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Structure-Function Relationships in Fructose Dehydration to 5-Hydroxymethylfurfural under Mild Conditions by Porous Ionic Crystals Constructed with Analogous Building Blocks

Takumi Yamada,^[a] Keigo Kamata,^[b] Eri Hayashi,^[b] Michikazu Hara,^[b] and Sayaka Uchida*^[a]

Abstract: 5-Hydroxymethylfurfural (HMF) is an important bio-based chemical, which has been recognized as a key platform chemical for furan-based polymers, biomass-derived fuels, fine chemicals, and pharmaceuticals. Catalytic conversion of fructose into HMF is an important reaction, and the development of an efficient heterogeneous catalysts with high selectivity towards HMF is highly desired. In this study, several porous ionic crystals with a Keggin-type $[PW_{12}O_{40}]^{3-}$ polyoxometalate and а macrocation [Cr₃O(OOCCH₂CN)₆(H₂O)₃]⁺ as building blocks are synthesized, and the structures are solved by single crystal X-ray diffraction analysis. The catalytic activities are basically dependent on the porosity, and the compound with a mesopore (aperture: 3 nm × 2 nm) showed the highest HMF yield (30% at 353 K in methanol/toluene solvent).

Biofuels are promising alternative fuels for replacement of limited fossil fuels and have fewer environmental problems. Among the current biofuel resources, 5-hydroxymethylfurfural (HMF) converted from C6 monosaccharides such as fructose is a versatile and key intermediate that is attracting much attention.^{[1-} ^{3]} Solid acid catalysts such as zeolites,^[4] sulfated zirconia,^[5] metal phosphates and phosphonates,^[6] acidic resins,^[7] and heteropolyacids^[8,9] have been reported to catalyze this reaction. A drawback with these solid acid catalysts is that they cause various side reactions, leading to by-products such as levulinic acid and formic acid. A landmark work in this research area is a biphasic system (water/methylisobutylketone modified with 2butanol) with hydrochloric acid or acidic resins: HMF is extracted spontaneously into the organic phase and undesirable side reactions are suppressed, leading to high fructose conversion (90%) and HMF selectivity (80%) at 453 K and < 3 min.^[10] On the other hand, it has been recently reported by Yi et al.[11] that a porous ionic crystal Cs₂[Cr₃O(OOCC₂H₅)₆(H₂O)₃]₂[SiW₁₂O₄₀] synthesized by one of us^[12] catalyzes the dehydration of fructose to HMF (yield 33-45%) at 403 K and 90 min, due to the mild Brønsted acid sites generated from water molecules coordinating to Cr³⁺ because of the polarizing effect due to the neighboring Keggin-type polyoxometalate (POM) (i.e., [SiW₁₂O₄₀]⁴⁻). However, the pore size of this ionic crystal (5.2 Å) is too small to

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accommodate fructose molecules, so that this reaction presumably took place on the surface of the solid particles.

We have previously reported the synthesis and crystal of structure mesoporous ionic crystal а $Cr[Cr_{3}O(OOCCH_{2}CN)_{6}(H_{2}O)_{3}]_{3}[PW_{12}O_{40}]_{2} \cdot 69H_{2}O$ with [1] а POM [PW₁₂O₄₀]³⁻ Keggin-type and macrocation а $[Cr_3O(OOCCH_2CN)_6(H_2O)_3]^+$ with polar cyano groups (CN) and water ligands.^[13] Compound I possesses one-dimensional mesopores with an aperture of 3 nm × 2 nm, and the mesoporous structure is maintained by the water of crystallization as templates. The void volume of I is 44.2% of the crystal lattice and the largest among the porous ionic crystals reported to date. While I does not contain any acidic functional groups, IR spectroscopy with pyridine as a basic probe molecule suggests the existence of Brønsted acid sites, and I shows moderate catalytic activity in allylation of benzaldehyde with allyltin in water at 353 K.^[13]

Based on the mesoporous structure of I and previous reports on fructose dehydration to HMF, we reached an idea that I may show promising performance as a catalyst for this reaction. In this work, we show that I can catalyze fructose dehydration to HMF without any apparent by-products and at mild conditions in a methanol/toluene solvent (HMF yield 30% at 353 K and 30 min). In order to prove the importance of the *mesoporous* structure, we synthesized *microporous* ionic crystals with analogous building blocks: Cr[Cr₃O(OOCCH₂CN)₆(CH₃OH)₂(H₂O)]₆[PW₁₂O₄₀]₃ ·18CH₃OH [II] and Cr[Cr₃O(OOCCH₂CN)₆(H₂O)₃]₆[PW₁₂O₄₀]₃ ·50H₂O [III]. Compounds II and III show lower catalytic activity (HMF yield ca. 10%) than I in fructose dehydration to HMF.

