

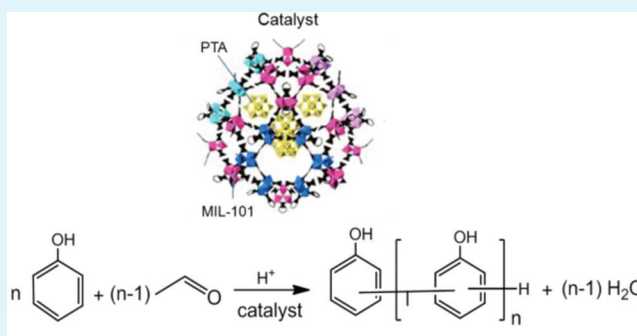
# Aldehyde-Alcohol Reactions Catalyzed under Mild Conditions by Chromium(III) Terephthalate Metal Organic Framework (MIL-101) and Phosphotungstic Acid Composites

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## Supporting Information

**ABSTRACT:** Porous materials based on chromium(III) terephthalate metal organic frameworks (MIL-101) and their composites with phosphotungstic acid (PTA) were studied as heterogeneous acid catalysts in aldehyde-alcohol reactions exemplified by acetaldehyde-phenol (A-P) condensation and dimethylacetal formation from benzaldehyde and methanol (B-M reaction). The MIL-101 was synthesized solvothermally in water, and the MIL101/PTA composite materials were obtained by either impregnation of the already prepared MIL-101 porous matrix with phosphotungstic acid solution or by solvothermic treatment of aqueous mixtures of  $\text{Cr}(\text{NO}_3)_3$  and terephthalic and phosphotungstic acids. The MIL101/PTA materials appeared to be effective catalysts for both A-P and B-M reactions occurring at room temperature, with half-lives ranging from 0.5 h (A-P) to 1.5–2 h (B-M) and turnover numbers over 600 for A-P and over 2900 for the B-M reaction, respectively. A synergistic effect of the strong acidic moieties (PTA) addition to mildly acidic Brønsted and Lewis acid sites of the MIL-101 was observed with the MIL101/PTA composites. The ability of the PTA and MIL101/PTA materials to strongly absorb and condense acetaldehyde vapors was discovered, with the MIL101/PTA absorbing over 10-fold its dry weight of acetaldehyde condensate at room temperature. The acetaldehyde was converted rapidly to crotonaldehyde and higher-molecular-weight compounds while in contact with MIL-101 and MIL101/PTA materials. The stability of the MIL-101 and MIL101/PTA catalysts was assessed within four cycles of the 1-day alcohol-aldehyde reactions in terms of the overall catalyst recovery, PTA or Cr content, and reaction rate constants in each cycle. The loss of the catalyst over 4 cycles was approximately 10 wt % for all tested catalysts due to the incomplete recovery and minute dissolution of the components. The reaction rates in all cycles remained unchanged and the catalyst losses stopped after the third cycle. The developed MIL101/PTA composites appear to be feasible for industrial catalytic applications.



**KEYWORDS:** chromium terephthalate, phosphotungstic acid, framework, composite, aldehyde-alcohol reaction, catalysis

## INTRODUCTION

Metal organic frameworks (MOF) constituted by metal ions or metal ion clusters occupying nodal framework positions coordinated with di- or multipodal organic ligands are rapidly emerging as an important family of crystalline materials to be utilized as catalysts in organic reactions.<sup>1–3</sup> Some of these MOFs are crystalline materials with the lowest framework densities and the highest pore volume known to date. Among more than 10 000 known MOF materials, there are several transition-metal MOFs that have been shown to be stable under liquid-phase reaction conditions. These include mesoporous chromium(III) terephthalate (MIL-101), which possesses acceptable resistance to water, common solvents and temperatures (up to 320 °C).<sup>4</sup> MIL-101 has a rigid zeotype crystal structure, consisting of 2.9 and 3.4 nm quasi-spherical cages accessible through windows of ca. 1.2 and 1.6 nm, respectively. Because of its high stability, MIL-101 exhibits no

detectable leaching of chromium into nonaqueous solutions, allowing its safe use in different applications. In addition, MIL-101 possesses a high density of chromium ions (three per elementary cell) with Lewis acid properties,<sup>5</sup> which can be stable under reaction conditions. The open-pore structure of MIL-101 can be further functionalized by Pd or Au nanoparticles or polyoxometalate (POM) anions, making the resulting composite materials effective in hydrogenation reactions and as oxidation catalysts.<sup>6</sup> Among other POM materials that can be utilized to functionalize the MIL-101 framework, we have taken interest in phosphotungstic acid (PTA), which was incorporated to enhance the acidic properties of the MOF.<sup>7</sup> PTA is the strongest heteropolyacid

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known.<sup>8,9</sup> There have been several reports on MIL-101 and PTA composites (MIL101/PTA) and their uses in oxidation of alkenes using molecular oxygen and aqueous hydrogen peroxide as oxidants,<sup>6</sup> H<sub>2</sub>O<sub>2</sub>-based alkene epoxidation,<sup>10</sup> Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate, liquid and gas-phase acid-catalyzed esterification (acetic acid with n-butanol, methanol dehydration),<sup>11</sup> and carbohydrate dehydration.<sup>12</sup> However, to the best of our knowledge, Baeyer condensations of aldehydes and phenols or aldehyde or ketone acetalizations in the presence of MIL-101 or MIL101/PTA composite materials have not been reported. Our current interest in the chemical conversion of aldehyde pollutants emitted by incomplete combustion of hydrocarbons or tobacco products,<sup>13</sup> and the well-documented catalysis of the Baeyer condensations by acids, provided an incentive for the inquiry into and discovery of volatile aldehyde capture by MIL101/PTA composites and subsequent kinetic studies of the aldehyde reactions reported herein. In particular, we studied the Baeyer acetaldehyde-phenol (A-P) condensation reaction known to be catalyzed by strong acids in homogeneous systems. This reaction, along with the formaldehyde-phenol condensation, is the basis for the production of novolac resins.<sup>14–18</sup> Likewise, acid-catalyzed acetalization of aldehydes with alcohols is an industrially important reaction used in preparative chemistry to protect the carbonyl group of aldehydes and ketones.<sup>19–21</sup> The acetalization exemplified by the benzaldehyde and methanol (B-M) reaction was studied herein under ambient conditions. The B-M reaction has been reported previously to occur at room temperature when catalyzed by the copper-based MOF, Cu<sub>3</sub>(BTC)<sub>2</sub> (BDC = 1,3,5-benzenetricarboxylate) and such a catalyst compared favorably with zinc chloride, zeolite, and clay.<sup>21</sup> As demonstrated in the present work, MIL101/PTA composites are even more potent catalysts than the copper-based MOF.

