework structure MOF-5/20% calix[4]arene have been synthesized and characterized by physical and chemical methods for the first time. The catalytic activity of the 3% Pd/MOF-5/20% calix[4]arene composite in partial 1,3-cyclohexadiene hydrogenation into cyclohexene is fairly high and is comparable with that of the 5% Pd/C reference catalyst.

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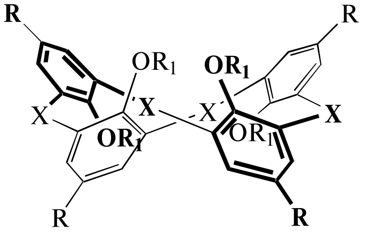
Metal-organic frameworks (MOFs) are crystalline porous materials formed by multidentate organic ligands and metal ions or clusters. An analogy is often drawn between MOFs and aluminosilicate zeolites—another class of porous materials [1, 2]. MOFs indeed possess properties significant for heterogeneous catalysis, namely, a large specific surface area and uniform pore and cavity size distributions. The unique feature of the MOFs differentiating them from metal oxides is the absence of inaccessible ("dead") spaces [3] like those existing in zeolites. Due to the large specific surface area of the MOF structures, the MOF-based catalysts can have a high volume concentration of active sites ensuring an extraordinarily high degree of dispersion of the metal [4]. MOF-5 is the metal-organic framework structure that has most extensively been studied to date. It consists of Zn_4O clusters and terephthalate (1,4-benzenedicarboxylate) bridging ligands.

Some authors note the vague resemblance between calix[n]arenes and MOFs, including the existence of a macrocycle cavity suitable for host–guest interaction [5] and, in some cases, the formation a supramolecular structure having ordered one-dimensional channels (calix[8]arenes) [6]. Calix[n]arenes have attracted keen attention from researchers owing to their excellent extraction and coordination properties. Note that calix[n]arenes are mentioned in the literature as convenient objects for modeling of catalytic systems [6, 7].

We have recently synthesized new materials based on the 1,4-benzenedicarboxylate framework MOF-5 and calix[4]arenes with different structures [8]. It was demonstrated that the systems containing 5–20 wt % calixarene are characterized by a high degree of crystallinity and a large specific surface area. The purpose of this study is to understand whether these composites are usable as supports for palladium-containing catalysts. The object of this study is the system containing, in the cavities of the MOF-5 structure, 20 wt % calix[4]arene in the cone conformation (Fig. 1). The palladium-containing system 3% Pd/MOF-5/20% calix[4]arene was prepared by incipient-wetness impregnation. This palladium content of the composite is equal the catalytic metal content of the heterogeneous catalysts commonly used in hydrogenation (1–5 wt %). Note that the literature contains no information concerning the synthesis of Pd/MOF-5/calix[4]arene composites and their catalytic applications. The catalytic performance of the synthesized material was studied in 1,3-cyclohexadiene (CHD) hydrogenation as a model reaction. The parameters of



$R = H$, $R_1 = CH_2COOH$, $X = CH_2$

Fig. 1. Structure of calix[4]arene introduced into MOF-5.

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

Support	S_{BET}, m^2/g	Total pore volume, cm^3/g	Micropore volume V_{micro}, cm^3/g	Mesopore volume V_{meso}, cm^3/g
Carbon SKT-4A	1269	0.66	0.54	0.12
MOF-5/20% calix[4]arene	550	0.29	–	–

this reaction will be compared with the characteristics of the same reaction over the conventional hydrogenation catalyst Pd/C.

EXPERIMENTAL

Preparation of the Catalysts

3% Pd/MOF-5/20% calix[4]arene. The MOF-5/20% calix[4]arene composite was obtained by direct mixing [8]. A mixture of terephthalic acid (0.507 g, 3.5 mmol), calix[4]arene (0.11 g), and triethylamine (0.85 ml) was dissolved in 40 ml of *N*,*N*-dimethylformamide (DMF) at room temperature. Simultaneously, $Zn(OAc)_2 \cdot 2H_2O$ (1.699 g, 7.74 mmol) was dissolved in 50 ml of DMF. The solution of the zinc salt was gradually added to the solution of the organic reactants (0.5 h, 20°C). The resulting white crystalline precipitate was separated by centrifugation, washed with DMF (three times, 10-ml portions), and dried in vacuo (10^{-3} Torr, 200°C). Calix[4]arene to be introduced into the MOF cavities was synthesized using a standard procedure [9].

The Pd-containing catalyst (3% Pd/MOF-5/calix[4]arene) was prepared by the incipient-wetness impregnation of the MOF composite with a $Pd(OAc)_2$ solution in absolute chloroform in a similar way to the Pd/MOF-5 system (in the latter case, MOF-5 was impregnated with a $Pd(acac)_2$ solution) [10]. The solution of $Pd(OAc)_2$ (0.032–0.050 g, 0.050–0.074 mmol) in chloroform (0.30 ml) was added slowly to a pre-evacuated MOF-5 sample (0.5 g), and the solvent was then distilled off under continuous stirring. Next, the $Pd(OAc)_2$/MOF-5/calix[4]arene system was pumped at 20°C for 4 h and at 150°C for another 4 h.