Compound was synthesized from L $[Cr_{3}O(OOCCH_{2}CN)_{6}(H_{2}O)_{3}](NO_{3}),$ $Cr(NO_3)_3$, and $H_3PW_{12}O_{40}$ · nH_2O in water with slight modification from our previous work.^[13] As shown in Figure 1a, POM $[PW_{12}O_{40}]^{3-}$ and macrocation $[Cr_3O(OOCCH_2CN)_6(H_2O)_3]^+$ were arranged alternately forming a ring, and a mesopore with an aperture of 3 nm × 2 nm was formed. Hydrogen-bonded water clusters served as a template to construct and maintain the mesoporous structure, and Cr³⁺ as a counter cation existed in the mesopore. Powder Xray diffraction pattern (PXRD) of I well agreed with the calculation (Figures 2a and 2b) showing that the structure of the whole bulk solid is well represented by the single crystal data.

Compound Ш was synthesized from $[Cr_{3}O(OOCCH_{2}CN)_{6}(H_{2}O)_{3}](NO_{3})$ and $H_{3}PW_{12}O_{40}\cdot nH_{2}O$ in methanol with toluene as a poor solvent for crystallization. Methanol was utilized as a solvent to construct micropores instead of mesopores, because water and methanol have two and one hydrogen atoms, respectively, to form hydrogen bonds, and methanol molecules would form a smaller hydrogen-bonded cluster as a template.^[14] IR spectrum of II contained the absorption bands of the two ionic components (see experimental section and Figures S1a, S1b, and S1d). Elemental analysis of II suggested that the macrocation and POM exist with a ratio of 6 : 3 (2 : 1) along with one Cr³⁺ as a counter cation to compensate

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the surplus anion charge. Thermogravimetry suggested that 18 CH_3OH existed as solvent molecules (Figure S2a).



Figure 1. Crystal structures of (a) I, (b)(c) II, and (d)(e) III. (c) and (e) show the void analysis of II and III, respectively, with a probe diameter of 1.2 Å and grid spacing 0.7 Å. Surface of the voids are shown in yellow. Solvent molecules are removed from the crystal structure. Gray, dark blue, and green spheres in (a), (b), and (d) show the carbon atoms, nitrogen atoms, and Cr^{3+} as counter cations, respectively. Light green, orange, and purple polyhedra in (a), (b), and (d) show the [WO₆], [CrO₆], and [PO₄] units, respectively.

The crystal structure of II along with void analysis are shown in Figures 1b and 1c, respectively. Crystallographic parameters are summarized in Table 1. Compound II possessed winding onedimensional channels along the c-axis with an aperture of ca. 1 nm. The void volume was 16.1% of the crystal lattice. While the positions of methanol solvent molecules could not be resolved by single crystal XRD (SXRD), they probably existed in the onedimensional channels. Cr3+ as a counter cation could be located in the one-dimensional channel and was disordered between two positions. Two out of the three terminal water ligands of Cr³⁺ in the macrocation were exchanged with methanol (i.e.. $[Cr_3O(OOCCH_2CN)_6(CH_3OH)_2(H_2O)]^+$). The macrocations were arranged along the a-axis, and each water ligand was hydrogenbonded to the terminal oxygen of the neighboring POM (Figure S3a). These hydrogen bonds as well as Coulomb interactions between the oppositely charged ionic components probably contribute to stabilize the crystal structure of II. PXRD of II well agreed with the calculation (Figures 2e and 2f) showing that the structure of the whole bulk solid is well represented by the single crystal data.