## EXPERIMENTAL SECTION

**Materials.** Chromium(III) nitrate nonahydrate (99%), terephthalic acid (≥99%), acetaldehyde (≥99.5%), benzaldehyde (purified by redistillation, ≥99.5%), phenol (≥99%), and methanol (anhydrous, 99.8%) were all obtained from Sigma-Aldrich Chemical Co. and were used as received. Hydrated 12-tungstophosphoric acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, PTA) (Sigma-Aldrich, >99%) was dried at 70 °C for 8 h to obtain H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O.<sup>8,9</sup> All other chemicals and solvents used were obtained from commercial sources and were of highest purity available.

**Syntheses.** *MOF MIL-101 Particle Synthesis.* Particles of MOF MIL-101 were synthesized hydrothermally, utilizing autoclave oven heat supply. Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (2.0 g, 5 mmol), terephthalic acid (0.83 g, 5 mmol) and deionized water (20 mL) were blended and briefly sonicated resulting in a dark blue-colored suspension with a pH of 2.58. The suspension was placed in a Teflon-lined autoclave bomb and kept in an oven at 218 °C for 18 h without stirring. After the synthesis and equilibration at room temperature, pH 0.5 was recorded in the suspension. After the synthesis, the MOF solids were separated from water using centrifuge (5,000 g, 10 min) and washed with water, methanol and acetone. The suspension in acetone was centrifuged and separated, the solids were placed in N,N-dimethylformamide (20 mL) and the suspension was sonicated for 10 min and then kept at 70 °C overnight. The resulting solids were separated by centrifugation, repeatedly washed with methanol and acetone, dried at 75 °C overnight and then under vacuum (1 × 10<sup>-5</sup> Torr) at ambient temperature for 2 days. Total yield of dry MIL-101 particles based on chromium was 54–63 wt %. Typical elemental analysis, found (wt %): C, 48.1; Cr, 10.3.

*Synthesis of MIL-101 and Phosphotungstic Acid (PTA) Hybrid Materials (MIL101/PTA).* The hybrid materials were synthesized by either autoclaving chromium nitrate, terephthalic acid and phosphotungstic

acid mixtures in water or by impregnating already prepared MIL-101 by aqueous solution of phosphotungstic acid in water. In a typical "joint autoclaving" synthesis (resulting MOF designated MIL101/PTA<sub>ja</sub>), Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (2.0 g, 5 mmol), terephthalic acid (0.83 g, 5 mmol), phosphotungstic acid (2 g, 0.7 mmol), and deionized water (20 mL) were blended and briefly sonicated resulting in a dark blue-colored suspension with a pH of 2.58. The suspension was placed in a Teflon-lined autoclave bomb and kept in an oven at 218 °C for 18 h without stirring. The resulting MIL101/PTA<sub>aj</sub> solids were separated by centrifugation and washed with water, methanol, acetone and then dried under vacuum until constant weight. Elemental analysis (found, wt%): C, 33.1; Cr, 7.58; W, 21.8.

In the "impregnation" method, 1 g of dry MIL-101 synthesized in autoclave as described above were suspended in aqueous solution of phosphotungstic acid (1.0 g in 20 mL). The suspension was sonicated and shaken at 300 rpm at ambient temperature for 2 days. The solids were separated by centrifugation and dried under vacuum. The resulting MOF was designated MIL101/PTA<sub>imp</sub>. Typical elemental analysis (found, wt%): C, 33.5; Cr, 9.23; W, 19.9.

Based on the elemental analysis results and molecular weight of the Keggin structure (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, 2880 Da), we estimated the PTA content of the MIL101/PTA<sub>ja</sub> and MIL101/PTA<sub>imp</sub> materials to be approximately 31 wt %.

**Capture and Condensation of Acetaldehyde Vapors on MOF Materials.** For acetaldehyde capture, borosilicate glass vials, each containing a weighed amount of dry powder of MIL-101, MIL101/PTA<sub>ja</sub>, MIL101/PTA<sub>imp</sub>, or PTA were placed next to an open Petri dish containing 10 g of liquid acetaldehyde, initially poured into the dish at -20 °C. Both the vials and the Petri dish were placed in a glass desiccator, which was sealed immediately after pouring liquid acetaldehyde into the Petri dish. Acetaldehyde rapidly evaporated from the Petri dish at room temperature, with the vapors contained inside of the sealed desiccator. The open vials were kept in the desiccator for 7 days at room temperature, while weighing the uptake periodically by withdrawing the vials from the desiccator, immediately sealing them and measuring weight. Liquid acetaldehyde was added into the Petri dish within the desiccator each time the desiccator was open for the samples withdrawal, to maintain the saturated vapor atmosphere inside the desiccator. Equilibrium weight uptake was reached after 2 days, at which point no further weight increase of the vials was observed. Small samples (0.1 mL) of liquid formed in the vials were withdrawn intermittently. Rapid change of color from white to yellow to brown to black was observed in the liquid condensed in the vials. The catalyst samples were prepared and weight uptake measured in triplicates. The weight uptake was calculated as WU, % = 100 × (sample weight after equilibration - initial sample weight)/initial sample weight.

The liquid condensed over the samples of the study was analyzed for composition by Matrix Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectrometry using an Applied Biosystems model Voyager DE-STR spectrometer, with  $\alpha$ -cyano-4-hydroxycinnamic acid (ACHCA) as a matrix. A typical MALDI-TOF spectrum overlapped with the ACHCA spectrum is shown in the Supporting Information (S-1). The condensate was further analyzed by <sup>1</sup>H NMR. Solid sample (20–30 mg) with adsorbed acetaldehyde condensate was collected and quickly placed in 1 mL of CDCl<sub>3</sub> for the adsorbed material extraction. Followed by brief sonication and vortexing, the solids were separated by centrifugation (14 000 g, 1 min) and the supernatant was analyzed by <sup>1</sup>H NMR.