5% Pd/C. The reference catalyst was prepared by impregnating the support—activated carbon SKT-4A (1 g, $S_{BET} = 1269$ m^2/g)—with an aqueous solution of H_2PdCl_4 (1 ml) containing 0.015 g/ml Pd. The product was dried in air at 90°C (3 h) and was then calcined at 300°C (2 h) in flowing air (10 ml/min). Before performing the reaction, the catalyst samples were reduced in flowing hydrogen (10 ml/min) at 200°C for 1 h.

The specific surface area of the supports was calculated from nitrogen adsorption data using the BET equation by the procedure described by Klyachko-Gurvich [11]. X-ray diffraction patterns were obtained on a DRON 3M diffractometer using $CuK_{\alpha 1}$ radiation (λ = 1.54 Å), the Bragg–Brentano reflection technique, and the Debye–Scherrer transmission geometry. Infrared diffuse reflectance spectra were recorded at room temperature on a Nicolet Protégé 460 spectrometer. Before examination, the samples were pumped at 200°C for 1 h. For a satisfactory signal-to-noise ratio, 500 spectra were coadded. CO (10 Torr) was adsorbed at room temperature and was then desorbed in vacuo. Deuterated acetonitrile CD_3CN was adsorbed at room temperature and a saturation vapor pressure of 96 Torr.

Performing the Reaction in a Flow Reactor

CHD was fed into the reactor using a syringe dosing pump. The catalyst charge was 0.1 cm^3. The H_2/CHD ratio was 2.5. The reaction was carried out at atmospheric pressure, $T = 40–170$°C, and a CHD liquid hourly space velocity (LHSV) of 2–12 h^{-1}. The catalysate was analyzed on a Model 3700 chromatograph (Soviet Union) using a capillary column (25 m) and the SE-54 phase in the isothermal mode at 80°C.

RESULTS AND DISCUSSION

The initial composite system, MOF-5/20% calix[4]arene, is characterized by a large specific surface area of 550 m^2/g (Table 1) and a high degree of crystallinity (Fig. 2). According to X-ray diffraction data, the crystallinity of the MOF structure persists both after the introduction of Pd and after the catalytic reaction.

The IR spectrum of acetonitrile-d^3 adsorbed on the MOF-5/20% calix[4]arene composite (Fig. 3) indicates the presence of strong Lewis acid sites (Zn^{2+}). The shift of the C≡N stretching frequency for adsorbed acetonitrile-d^3 (2306 cm^{-1}) relative to the same frequency for gaseous acetonitrile (2253 cm^{-1}) is 53 cm^{-1}.

As follows from the IR spectra of adsorbed CD_3CN, the introduction of 3 wt % Pd into MOF-5/20% calix[4]arene does not affect the strength of the Lewis acid sites (Fig. 3).

The electronic state of palladium in 3% Pd/MOF-5/20% calix[4]arene was studied by IR spectroscopy of adsorbed CO. The IR spectra of adsorbed CO (Fig. 4) show stretching bands typical of carbon monoxide adsorbed on palladium [12, 13]. The band at 2128 cm^{-1} is due to CO adsorbed on Pd^+ sites in a linear configuration. The band at 2079 cm^{-1} is due to CO adsorbed linearly on metallic palladium. The band at 1938 cm^{-1}

Table 2. 1,3-Cyclohexadiene hydrogenation at atmospheric pressure*

Catalyst	LHSV, h^{-1}	T, °C	X, %	S, wt %	Concentration, wt %**			
					CH	benzene	CH=	1,3-CH==
3% Pd/MOF-5/20% calix[4]arene	2	40	100	0.9	99.1	–	0.9	–
	8	40	99.2	**42.2**	58.8	–	40.4	0.8
	12	40	76.8	40.1	46.0	–	30.8	23.2
	8	60	100	27.0	73.0	–	27.0	–
	8	80	100	0.4	99.6	–	0.4	–
5% Pd/C	2	40	100	2.5	97.5	–	2.5	–
	8	40	99.8	**6.5**	93.4	–	6.4	0.2
	12	40	99.1	6.8	92.4	–	6.7	0.9
	2	80	99.2	14.6	83.1	1.6	14.5	0.8
	2	160	83.6	2.2	78.0	2.7	1.8	16.4

*X is the CHD conversion and S is selectivity in terms of partial CHD hydrogenation into cyclohexene.

**CH, saturated hydrocarbons; CH=, unsaturated hydrocarbons; 1,3-CH==, CHD.

pertains to bridging CO adsorbed on metallic palladium. CO desorption in vacuo reduces the stretching frequency for CO linearly adsorbed on metallic palladium to 2045 cm^{-1}.

