Coordinatively Unsaturated Hf-MOF-808 Prepared via Hydrothermal Synthesis as a Bifunctional Catalyst for the Tandem N-Alkylation of Amines with Benzyl Alcohol

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ABSTRACT: The modulated hydrothermal (MHT) synthesis of an active and selective Hf-MOF-808 material for the N-alkylation reaction of aniline with benzyl alcohol under base-free mild reaction conditions is reported. Through kinetic experiments and isotopically labeled NMR spectroscopy studies, we have demonstrated that the reaction mechanism occurs via borrowing hydrogen (BH) pathway, in which the alcohol dehydrogenation is the limiting step. The high concentration of defective −OH groups generated on the metallic nodes through MHT synthesis enhances the alcohol activation, while the unsaturated Hf⁴⁺, which acts as a Lewis acid site, is able to borrow the hydrogen from the methylene position of benzyl alcohol. This fact makes this material at least 14 times more active for the N-alkylation reaction than the material obtained via solvothermal synthesis. The methodology described in this work could be applied to a wide range of aniline and benzyl alcohol derivates, showing in all cases high selectivity toward the corresponding N-benzylaniline product. Finally, Hf-MOF-808, which acts as a true heterogeneous catalyst, can be reused in at least four consecutive runs without any activity loss.

KEYWORDS: MOF-808, hydrothermal synthesis, tandem reaction, N-alkylation, borrowing hydrogen

INTRODUCTION

Industry is more than ever directed toward the development of efficient synthetic routes that minimize chemical waste, the use of hazardous raw sources, and/or the number of required steps. To this respect process intensification by cascade reactions that imply multiple consecutive transformations in the same reaction system is attracting a lot of attention in the field of catalysis.¹⁻⁴ These types of intensive processes present several advantages, including separation and purification intermediate steps that may also result in kinetic and production advantages.⁴

Among different chemical reactions, those comprising hydrogen auto-transfer mechanisms (borrowing hydrogen, BH)⁵ stand out as a powerful approach for the one-pot formation of C−C⁶ or C−N⁸⁻¹¹ bonds without requiring intermediate purification steps. The direct N-alkylation reaction of amines with alcohols offers an attractive pathway for the synthesis of secondary amines with high applicability in the pharmaceutical industry, materials science, agrochemistry, and biological systems. It is worth noting that the synthesis of secondary amines through the direct N-alkylation reaction of amines with alcohols shows outstanding benefits: (a) no hydrogen acceptor or oxidant is required, (b) water is only generated as a byproduct, a fact that improves the sustainability of the process compared to the generation of inorganic salts produced in classical amination reactions (i.e., from alkyl or aryl halides),⁶ (c) high atomic efficiency can be achieved, (d) alcohols are employed as both alkylating agents and hydrogen sources, being then cheaper, less flammable, and better manipulated compared to H₂, and (e) side reactions are minimized (i.e., aldol condensation between alcohols and/or over alkylation reaction).

The N-alkylation of amines using alcohols has been mostly associated in the literature with a hydride-capture mechanism by metal-containing catalysts, where the general mechanism consists of three well-defined stages:⁵ (1) alcohol dehydrogenation and hydride capture by the metal-containing catalyst, (2) condensation between the carbonyl group generated and the amine giving rise to an imine, and (3) imine hydrogenation by the metal hydride produced in the initial dehydrogenation stage (Scheme 1). However, it is worth noting that recent descriptions have also reported that the stripped hydrogen

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during the alcohol dehydrogenation can be stored in the form of hydrazo in the ligand backbone without metal–hydride formation.12

Numerous studies have shown that noble and non-noble metal complexes, mainly based on Ru13,14 H215, Ni12,16,17 Mn18, Co19,20 Cu21 and Fe22 combined with co-catalysts, such as bases and stabilizing ligands to undergo the alcohol deprotonation, are efficient multifunctional catalytic systems for the N-alkylation reaction. However, these homogeneous catalytic systems offer some drawbacks associated with their high cost and/or their limited recovery/regeneration. To circumvent these limitations, different heterogeneous catalysts based on supported transition metals have been described in the literature,5,10,23 but most of these solids still present some disadvantages, including uncertain stability/recyclability and/or the use of homogeneous bases.