**Condensation of Acetaldehyde and Phenol.** The reactions between acetaldehyde and phenol in deuterated THF (THF-*d*<sub>6</sub>) were followed by <sup>1</sup>H NMR spectroscopy, with the reactions conducted in triplicate at 25 °C. Initial concentrations of phenol and acetaldehyde were C<sub>pi</sub> = 0.165 or 0.33 M and C<sub>a0</sub> = 0.33 M, respectively. In a typical experiment, phenol (188 mg, 2 mmol) and 10 mg of powdered catalyst were dissolved/suspended in THF-*d*<sub>6</sub> (2 mL), and 38  $\mu$ L of acetaldehyde (previously chilled at 0 °C) were injected into the reaction mixture through a syringe. By varying MIL101/PTA concentration, we conducted a series of control measurements to establish an optimum catalyst concentration. Addition of 5 mg MIL101/PTA<sub>imp</sub> or MIL101/PTA<sub>ja</sub> into the initial acetaldehyde/phenol/THF-*d*<sub>6</sub>

reaction mixture resulted in 1.1 to 1.6-fold lower conversion within 30 to 60 min than with 10 mg of the corresponding catalyst species, whereas addition of 20 mg did not change the reaction rate under otherwise identical conditions. Therefore, all further studies, except for stability studies, were conducted with 10 mg catalyst addition. All catalysts were kept under vacuum ( $1 \times 10^{-5}$  Torr) prior to the reactions. The reaction mixture was kept at 25 °C in a sealed 7 mL glass vial vigorously stirred at 800 rpm by a small magnetic bar. While phosphotungstic acid completely dissolved in THF, thus resulting in a homogeneous catalytic reaction, particles of MIL-101 and MIL101/PTA formed suspensions and therefore, in these cases the catalysis was heterogeneous. Samples (350  $\mu$ L) were withdrawn from the vials intermittently, diluted 2-fold by THF- $d_8$  and centrifuged for 30 s at 14 000 g to remove the catalyst. The catalyst was returned to the vial.  $^1\text{H}$  NMR spectra of the clear supernatant were then recorded. The time point was taken as a median of the measurement duration. In the catalyst stability/reuse studies, the reactions were performed with 20 mg catalyst. The catalyst was removed from the reaction mixture by centrifugation (14 000 g, 30 s), the resulting tablet was dispersed in 3 mL THF with brief sonication and the particles were again separated by centrifugation. The procedure was repeated twice and the resulting particles were separated and dried under vacuum. The recycled catalyst was weighed and analyzed for W or Cr content by elemental analysis, conducted in duplicates. The catalyst recovery (wt%) was measured as  $100 \times \text{mass of catalyst in } n\text{-th cycle}/\text{initial mass of catalyst}$ . The performance of the catalyst in each cycle was measured as described above.

**Reaction between Benzaldehyde and Methanol.** The reactions between benzaldehyde and methanol were conducted in triplicate at temperatures ranging from 25 to 55 °C. Initial concentrations of methanol and benzaldehyde were  $C_{\text{mi}} = 23.5$  and  $C_{\text{b0}} = 0.474$  M, respectively. In a typical experiment,<sup>22</sup> dry powdered catalyst (10 mg) was suspended in a mixture of methanol (6.7 mL, 166 mmol) and benzaldehyde (340  $\mu$ L, 3.34 mmol) and the reaction commenced. All catalysts were kept under vacuum ( $1 \times 10^{-5}$  Torr) prior to the reactions. The reaction mixture was kept at 25 °C in a sealed 7 mL glass vial vigorously stirred at 800 rpm by a small magnetic bar. While phosphotungstic acid completely dissolved in methanol, particles of MIL-101 and MIL101/PTA were insoluble and no organic product such as terephthalic acid was detected to leach out by  $^1\text{H}$  NMR. Samples (200  $\mu$ L) were withdrawn from the vials intermittently and centrifuged for 30 s at 14,000 g to remove the catalyst. The catalyst was returned to the vial.  $\text{CDCl}_3$  was added to the clear supernatant and  $^1\text{H}$  NMR spectra of the resulting solutions were then recorded. In cases when the samples could not be measured immediately after withdrawal from the reaction vials, they were placed into NMR tubes immediately after separation of the catalyst and dilution by  $\text{CDCl}_3$ ; the tubes were kept on dry ice prior to the spectra measurement to quench the reaction fully. In the control experiment, no measurable change was observed in NMR spectra for 2 days in samples kept under such conditions. As in the case of the A-P reaction, by varying MIL101/PTA concentration, we attempted to establish an optimum catalyst concentration. Addition of 5 mg MIL101/PTA<sub>imp</sub> or MIL101/PTA<sub>ja</sub> into the initial B-M reaction mixture resulted in 1.5–1.8-fold lower conversion within 30–60 min than with 10 mg of the corresponding catalyst species, whereas addition of 20 mg did not change the reaction rate under otherwise identical conditions. Therefore, all further studies were conducted with 10 mg catalyst addition, except for stability studies wherein 20 mg of the catalyst were used. For recycling, the catalyst removed by centrifugation from the reaction mixture was washed with THF and chilled methanol twice, dried under a vacuum, and weighed. Other stability parameters were measured as described above for the acetaldehyde-phenol reactions.

Benzaldehyde dimethyl acetal obtained in reaction catalyzed by MIL101/PTA<sub>ja</sub> followed by the product purification by flash chromatography on silica gel<sup>22</sup> was observed to be a brownish paste material.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.38 (s, 6 H), 5.34 (s, 1 H), 7.28–7.39 (m, 3 H), 7.47–7.51 (m, 2 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  55.3, 108.9, 126.2, 127.8, 128.6, 137.3.

**Methods.** MOF surface area and pore parameters were measured using a Micromeritics' ASAP 2020 Accelerated Surface Area and

Porosimetry Analyzer (Micromeritics Corp., Norcross, GA). Thermogravimetric Analysis (TGA) was conducted using a Q5000IR thermogravimetric analyzer (TA Instruments, Inc.). Samples were subjected to heating scans (20 °C/min) in nitrogen atmosphere and in a temperature ramp mode.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were collected at  $25 \pm 0.5$  °C using a Bruker Avance-400 spectrometer operating at 400.01 and 100 MHz, respectively. Particle size distribution in MOF suspensions in methanol was measured using a ZetaPALS instrument (Brookhaven Instruments Corp.). Elemental analysis was conducted in a commercial laboratory.

## RESULTS AND DISCUSSION

**Catalyst Characteristics.** In the present study, the MIL-101 framework was synthesized solvothermally in deionized water, without the addition of toxic and corrosive hydrofluoric acid that is typically used in the standard preparation of MIL-101.<sup>4</sup> Despite the absence of HF, the crystal structure of MIL-101 in the present work corresponds to the one published previously.<sup>7</sup> Doping of the MIL-101 porous structure with PTA ions results in robust particles, which possess 4–5-fold less surface area than the original MOF due to a significant portion of the pores being occupied by the PTA. The Keggin anion of PTA is relatively large in size (ca. 1.3 nm diameter and 2.25 nm<sup>3</sup> volume) and hence, only the large cages of MIL-101 (3.6-nm diameter, Table 1) can host it. Férey et al.<sup>4</sup> showed

**Table 1. Properties of MIL-101 Metal Organic Framework and MIL101/PTA Composite Materials Synthesized by Impregnation of MIL-101 by PTA in Water (MIL101/PTA<sub>imp</sub>) or by Joint Autoclaving of the MIL-101 Components and PTA in Deionized Water (MIL101/PTA<sub>ja</sub>)**