Compound III was synthesized from $[Cr_3O(OOCCH_2CN)_6(H_2O)_3](NO_3)$, $Cr(NO_3)_3$, $H_3PW_{12}O_{40}\cdot nH_2O$, and anhydrous MgSO₄ in an aqueous methanol solution. IR spectrum of III contained the absorption bands of the two ionic components (see experimental section and Figures S1a, S1b, and S1e). Elemental analysis of III suggested that the

macrocation and POM exist with a ratio of 6:3 (2:1) along with one Cr³⁺ as a counter cation to compensate the surplus anion charge. Therefore, **II** and **III** have the same chemical formula and can be considered as polymorphs. We have previously reported that ionic crystals based on POMs often show polymorphism because of the flexible crystal structure due to Coulomb interaction, which works isotropically and in a long range.^[15] Elemental analysis of **III** showed that the amount of Mg is negligible (0.25wt%). However, crystals did not appear without the addition of anhydrous MgSO₄, which probably acts as a buffer to control the water content in the synthetic solution. Thermogravimetry suggested that 50 H₂O existed as solvent molecules (Figure S2b).

Table 1.	Crystallographic data
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Crystal system	Triclinic	Monoclinic		
Space group	<i>P</i> -1	C2		
Unit cell	a = 17.116(17) b = 18.776(19) c = 21.76(2) $\alpha = 112.649(6)$ $\beta = 89.983(16)$ $\gamma = 117.265(4)$	a = 27.941(4) b = 19.1673(19) c = 13.034(2) $\beta = 117.270(6)$		
Volume	5603(9)	6204.6(16)		
Z	2	2		
D_{calc} (g cm ⁻³)	2.588	2.431		
F(000)	3909.84	4086.08		
h, k, l range	–19/19, –21/21, –23/24	-33/26, -30/32, -27/27		
μ (Mo K α) (mm ⁻¹)	12.971	11.727		
$R_1(l > 2\sigma(l))$	0.1457	0.0452		
wR₂ (all data)	0.4360 0.1446			
GOF on F ²	1.201	1.100		

The crystal structure of III along with void analysis are shown in Figures 1d and 1e, respectively. Crystallographic parameters are summarized in Table 1. Compound III possessed winding one-dimensional channels along the *c*-axis with minimum and maximum apertures of ca. 0.7 nm and 1.3 nm, respectively. The void volume was 30.6% of the crystal lattice. Thus the porosity decreased in the order of I (aperture 3 nm × 2 nm, void volume 44.2%) > III (aperture 1.3 nm (max) and 0.7 nm (min), void volume 30.6%) > II (aperture 1 nm, void volume 16.1%). SXRD could locate 42 out of the 50 solvent water molecules, which existed in the one-dimensional channel. Cr³⁺ as a counter cation was also located in the one-dimensional channel. The macrocations were arranged along the c-axis, and cyano groups of the neighboring macrocations were aligned parallel to each other with C-C or C-N distances of 3.487-3.617 Å, suggesting weak dispersion force between the cyano groups. Such kind of interaction with vinyl groups has been observed in our previous work with a porous ionic crystal of [Cr₃O(OOCCH=CH₂)₆(H₂O)₃]₃ [PW₁₂O₄₀]·15H₂O.^[16] PXRD of **III** well agreed with the calculation

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(Figures 2g and 2h) showing that the structure of the whole bulk solid is well represented by the single crystal data.



Figure 2. Powder XRD patterns of (a) I (calc), (b) I (exp, before reaction), (c) I (exp, after reaction), (d) I (exp, after evacuation at rt), (e) II (calc), (f) II (exp), (g) III (calc), and (h) III (exp).