In this study, we compared the 3% Pd/MOF-5/20% calix[4]arene and 5% Pd/C catalysts in terms of CHD conversion and hydrogenation selectivity. The results of these catalytic tests are presented in Table 2. In the case of the composite catalyst 3% Pd/MOF-5/20% calix[4]arene, selectivity for partial CHD hydrogenation into cyclohexene increases markedly as LHSV is raised to 8–12 h^{-1}, reaching ~40%, and decreases with increasing temperature at a fixed LHSV. Note that the cyclohexene selectivity is ~40% even for mixtures containing excess hydrogen at an H_2/CHD molar ratio of 2.5.

For 5% Pd/C, we observed that, under severe reaction conditions (LHSV = 2 h^{-1}, $T > 80°C$), partial CHD hydrogenation is accompanied by cyclohexene disproportionation into benzene and cyclohexane. No benzene results from CHD hydrogenation over 3% Pd/MOF-5/20% calix[4]arene under the same conditions. No side disproportionation reaction was also observed in cyclohexene hydrogenation over the palladium-containing system 3% Pd/MOF-5 [14]. The

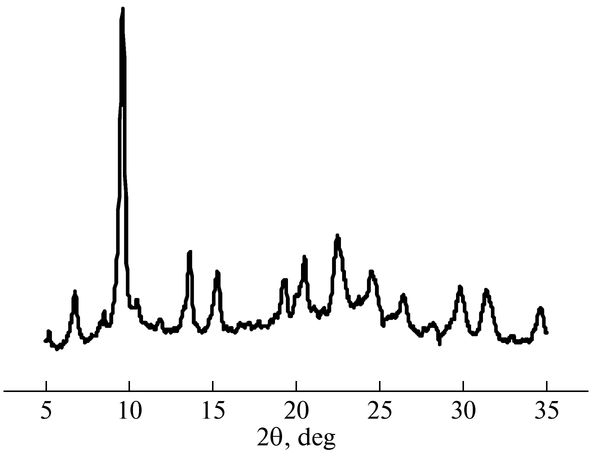


Fig. 2. X-ray diffraction data for the MOF-5/calix[4]arene composite.

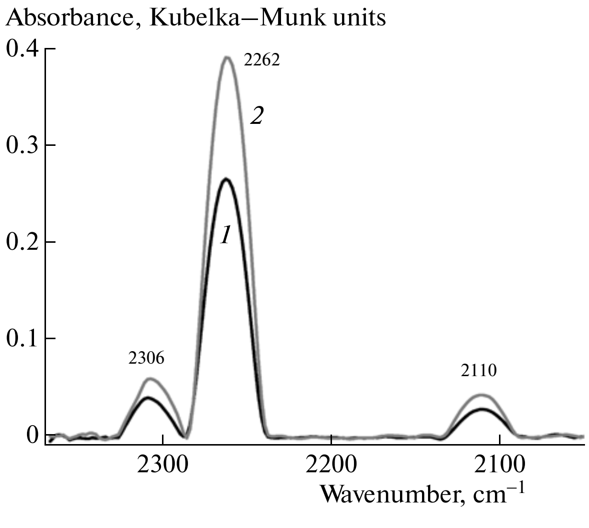


Fig. 3. IR spectra of CD_3CN adsorbed on (*1*) MOF-5/20% calix[4]arene and (*2*) 3% Pd/MOF-5/20% calix[4]arene.

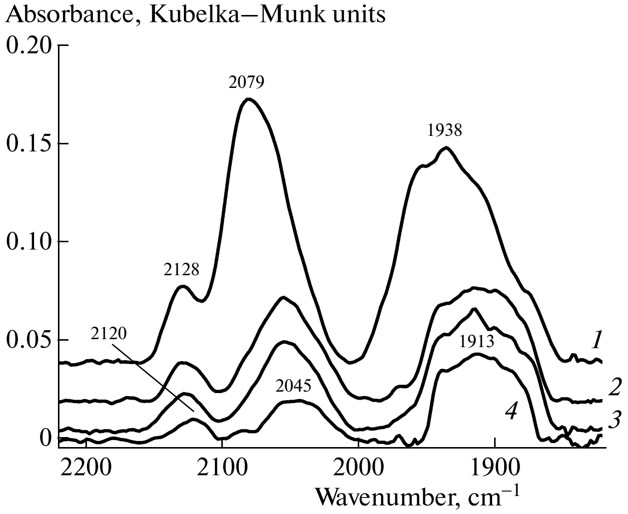


Fig. 4. IR spectra of CO adsorbed on 3% Pd/MOF-5/20% calix[4]arene recorded (*1*) after adsorption and (*2–4*) after adsorption followed by pumping at 23°C for (*2*) 1 and (*3*) 2 h and (*4*) thereafter at 50°C for 30 min.

above experimental data point to the advantages of the highly ordered MOF and MOF/calixarene systems over activated carbons with an irregular structure as supports for heterogeneous catalysts [15].

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