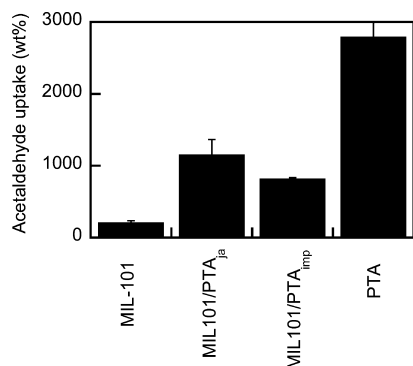
parameter	MIL-101	MIL101/ PTA <sub>imp</sub>	MIL101/PTA <sub>ja</sub>
average Keggin ion content (wt%) <sup>a</sup>	0	30.9	30.5
particle size (nm) <sup>b</sup>	396 $\pm$ 4	390 $\pm$ 11	2000–10000
average pore diameter (nm) <sup>c</sup>	3.6	2.4	2.3
BET surface area (m <sup>2</sup> /g) <sup>c</sup>	3460	1020	860

<sup>a</sup>Obtained from elemental analysis and calculations based on Keggin structure ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ). <sup>b</sup>Measured by dynamic light scattering in particle suspension in methanol or estimated from SEM measurements. <sup>c</sup>Determined from nitrogen adsorption isotherms.

that each cage can accept up to five Keggin ions, representing 50% of the volume of the cage. Crystals grown as a result of joint autoclaving of the MIL-101 components and PTA resulted in particles sized 5–25-fold larger than those of the original MIL-101 or MIL101/PTA<sub>imp</sub>. Despite the larger particle size, as shown below, the catalytic activity of the MIL101/PTA<sub>ja</sub> was virtually the same as that of the MIL101/PTA<sub>imp</sub> with its smaller particles, indicating that the mass transport through the MOF pores did not limit the activity.

**Capture and Conversion of Acetaldehyde.** MOF materials have been reported as selective adsorbents of gases as well as volatile organic compounds.<sup>23–27</sup> Because MIL-101 and MIL101/PTA composites are potential catalysts in the aldehyde and alcohol reactions, the adsorption of aldehydes, in particular, acetaldehyde ( $\text{CH}_3\text{CHO}$ ) by these materials, is of interest. Acetaldehyde is extremely volatile, with a boiling point of 20.16 °C and vapor pressure at 20 °C of 0.97 atm. The acetaldehyde concentration in cigarettes ranges from 0.5 to 1.2 mg/cigarette and 98% of the compound is found in the

vapor phase/smoke. We conducted experiments illustrating the capture of acetaldehyde from the vapor phase and its catalytic conversion into less volatile products as follows. Figure 1 shows



**Figure 1.** Equilibrium acetaldehyde uptake by MIL-101, MIL101/PTA composites, and PTA at 25 °C.

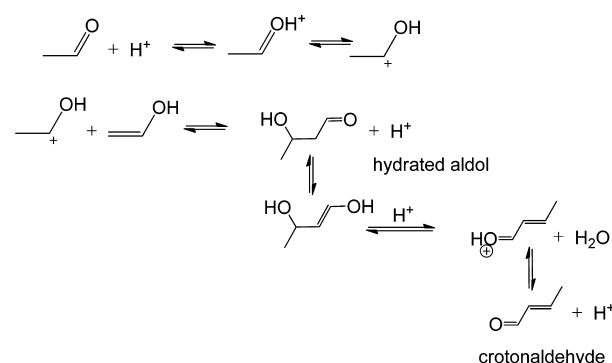
the results of the mass uptake of acetaldehyde by MIL-101 and MIL101/PTA materials. As is seen, more than 200 wt % acetaldehyde uptake by porous MIL-101 matrix was observed. The uptake was enhanced dramatically, over 4–5-fold, by doping the MOF matrix with phosphotungstic acid (PTA), resulting in MIL101/PTA<sub>ia</sub> and MIL101/PTA<sub>imp</sub> matrices being filled with liquid. The sample of solid PTA powder dissolved completely in the aldehyde condensate liquid formed around it, with an uptake exceeding 2780 wt %. It appeared that we unexpectedly discovered that PTA and PTA-doped MOF are powerful condensing agents for acetaldehyde. The liquid condensed over the samples of the study was analyzed for composition by MALDI-TOF mass spectrometry (S-1).

We observed that the initial acetaldehyde ( $m/z = 44$ , b.p. = 20 °C) was almost entirely (over 97%) converted to crotonaldehyde ( $m/z = 70$ , b.p. = 104 °C), ethyl acetate ( $m/z = 88$ , b.p. = 77.1 °C), 2-methyl-2-pentenal ( $m/z = 98$ , b.p. = 133–134 °C), 3-hydroxy-2-methylpentanal ( $m/z = 116$ , b.p. = 180 °C), unsaturated aldehyde products of metaldehyde (aldehyde tetramer) dehydration ( $m/z = 158$ , b.p. 170 °C), and other products of higher molecular weight after 2 days of equilibration with MIL101/PTA composites and PTA at room temperature. Formation of crotonaldehyde with almost complete conversion of the initial acetaldehyde was observed after only 1–2 h of the experiment with all the catalytic solids studied (S-2). Heterogeneous aldol condensation of acetaldehyde (Scheme 1) over acid catalysts, but not MIL-101 and its composites with PTA, is well-documented.<sup>28,29</sup>

The condensation is followed by polymerization, including rapid polymerization of unsaturated crotonaldehyde, in the presence of Lewis acids and other acids.<sup>30</sup> Over the course of measurements, a fraction of products with higher molecular weight (up to 1–5 kDa) appeared and grew. Notably, the boiling points of the condensation products show that these products are considerably less volatile than the initial acetaldehyde.

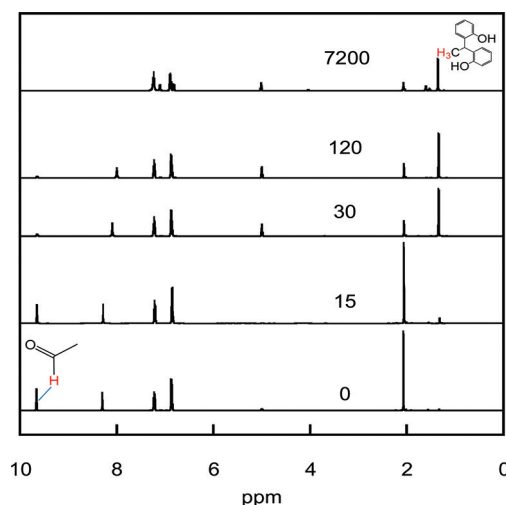
**Reaction between Acetaldehyde and Phenol.** The kinetics of the A-P condensation reaction at room temperature was studied by <sup>1</sup>H NMR. Acetaldehyde is readily miscible with most organic solvents as well as phenol at ambient temperatures. In the presence of the catalyst, the exothermic A-P condensation is extremely rapid. The rise of temperature causes

### Scheme 1. Acid-Catalyzed Aldol Condensation of Acetaldehyde



further increases in the reaction rate, which in turn cause a further temperature rise. As in the industrial processes of novolak resin production,<sup>30</sup> we needed to utilize a nonreactive diluent as a means of cooling. Deuterated tetrahydrofuran (THF- $d_8$ ), which also served as an NMR lock, appeared to be an efficient diluent under the chosen conditions, which afforded no significant spike of temperature upon addition of acetaldehyde into the reaction mixture.