Table 2. Fructose dehydration to HMF with various catalysts^[a]

Entry	Catalyst	Temp [K]	Time [min]	Conv. ^[d] [%]	HMF yield ^[e] [%]
1	I	353	15	30	10
2	I	353	30	35	30
3	I	373	15	35	30
4	I (2 nd run)	353	30	35	25
5	l (3 rd run)	353	30	30	22
6	II	353	30	15	5
7	II	353	75	15	10
8	III	353	30	15	12
9	K ₃ PW ₁₂ O ₄₀ ^[b]	353	30	5	< 2
10	[Cr ₃ O(OOCCH ₂ CN) ₆ (H ₂ O) ₃](NO ₃) ^[b]	353	30	5	5
11	no catalyst ^[c]	353	30	< 2	< 2

^[a]Reaction conditions: Fructose (0.4 g, 2.2 mmol), naphthalene (0.5 mmol, internal standard), anhydrous MgSO₄ (0.6 g, added to remove excess water in the reaction solution), and catalysts (0.2 g) in methanol/toluene (5 mL/10 mL). ^[b]Partial dissolution was observed. ^[c]Anhydrous MgSO₄ was added to the reaction solution. ^[d]Amount of fructose was analyzed as follows: The solution was filtered and the filtrate was evaporated to dryness. Water was added to the residue, the solution was filtered again, and the filtrate was collected and injected into the HPLC system with butanol as an internal standard. ^[e]Only HMF was detected as a product. The discrepancy between fructose conversion and HMF yield is probably due to fructose adsorbed in the catalysts. We attempted to analyze the amount of fluctose adsorbed in the catalysts by dissolving the catalyst in methanol followed by evaporation to dryness and dissolving the residue in water. However, unknown HPLC peaks, which overlapped with fructose and the internal standard, were observed.

Table 2 summarizes the results of fructose dehydration to HMF with I as a solid catalyst. A mixed solution of methanol : toluene = 1 : 2 (v/v) was chosen as a reaction solvent. Methanol is necessary to dissolve fructose into the reaction solution and toluene is added to prevent dissolution of the solid catalyst. Temperature programmed desorption mass spectrometry (TPD-MS) of the spent catalyst I showed that methanol and toluene were absorbed in and excluded from the solid bulk, respectively. Anhydrous MgSO₄ is added to adsorb excess water, which formed by the dehydration reaction of fructose, otherwise the solid catalyst would become pasty and the reaction would stop. The reaction did not proceed without a catalyst (entry 11), and ionic components showed low activities (entries 9 and 10). Notably, [Cr₃O(OOCCH₂CN)₆(H₂O)₃](NO₃) was slightly active (entry 10, HMF yield 5%), suggesting that mild Brønsted acid sites generated from water molecules coordinating to Cr3+ might exist as in ref. 11. A maximum HMF yield of 30% was obtained after 30 min at 353 K (entries 1 and 2). Note that products other than HMF (cf. levulinic acid and methyl levulinate) were not observed under this reaction condition (see ¹H-NMR of the reaction product, Figure S4). We assume that the high HMF selectivity is due to the mild acidity,^[11] which prevents further hydrolysis to levulinic acid. PXRD pattern of I after the reaction fairly agreed with that before the reaction (Figures 2b and 2c), showing that the mesoporous structure is maintained under the reaction condition. The maximum HMF yield of this reaction at 353 K was 30% (30 min), which slightly decreased upon prolongation of reaction time. Gas chromatography mass spectrometry (GC-MS) suggested the formation of polymerized products.

Furthermore, I can be easily recovered from the reaction solution by filtration followed by washing with water to remove MgSO₄, and reused without significant loss of catalytic activity (entries 4 and 5). Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of the reaction solution showed that leaching of I into the reaction solution is < 3%. In order to prove the importance of the mesoporous structure, I was evacuated at room temperature prior to the reaction, and PXRD pattern showed that I became amorphous by this treatment (Figure 2d). The solid catalyst became pasty immediately and dissolved into the reaction solution, suggesting that the mesoporous structure of ${\bf I}$ is the key to the structural stability as well as the catalytic activity. When the reaction was carried out at a higher temperature (373 K), the reaction rate increased while the HMF yield remained almost the same (entry 3). At 383 K, byproducts due to the reaction between HMF and methanol (ether and acetal) were observed (see GC-MS data, Figure S5), and PXRD showed that the crystal structure of I changed under this reaction condition.