Typical <sup>1</sup>H NMR spectra representing the kinetics of the acetaldehyde and phenol condensation reaction catalyzed by MIL101/PTA<sub>ia</sub> in THF- $d_8$  at 25 °C are shown in Figure 2.



**Figure 2.** Typical <sup>1</sup>H NMR spectra representing the kinetics of the acetaldehyde and phenol condensation reaction catalyzed by MIL-101/PTA<sub>ia</sub> in THF- $d_8$  at 25 °C.  $C_{a0}/C_{p0} = 2:1$  (mol/mol). Numbers denote time in minutes since the reaction commencement. Protons of aldehyde and product corresponding to NMR signals are shown in red. The positions of the triplet centered at 7.2 ppm (two meta-positioned protons in phenol and products) and multiplet centered at 6.9 ppm (two ortho- and one para-positioned protons in phenol rings) were independent of the solvents used in the present study and did not change as the reaction proceeded. It is interesting to observe that the signals corresponding to the phenolic hydroxyl groups in the areas 7.9–8.3 and 5 ppm were labile, depending on the extent of the reaction. Previous studies of the model phenol-aldehyde oligomers documented that the chemical shifts of the phenol hydroxyls are highly sensitive to the formation of intramolecular complexes, wherein phenolic and forming methylolic hydroxyls form hydrogen bonds, resulting in changes in chemical shifts of up to 3 ppm.<sup>31,32</sup> Formation and dissociation of such complexes explain the observed changes in chemical shifts.

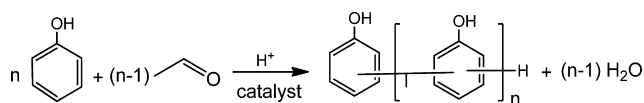
During the course of the reaction, the signal for the aldehyde group proton ( $-HC=O$ ) at 9.7 ppm disappeared, while a strong signal for the methyl groups belonging to the ethylidene links between phenolic rings of the condensate product ( $-CHCH_3$ )<sup>16</sup> appeared at 1.34 ppm and grew. These signals were a good reference for calculation of the aldehyde conversion ( $F$ ), which was obtained from the expression

$$F = \frac{\frac{1}{3}I_{1.3}}{I_{9.7} + \frac{1}{3}I_{1.3}} \quad (1)$$

where  $I_{1.3}$  and  $I_{9.7}$  are relative integrations of the corresponding methyl and aldehyde protons, respectively, measured at time  $t$ .

The overall reaction of the acetaldehyde-phenol condensation is shown in Scheme 2.<sup>32–37</sup>

### Scheme 2. Baeyer Condensation of Acetaldehyde and Phenol



In the above schematic, we deliberately did not specify the position of the methylene bridges between the phenol rings, as the ortho and para positions of the aromatic phenol ring possess the same reactivity in acid-catalyzed reactions.<sup>37</sup> It is possible, however, to obtain all-ortho phenol-acetaldehyde novolac resins with uniform constitution in other catalytic reactions such as bromomagnesium ion mediated reaction of phenol with acetaldehyde derivatives.<sup>16</sup>

From the formal definition of a reaction rate, we can define the rate of the condensation (Scheme 2) as

$$r = kC_p^\alpha C_a^\beta$$

where  $C_p$  and  $C_a$  are the phenol and acetaldehyde concentrations, respectively. Assuming that the  $-OH$  group does not react, the change in the aldehyde concentration with time is as follows

$$-\frac{dC_a}{dt} = k_1 C_{pp} C_a + k_2 C_{po} C_a$$

where  $C_{pp}$  and  $C_{po}$  are the total concentrations of the para and ortho positions, respectively, available for reaction.

Approximating  $k_1 = k_2 = k$ , we obtain

$$-\frac{dC_a}{dt} = k(C_{pp} + C_{po})C_a$$

The concentration of reacted aldehyde at a given time is  $C_{a0} - C_a$ , where  $C_{a0}$  is the initial aldehyde concentration. The total concentrations of the remaining ortho and para positions of phenol are then found from the expression  $C_{pp} + C_{po} = 3C_{pi} - C_{a0} + C_a$ , where  $C_{pi}$  is the initial phenol concentration.

The rate expression can then be written as follows

$$-\frac{dC_a}{dt} = k(3C_{pi} - C_{a0} + C_a)C_a$$

Denoting  $q = (3C_{pi} - C_{a0})$ , the above expression becomes  $((dC_a)/(q + C_a)C_a) = -kdt$ , which after integration results in the following relation

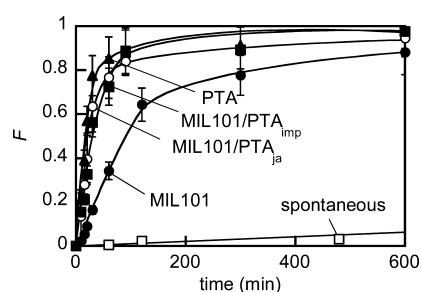
$$\ln \frac{C_a}{q + C_a} = \ln \frac{C_{a0}}{q + C_{a0}} - kqt$$

Thus, expressing the initial reaction results in the coordinates

$$P = \ln \left( \frac{q + C_a}{q + C_{a0}} \right) \text{ vs time} \quad (2)$$

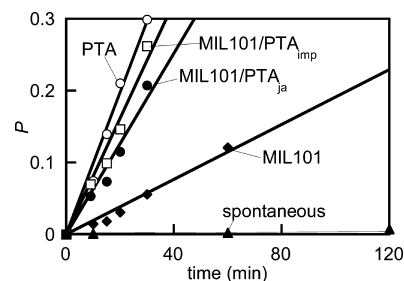
we will obtain a straight line with a slope proportional to  $kq$ , and hence, arrive at an estimate of the reaction rate constant,  $k$ .

As is seen in Figure 3, the reaction catalyzed by PTA, MIL101/PTA and MIL101 proceeded with considerable rates



**Figure 3.** Acetaldehyde conversion ( $F$ ) vs time in the acetaldehyde-phenol (A-P) condensation reaction in deuterated THF. Initial acetaldehyde and phenol concentrations were  $C_{a0} = C_{pi} = 0.33$  M.  $T = 25$  °C. For the definition of  $F$ , see eq 1.

in the first 30 min, at which point over 50% of the initial acetaldehyde was reacted. Complete conversion of acetaldehyde in the catalyzed reactions was reached within approximately 5 days. Spontaneous reaction without any added catalyst resulted in only ca. 5% conversion after 5 days at room temperature. The rate constant of the initial reaction was determined from the plot of the time-dependent acetaldehyde concentration function ( $P$ ) vs time (eq 2) as shown in Figure 4.



**Figure 4.** Initial kinetics of acetaldehyde conversion in the Baeyer acetaldehyde-phenol condensation expressed in terms of  $P = \ln((q + C_a)/(q + C_{a0}))$  vs time (eq 2).

The slope of the linear fits ( $R^2 > 0.96$  in all cases) yielded the A-P condensation rate constants,  $k$ , values of which are collected in Table 2, along with the catalyst turnover number (TON) and frequency (TOF) values. The TOF was obtained from the initial slope of the time-dependent concentration of

**Table 2. Effective Catalyst Concentration ( $C_{\text{cat}}$ ), Reaction Half-Life ( $t_{1/2}$ ), Kinetic Rate Constant, and Turnover Number (TON) and Frequency (TOF) of the Acetaldehyde-Phenol Condensation Conducted in THF- $d_8$  at 25 °C and  $C_{\text{a0}} = C_{\text{pi}} = 0.33 \text{ M}$**

catalyst	$C_{\text{cat}}$ (mM)	$t_{1/2}$ (min)	$k \times 10^3$ ( $\text{M}^{-1}\text{min}^{-1}$ )	TON <sup>d</sup>	TOF ( $\text{min}^{-1}$ )
PTA	1.7 <sup>a</sup>	16	21	170	8.5
MIL101/PTA <sub>imp</sub>	0.52 <sup>b</sup>	26	17	630	17
MIL101/PTA <sub>ja</sub>	0.52 <sup>b</sup>	31	15	630	14
MIL-101	10 <sup>c</sup>	127	1.7	30	0.18

<sup>a</sup>Concentration of PTA in solution. <sup>b</sup>Concentration of PTA in the MIL101/PTA calculated per L of the suspension. <sup>c</sup>Total concentration of Brønsted and Lewis acid sites per L of the suspension. <sup>d</sup>Calculated from the expression  $\text{TON} = C_{\text{a0}} \times F / C_{\text{cat}}$ . Here,  $F$  (eqn1) is measured at 10 h after the reaction commencement.

the converted aldehyde  $C_{\text{a}}/t = (C_{\text{a0}} - C_{\text{a0}}F)/t$  and effective catalyst concentration ( $C_{\text{cat}}$ )

$$\text{TOF} = (C_{\text{a0}}/C_{\text{cat}})(\Delta F/\Delta t) \quad (3)$$

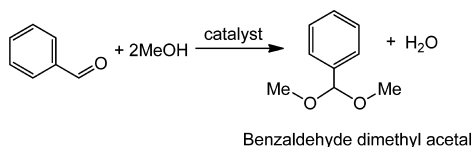
Similarly, the reaction half-life was calculated from the expression  $t_{1/2} = \ln(2)/(\Delta F/\Delta t)$ .

In the case of MIL-101 without PTA, we assumed that the total concentration of Brønsted and Lewis acid sites ( $\sim 2 \text{ mmol/g}$ )<sup>38</sup> rather than the concentration of coordinatively unsaturated sites in MIL-101 ( $0.7 \text{ mmol/g}$ )<sup>39</sup> provides an adequate estimate of the catalytic site concentration, which we utilized in the  $C_{\text{cat}}$  calculation.

As is seen in Table 2, TON and TOF values obtained with the MIL101/PTA composites exceeded those for PTA itself due to the lower effective concentration of PTA in these composites. Since the reaction rates and the TON and TOF values with MIL-101 were significantly (5–10-fold) lower than the respective parameter values for PTA, we conclude that there is a positive synergistic effect in the case of heterogeneous catalysis by the composites due to the combination of the Brønsted and Lewis sites of the MOF and the strong acidic sites of the PTA in the MIL101/PTA conjugates. The rate constant found herein for MIL101/PTA and PTA materials at 25 °C exceeded by 2–3-fold that reported in the acetaldehyde-phenol reaction catalyzed by concentrated hydrochloric acid at 30 °C in dioxane, dichloroethane, benzene, and water.<sup>36</sup> We have thus discovered a family of highly efficient catalysts for these reactions.

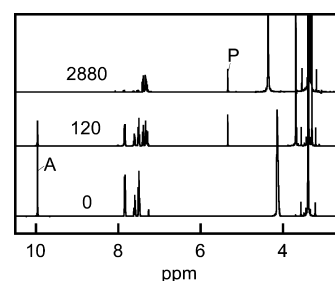
**Acetalization of Benzaldehyde with Methanol.** The reaction of acetalization of benzaldehyde (Scheme 3) using

**Scheme 3. Reaction between Benzaldehyde and Methanol**<sup>22</sup>



excess methanol with the formation of benzaldehyde dimethyl acetal was readily followed by <sup>1</sup>H NMR, which enabled measurement of the reaction kinetics (Figure 5).

As is seen in Figure 5, in the course of the reaction, the signal of the benzaldehyde proton ( $-\text{HC}=\text{O}$ ) at 9.9 ppm disappeared, while signals at 5.3 ppm for the methine group



**Figure 5.** Typical <sup>1</sup>H NMR spectra illustrating the kinetics of the reaction of benzaldehyde acetalization by methanol catalyzed by MIL101/PTA<sub>ja</sub> at 25 °C. Initial concentrations of methanol and benzaldehyde are  $C_{\text{mi}} = 23.5$  and  $C_{\text{b0}} = 0.474 \text{ M}$ , respectively. Samples of the reaction mixture withdrawn at time points indicated were dissolved in  $\text{CDCl}_3$  at 2:5 vol/vol ratio after catalyst separation. Numbers denote time in minutes since the reaction commencement. Letters A and P indicate the aldehyde (substrate) and product (acetal) signals, respectively.

located  $\alpha$  to both  $-\text{C}-\text{O}-$ , as well as the benzyl group and the six protons of the methyl groups of the dimethyl acetal at 3.3 ppm ( $-\text{CH}-\text{O}-\text{CH}_3$ ) appeared and grew. The aldehyde conversion ( $F$ ) in this reaction was obtained from the expression

$$F = \frac{I_{5.3}}{I_{9.9} + I_{5.3}} \quad (4)$$

where  $I_{5.3}$  and  $I_{9.9}$  are relative integrations of the signals belonging to the corresponding methylene and aldehyde protons, respectively, measured at time  $t$ .