The results of fructose dehydration to HMF with **II** and **III** as solid catalysts are also summarized in Table 2. As for **II**, the HMF yields after 30 and 75 min at 353 K were 5 and 10%, respectively (entries 6 and 7). HMF yield did not increase further with the reaction time. The reaction rate and activity were much lower than that of **I** (HMF yield 30% at 353 K and 30 min). As for **III**, the HMF yield after 30 min at 353 K was 12%, and did not increase further with the reaction time. Therefore, the catalytic activities decreased in the order of **I** (30%) >> **III** (12%) > **II** (10%), which is in line with the porosity of the crystal structures **I** (aperture 3 nm × 2 nm, void volume 44.2%) > **III** (aperture 1.3 nm (max) and 0.7

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nm (min), void volume 30.6%) > **II** (aperture 1 nm, void volume 16.1%). These results clearly show the significance of porosity of the ionic crystals in this reaction system. In contrast, pinacol rearrangement with **I-III** as catalysts was performed: Pinacol rearrangement is a typical acid reaction, and the molecular size of pinacol ($C_6H_{14}O_2$, MW = 118) is smaller than that of fructose ($C_6H_{12}O_6$, MW = 180). The catalytic activities at 373 K were quite similar among **I-III**, suggesting that the intrinsic acidities of **I-III** are similar to each other.

In conclusion, porous ionic crystals I-III were crystallized with a Keggin-type POM $[\text{PW}_{12}\text{O}_{40}]^{3-}$ and a macrocation $[Cr_3O(OOCCH_2CN)_6(H_2O)_3]^{\scriptscriptstyle +}$ as ionic components by the appropriate choice of synthetic conditions. Compound I possessed mesopores while II and III possessed micropores, and as expected, the catalytic activities on fructose dehydration to HMF were I > II, III. The main features of the present reaction system can be summarized as follows (Figure 3): No apparent byproducts due to mild acidity, monophase and easy work-up, and reaction proceeding guickly under mild conditions (30 min at 353 K). Ongoing and future works are to increase the acidity slightly by substituting the metal center of the macrocation (e.g., $Cr^{3+} \rightarrow$ Fe³⁺)^[17] and to increase the structural stability by strengthening the Coulomb interaction among ionic components (e.g., $[PW_{12}O_{40}]^{3-} \rightarrow [SiW_{12}O_{40}]^{4-}$). If we could increase the structural stability of the porous ionic crystals and work at slightly higher temperatures, it would be possible to make use of Lewis acid sites generated from the metal center. These crystals may serve as a bifunctional catalyst with both Brønsted and Lewis acidity, and glucose as well as fructose may be used as a reactant for HMF production.[18]



Figure 3. Schematic illustration of the catalytic conversion of fructose to HMF with I as a catalyst.

Experimental Section

Materials: Na₂WO₄·9H₂O, Na₂HPO₄·9H₂O, Cr(NO₃)₃·9H₂O, anhydrous MgSO₄, conc. HCl, cyano acetic acid, acetone, methanol, butanol, toluene, diethylether and distilled water were purchased from Kanto Chemical Co. Inc. and used as received. H₃PW₁₂O₄₀·*n*H₂O was synthesized according to the literature.^[19] Fructose, naphthalene (internal standard), 5-hydroxymethylfurfural, and levulinic acid (as reference standards) were purchased from TCI Co. Ltd. and used as received. **Synthesis**: [Cr₃O(OOCCH₂CN)₆(H₂O)₃](NO₃) was synthesized as follows:

Cr(NO₃)₃·9H₂O (54 g, 0.14 mol) and cyano acetic acid (27 g, 0.32 mol) were dissolved in 300 mL of acetone, and the solution was stirred at 323 K for 6 h. The solution was concentrated by evaporation, water was added as a poor solvent, and [Cr₃O(OOCCH₂CN)₆(H₂O)₃](NO₃) was obtained as a green powder (21 g, yield 90% based on cyano acetic acid). Compound I was synthesized as follows with slight modification from our previous work:^[13] [Cr₃O(OOCCH₂CN)₆(H₂O)₃](NO₃) (2.8 g, 3.6 mmol) was dissolved in 200 mL of water followed by filtration. Cr(NO₃)₃·9H₂O (4.0 g, 10 mmol) and H₃PW₁₂O₄₀·nH₂O (5.0 g, 1.7 mmol) were dissolved in a minimum amount of water and added slowly to the filtrate. Green crystals of I were obtained after 24 h (6 g, yield 55% based on $H_3PW_{12}O_{40} \cdot nH_2O$). Compound н was synthesized follows: as [Cr₃O(OOCCH₂CN)₆(H₂O)₃](NO₃) (0.2 g, 0 25 mmol) and H₃PW₁₂O₄₀·nH₂O (1.0 g, 0.34 mmol) were dissolved into 50 mL of methanol with stirring at 333 K. The solution was cooled to rt (room temperature) followed by the addition of 50 mL of toluene as a poor solvent. Green crystals of II were obtained after 24 h (0.22 g, yield 38% based on [Cr₃O(OOCCH₂CN)₆(H₂O)₃](NO₃)). Cr³⁺ as a counter cation probably formed by the solvolysis of [Cr₃O(OOCCH₂CN)₆(H₂O)₃]⁺ in hot methanol. IR: 1656 $\nu_{asym}(OCO)$, 1436 $\nu_{asym}(CH)$, 1382 $\nu_{sym}(OCO)$, 1079 $\nu_{asym}(P-O)$, 981 vasym(W=O), 897 vasym(W-Oc-W), 814 vasym(W-Oe-W), 597 vasym(Cr3-O). Elemental analysis (%) calcd for II: C 10.89, H 1.01, N 3.81, Cr 7.47, P 0.70, W 50.01; found: C 10.54, H 0.79, N 3.83, Cr 7.47, P 0.70, W 49.05. Prior to the elemental analysis, II was pretreated at 323 K under vacuum to remove the methanol solvent molecules. Compound III was synthesized as follows: [Cr₃O(OOCCH₂CN)₆(H₂O)₃](NO₃) (0.2 g, 0.25 mmol), MgSO₄ (0.6 g, 5 mmol), and Cr(NO₃)₃·9H₂O (0.2 g, 0.5 mmol) were added to 100 mL of an aqueous methanol solution (25vol%) with stirring at rt. To the solution, $H_3 PW_{12} O_{40} \cdot \textit{n} H_2 O$ (1.0 g, 0.34 mmol) was added with stirring. Green crystals of III were obtained after 24 h and washed with water (0.53 g, yield 89% based on [Cr₃O(OOCCH₂CN)₆(H₂O)₃](NO₃)). IR: 1657 $v_{asym}(OCO)$, 1439 $v_{asym}(CH)$, 1381 $v_{sym}(OCO)$, 1080 $v_{asym}(P-O)$, 981 vasym(W=O), 898 vasym(W-Oc-W), 818 vasym(W-Oe-W), 595 vasym(Cr3-O). Elemental analysis (%) calcd for III: C 9.92, H 0.83, N 3.86, Cr 7.56, Mg 0, P 0.71, W 50.65; found: C 10.12, H 0.81, N 3.79, Cr 7.25, Mg 0.25, P 0.71, W 49.62. Note that while the amount of Mg in III is negligible, crystals do not appear without the addition of anhydrous MgSO4. Prior to the elemental analysis, III was pretreated at 323 K under vacuum to remove the water of crvstallization. Single-Crystal X-ray Diffraction (SXRD) Analysis: X-ray diffraction data

of II and III were collected at 93 K with a CCD 2-D detector by using Rigaku Saturn diffractometer with graphite monochromated Mo Ka radiation. Structures were solved by direct methods (SHELX97), expanded using Fourier techniques, and refined by full-matrix least squares against F² with the SHELXL-2014 package. Tungsten, chromium, and phosphorous atoms were refined anisotropically. Chromium as a counter cation, oxygen, carbon, and nitrogen atoms were refined isotropically. Hydrogen atoms were not included in the model. Thermogravimetry suggested the existence of 18 CH₃OH and 50 H₂O as solvent molecules in II and III, respectively. Methanol solvent molecules in **II** were not located with SXRD. 42 out of the 50 water of crystallization in III could be located with SXRD. Void analysis was carried out by a Mercury structure visualization software (CCDC) with a probe radius of 1.2 Å and approximate grid spacing of 0.7 Å. Crystal data for II: triclinic, P-1, a = 17.116(17), b = 18.776(19), c = 21.76(2), α = 112.649(6), β = 89.93(16), γ = 117.265(4), V = 5603(9), Z = 2, R1 = 0.1457, wR2 = 0.4360, GOF = 1.201. Crystal data for III: monoclinic, C2/c, a = 27.941(4), b = 19.1673(19), c = 13.034(2), $\beta = 117.270(6)$, V = 10.0006204.6(16), Z = 1, $R_1 = 0.0452$, $wR_2 = 0.1446$, GOF = 1.100. CCDC-1905293 and 1905294 contain the crystallographic data for II and III, respectively.