While the position of the signals of the methyl groups of methanol (3.38 ppm) remained constant throughout the course of the reaction, the position of the hydroxyl group signals varied over the range 3.7–4.3 ppm (Figure 5). The chemical shift of the hydroxyl groups of methanol ( $\delta_{\text{OH}}$ ) is known to depend strongly on the extent of the hydrogen bond formation, which depends on the solvent. In particular, the chemical shift of the  $-\text{OH}$  signal in the methanol-chloroform mixtures varies with the solvent composition in the 1.5–4.6 ppm range because of the hydrogen between the methanol and the solvent.<sup>40</sup> Slight variations in the methanol concentration in  $\text{CDCl}_3$  and the appearance of water, with its strong propensity for H-bonding, in the course of the reaction, lead to the changes in  $\delta_{\text{OH}}$ .

The kinetics and thermodynamics of the reaction of aldehyde with alkanols over solid acidic heterogeneous catalysts such as zeolites, clays and ion exchange resins have been studied.<sup>41–47</sup> A reaction mechanism for the alkanol-aldehyde reaction involving heterogeneous catalysis was proposed, consisting of three elementary steps (i) hemiacetal formation from the adsorbed aldehyde and the alcohol; (ii) formation of water (a limiting step); and (iii) formation of acetal. Detailed studies involving the monitoring of the time-dependent activities of all reactants in the synthesis of acetaldehyde dimethylacetal on the acid resin Amberlyst-15 in a batch reactor revealed a kinetic law and rate constants of the reaction, and accounted for the acetaldehyde volatility.<sup>44</sup> However, to the best of our knowledge, no rate constants have been reported in the case of the formation of arylaldehyde acetals, although there have been reports on the formation of dimethyl acetals using trimethyl orthoformate as reagent and indium-layered MOFs as catalysts,<sup>46</sup> and from benzaldehyde and methanol using  $\text{Cu}(\text{II})$ ,

Fe(II), and Al benzene diand tricarboxylate MOFs as catalysts.<sup>21</sup>

In the present work, we evaluated the overall kinetics of the benzaldehyde dimethyl acetal formation reaction catalyzed by MIL-101 and its composites with PTA and compared the performance of these materials with those of the previously reported MOF catalysts. We avoid the description of the (unknown) elementary steps.

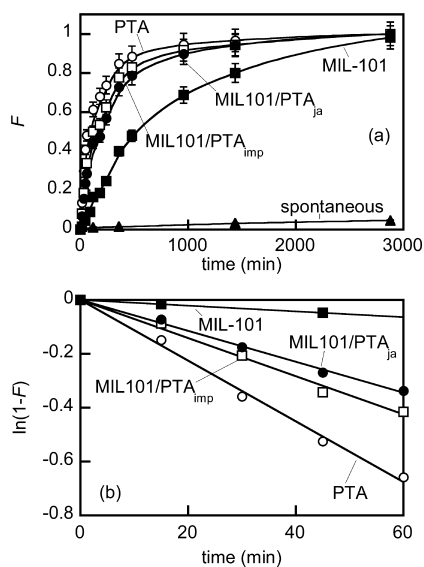
Owing to the 50-fold molar excess of methanol over benzaldehyde (see Experimental section), the change in benzaldehyde concentration ( $C_b$ ) with time (see Scheme 3) can be described by a pseudo-first-order rate equation

$$-\frac{dC_b}{dt} = k_{\text{obs}}C_b$$

From the integrated form of the above equation

$$\ln(C_{\text{bt}}/C_{\text{b0}}) = \ln(1 - F) = -k_{\text{obs}}t \quad (5)$$

we can obtain  $k_{\text{obs}}$  using experimental  $^1\text{H}$  NMR results cast in the form of  $F$  vs time data, wherein  $F$  is obtained from eq 4. The kinetics shown in Figure 6 depict rapid conversion of



**Figure 6.** Kinetics of benzaldehyde conversion in its acetalization by methanol catalyzed by MIL-101, MIL101/PTA<sub>ja</sub>, MIL101/PTA<sub>imp</sub> and PTA at 25 °C. (a) Overall kinetics, (b) initial reaction rate; the straight lines illustrate the initial reaction rates.

benzaldehyde to its dimethyl acetal in the presence of PTA and its composites with MIL-101. The data points obtained within the first 60 min (Figure 6b) appeared to be straight lines ( $R^2 > 0.98$  in all cases) in coordinates of eq 5, enabling estimates of  $k_{\text{obs}}$ , the reaction half-time  $t_{1/2} = \ln(2)/k_{\text{obs}}$ , and the turnover frequency  $\text{TOF} = C_{\text{b0}}k_{\text{obs}}/C_{\text{cat}}$  to be made. These parameters are collected in Table 2. Importantly, a very low (<5%) benzaldehyde conversion was observed without the catalysts at room temperature, while complete conversion was observed within 48 h in the presence of all catalysts; 93–95% conversion was observed within 24 h in reactions catalyzed by the MIL101/PTA composites as well as PTA. With MIL-101, the conversion reached 80% after 24 h. Activation energies for the B-M reactions catalyzed by MIL101/PTA<sub>imp</sub> and MIL101/PTA<sub>ja</sub> were measured in the temperature range of 25–55 °C to be 67 and 63 kJ/mol, respectively (S-3). These activation

energies are close to the  $E_a$  values determined for dimethyl acetal formation from benzaldehyde catalyzed by perchloric acid in methanol–water (95:5) mixtures (59.8 kJ/mol)<sup>46</sup> and dimethylacetal formation from methanol and acetaldehyde (72.4 kJ/mol) catalyzed by acid resin Amberlyst-15.<sup>43</sup>

For the catalyst efficiency comparison, less than 85% of benzaldehyde was converted at room temperature to dimethyl acetal in the B-M reaction catalyzed by MOFs based on  $\text{Cu}_3(\text{BTC})_2$  (BTC = 1,3,5-benzenetricarboxylate).<sup>21</sup> Approximating the molecular weight of the  $\text{Cu}_3(\text{BTC})_2$  MOF to be 605 Da,<sup>48</sup> the effective MOF catalyst loading in ref 21. was approximately 21 mM. Thus, the catalytic turnover number ( $\text{TON} = C_{\text{b0}} \times \text{conversion}/C_{\text{cat}}$ ) after 24 h reaction at room temperature with  $C_{\text{b0}} = 0.24$  M in that study was ca. 11. Calculated per total concentration of the Brønsted and Lewis acid sites per L of the suspension, the TON we obtained with MIL-101 at 80% conversion after 24 h was ca. 140 (Table 3).

**Table 3.** Effective Catalyst Concentration ( $C_{\text{cat}}$ ), Observed Rate Constant ( $k_{\text{obs}}$ ), Reaction Half-Life ( $t_{1/2}$ ), and Turnover Number (TON) and Frequency (TOF) of the Acetalization of Benzaldehyde with Methanol Conducted at 25 °C and  $C_{\text{b0}}=0.474$  M,  $C_{\text{mi}} = 23.5$  M

catalyst	$C_{\text{cat}}$ (mM)	$k_{\text{obs}} \times 10^3$ ( $\text{min}^{-1}$ )	$t_{1/2}$ (min) <sup>d</sup>	TON <sup>e</sup>	TOF ( $\text{min}^{-1}$ )
PTA	0.49 <sup>a</sup>	11	61	930	11
MIL101/PTA <sub>imp</sub>	0.15 <sup>b</sup>	7.1	98	2930	22
MIL101/PTA <sub>ja</sub>	0.15 <sup>b</sup>	5.7	120	2920	18
MIL-101	2.8 <sup>c</sup>	1.1	630	140	0.19

<sup>a</sup>Concentration of PTA in solution. <sup>b</sup>Concentration of PTA in the MIL101/PTA calculated per L of the suspension. <sup>c</sup>Total concentration of the Brønsted and Lewis acid sites per L of the suspension. <sup>d</sup>Calculated from the expression  $t_{1/2} = \ln(2)/k_{\text{obs}}$ . <sup>e</sup>Calculated from the expression  $\text{TON} = C_{\text{b0}}F/C_{\text{cat}}$ . Here,  $F$  (eq 4) is measured at 24 h after the reaction commencement.

The above estimates of TON indicate that MIL-101 is at least 10-fold more efficient a catalyst than is  $\text{Cu}_3(\text{BTC})_2$  MOF. Importantly, the reaction rates were 5-fold and TON values were 20-fold higher, with the MIL101/PTA composites than with the unmodified MIL-101, indicating that the presence of a strong heteropolyacid in these composites enhanced the catalysis efficiency drastically.

**Catalyst Recovery and Reuse.** From a practical standpoint, maximum catalyst productivity or kg of product produced per kg of catalyst is a figure of performance merit of a catalyst.<sup>3</sup> Highly stable catalysts that do not become easily deactivated during the reaction exhibit high productivity and many kg of product can be produced per kg of catalyst. Productivity data for MOFs as catalysts are necessary to determine the economics of the proposed processes based on MOF catalysis, but are available in only a few reports.<sup>3,49</sup> In the present work, we assessed the stability of the MIL-101 and MIL101/PTA catalysts over four cycles of the alcohol-aldehyde reactions. The stability parameters were (i) overall catalyst recovery by mass, (ii) structural stability in terms of PTA (Keggin ion) content in the MIL101/PTA composites or Cr content in MIL-101, and (iii) performance in terms of kinetic rate constants in each cycle. The results of the recovery and reuse studies are collected in Table 4. As is seen, the loss of the catalyst mass over 4 cycles was approximately 10 wt % for all

**Table 4.** Total Catalyst Recovery, Keggin Ion Content, Cr Content and Kinetic Rate Constants Measured in 4 Cycles of Catalyst Reuse<sup>a</sup>

cycle no.	total catalyst recovery (wt%) <sup>b</sup>			Keggin ion content (wt%) <sup>c</sup>		Cr content (wt%) <sup>c</sup>	$k \times 10^3$ (M <sup>-1</sup> min <sup>-1</sup> ) or $k_{\text{obs}} \times 10^3$ (min <sup>-1</sup> ) <sup>d</sup>		
	MIL101/PTA <sub>imp</sub>	MIL101/PTA <sub>ja</sub>	MIL-101	MIL101/PTA <sub>imp</sub>	MIL101/PTA <sub>ja</sub>	MIL-101	MIL101/PTA <sub>imp</sub>	MIL101/PTA <sub>ja</sub>	MIL-101
Acetaldehyde–Phenol Reaction									
1	93	94	93	30.9	30.5	11.1	17	15	1.7
2	88	87	88	29.1	28.3	11.4	18	13	1.8
3	82	83	82	25.3	27.1	11.5	15	14	1.5
4	81	83	82	25.2	27.1	11.2	16	14	1.6
Benzaldehyde–Methanol Reaction									
1	93	94	95	30.9	30.8	11.1	7.1	5.7	1.1
2	92	87	91	29.0	29.4	11.1	7.2	6.0	1.0
3	89	83	93	26.5	28.1	11.1	7.1	5.7	1.1
4	84	81	91	26.2	28.0	10.9	7.1	5.7	0.9

<sup>a</sup>Each cycle consisted of 1 day of the catalytic reaction at 25 °C. Catalyst recovery, workup and reuse are described in the Experimental Section.

<sup>b</sup>Calculated as  $100 \times \text{mass of catalyst in } n\text{-th cycle} / \text{initial mass of catalyst}$ . <sup>c</sup>Measured by elemental analysis in each cycle. <sup>d</sup>Rate constants  $k$  and  $k_{\text{obs}}$  are measured in the acetaldehyde–phenol and benzaldehyde–methanol reactions, respectively.

catalysts tested. This loss is attributable to the incomplete recovery of the catalyst after separation by centrifugation, due to a minute fraction dissolving in methanol in the process of catalyst washing, and to some small catalyst quantities staying on the walls of the centrifuge tubes. These losses essentially stopped after the third cycle, as did the losses of the PTA leaching out of the MIL-101 framework. We have previously demonstrated by XRD methods<sup>7</sup> that prolonged and repeated exposure of the MIL-101 and its composites with PTA to organic solvents such as methanol, THF and some others in the temperature range from ambient to 90 °C did not induce any changes to the framework crystal structure. These data, along with essentially unchanged reaction rate constants (Table 4) demonstrate outstanding stability of the MOF catalysts. In 4 cycles, 20 mg of the MIL/PTA catalyst converted approximately 750 mg of phenol and 140 mg of acetaldehyde, or 1.35 g of benzaldehyde. This finding indicates high performance figure of merit of the catalyst.

## CONCLUDING REMARKS

The present work describes our observation that strongly acidic MOF MIL-101 and especially its composites with phosphotungstic acid (MIL101/PTA) are capable of efficient catalysis of aldehyde self-condensation as well as aldehyde–alcohol reactions at ambient temperature. The MIL101/PTA composites are prepared via rather straightforward synthetic routes toward MIL101/PTA through an impregnation by aqueous PTA solution of the MIL-101 fabricated by autoclaving aqueous Cr(III) nitrate and terephthalic acid solutions or by a simple autoclaving of a mixture of Cr(NO<sub>3</sub>)<sub>3</sub>, terephthalic acid and PTA in water. The ready availability combined with the catalyst stability and high performance merit in the aldehyde–alcohol reactions indicate that MIL101/PTA could emerge as an industrially important catalyst.

## ASSOCIATED CONTENT

### Supporting Information

MALDI-TOF spectrum of the liquid condensed over MIL101/PTA matrix, <sup>1</sup>H NMR spectra of acetaldehyde and of the product of extraction from MIL101/PTA and Arrhenius plots of benzaldehyde–methanol reaction rate constants. This

material is available free of charge via the Internet at <http://pubs.acs.org/>.

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