Characterization: Combustion analysis (Elementar, vario MICRO cube) was used for the quantitative analysis of C, H, and N. Inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent Technologies, ICP-OES720) was used for the quantitative analysis of chromium, magnesium, phosphorous, and tungsten. Prior to the ICP-OES measurements, ammonium hydroxide solution (1 mL) was added to ca. 10

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mg (accurately weighed) of II or III to dissolve the solid completely into water (100 mL), FT-IR spectra were measured by the KBr pellet method with a JASCO FT/IR 4100 spectrometer (JASCO) equipped with a TGS detector. Thermogravimetry was conducted with a Thermo Plus 2 thermogravimetric analyzer (Rigaku) with α-Al₂O₃ as a reference under a dry N₂ flow (100 mL min⁻¹) in the temperature range of 298–773 K and an increasing rate of 10 K min-1. Powder XRD patterns were measured with a New advance D8 X-ray diffractometer (Bruker) by using Cu $K\alpha$ radiation $(\lambda = 1.54056$ Å, 40 kV-40 mA) at 1.8 deg min⁻¹. Catalytic Reaction: Reaction was carried out in a glass reactor equipped with a magnetic stirrer. In a typical run of fructose dehydration, a mixture of fructose (0.4 g, 2.2 mmol), naphthalene (0.5 mmol, internal standard), anhydrous MgSO₄ (0.6 g, added to remove excess water in the reaction solution), and catalysts (I-III 0.2 g, 0.015-0.020 mmol) in methanol/toluene (5 mL/10 mL) was stirred under air at 353-373 K. The amounts of products (HMF and levulinic acid) were followed by gas chromatography using a GC-2014 (Shimadzu) fitted with a TC-WAX (GL Sciences) or HP-5 (Agilent J&W) capillary column and a flame ionization detector. The reaction solution (with the solid catalyst) was sampled periodically and injected directly into the GC system. Gas chromatography mass spectrometry (GC-MS) was conducted with a GCMS-QP2010 SE (Shimadzu) to check the possible formation of by-products (5-dimethoxymethyl-2-furylmethanol and 5-methoxymethylfurfural). The amount of reactant (fructose) was followed by high-performance liquid chromatography (HPLC) using a Hitachi Chromaster 5450 (Hitachi) fitted with a Gelpack GL-C610-S (Hitachi Chemical) or a Inertsil ODS-3 (GL Sciences) with pure water as eluent and a RI detector. Prior to the HPLC analysis, the reaction solution was filtered and the filtrate was evaporated to dryness. Water was added to the residue, the solution was filtered again, and the filtrate was collected and injected into the HPLC system with butanol as an internal standard. ¹H-NMR spectra of the reaction solution (CDCl₃) were recorded on a Bruker Advance III 500 MHz (Bruker). Prior to the ¹H-NMR measurement, the reaction solution was filtered, the filtrate was evaporated to dryness, and CDCl₃ was added to dissolve the residue. Temperature programmed desorption mass spectrometry (TPD-MS) of the spent catalyst I was conducted with a BELCAT (Microtrac BEL) to check the absorption of the reaction solvent molecules (methanol and toluene).

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Three porous ionic crystals were synthesized with a Keggin-type polyoxometalate and a macrocation with Cr^{3+} as building blocks. The catalytic activities of the crystals toward fructose dehydration to HMF were dependent on the porosity, and the mesoporous crystal (aperture: 3 nm × 2 nm) showed the highest HMF yield.

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Structure-Function Relationships in Fructose Dehydration to 5-Hydroxymethylfurfural under Mild Conditions by Porous Ionic Crystals Constructed with Analogous Building Blocks