Metal–organic frameworks (MOFs) are a very versatile family of microporous materials formed by inorganic metallic nodes connected through organic ligands,24 where the nature of the metallic cluster and/or the organic ligand can be easily tuned by direct synthesis or postsynthetic treatments, offering unique capabilities as heterogeneous catalysts.25,26 Indeed, MOFs can be considered as interesting catalysts for tandem reactions since these materials allow the simultaneous introduction of different active sites.27,28 Despite the high-tunability of MOFs, only two examples of MOF-based materials have been reported as catalysts for the N-alkylation reaction.27,29 The first description was a heterogenized Ir complex on the organic ligand of the Zr-Uio-66-NH2 material, which allows performing the N-alkylation reaction under solvent and base-free conditions.27 This methodology describes excellent results for aliphatic reagents, but the overall efficiency of the process is considerably reduced when using aromatic substrates, such as benzyl alcohol and aniline. Moreover, the initial catalytic activity decreases along the different catalytic cycles, indicating a limited stability for the heterogenized Ir complex. More recently, a MOF-type material based on the MIL-125-NH2 structure has been described for this reaction.29 In this catalytic system, the unsaturated Ti4+ sites of the metallic nodes and the O-atoms of Ti–O clusters would provide vicinal Lewis acid and Lewis basic sites, respectively, facilitating alcohol adsorption and its subsequent dehydrogenation reaction (borrowing hydrogen). The selectivity toward the corresponding N-benzylaniline product obtained in this work is higher than 98%, but this catalytic system requires almost 15 h and 160 °C to achieve complete conversion values.

Recently, we have demonstrated that transition metal-containing beta zeolites, particularly Zr- and Hf-beta, show excellent activity, selectivity, and stability for the N-alkylation reaction of anilines with benzyl alcohol under base-free conditions.30 These previous results suggest that the Lewis acid strength offered by the isolated transition metal sites in the zeolite framework would play an important role on the alcohol dehydrogenation (step 1 in Scheme 1).30,31 Thus, the preparation of a MOF-type catalyst including tetravalent species other than Ti with enhanced Lewis acidity, such as Zr and Hf,32 can give rise to a faster metal hydride formation and, therefore, a remarkable activity improvement compared to Ti-containing MIL-125-NH2.29 It is worth noting that, in the last years, Zr- and Hf-MOFs have shown exceptional thermal, mechanical, and chemical stabilities,32–34 allowing their application as active and stable catalysts for a wide range of chemical processes.35–40

The control of the amount of coordinatively unsaturated open metal sites in MOFs has been demonstrated crucial in rationalizing the nature of the catalytically active sites, allowing fine-tuning the Lewis/Brensted acid properties of the resultant MOFs.41,42 Different strategies have been described in the literature to adequately generate these defective sites, such as the use of modulators (i.e., monocarboxylic or inorganic acids) during the solvothermal synthesis,43,44 or postsynthetic modifications through acid/base treatments.45 In fact, the amount of defective −OH groups on the metallic cluster of Hf-containing MOFs can be modulated by carrying out their synthesis via solvothermal or hydrothermal conditions.46

Herein, we propose the use of Zr- and Hf-containing MOF materials as efficient and active catalysts for the synthesis of secondary amines via N-alkylation reaction between amines and benzyl alcohols that does not require the use of an additional base and/or external H2, as required for instance when synthesizing secondary amines by the traditional condensation between amines and aldehydes. The metal-containing MOFs prepared via modulated hydrothermal synthesis conditions show a remarkably higher catalytic activity compared to the metal-containing MOFs prepared via modulated solvothermal synthesis, suggesting that a larger amount of −OH sites within the metal nodes substantially facilitates the N-alkylation reaction. Kinetic and NMR spectroscopy studies clearly reveal that the reaction occurs via a borrowing hydrogen pathway, in which the alcohol dehydrogenation is the limiting step. Finally, the Hf-MOF-808 catalyst has demonstrated good stability in this transformation, since it can be reused at least 4 times without observing any catalyst deactivation. The catalytic system can be expanded to the use of a large number of aromatic amines and benzyl alcohols.

### EXPERIMENTAL SECTION

**Metal–Organic Framework Synthetic Procedures.** *Modulated Hydrothermal Synthesis of M-MOF-808 H2O.* This synthesis has been carried out following a previously reported recipe.47 MClO2·8H2O (M = Hf/Zr) (3.60 mmol) and H3BTC (1.20 mmol, 252.17 mg) were dissolved in a mixture of H2O/acetic acid (1:1, v/v, 20 mL). The resulting solution was refluxed at 100 °C under magnetic stirring for 3 h. The white solid precipitate was washed three times with H2O, methanol, and, finally, aceton. The as-obtained material, denoted as M-MOF-808·H2O, was activated at 100 °C for 2 h (1.21 g of Hf-MOF-808·H2O, 3.06 mmol of Hf, 85% yield referred to H2O; 0.97 g of Zr-MOF-808·H2O, 2.81 mmol of Zr, 78% yield referred to as ZrCl3·8H2O).

**Modulated Solvothermal Synthesis of Hf-MOF-808 DMF.** This material has been synthesized according to a previously reported

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**Scheme 1. Hydrogen Auto-transfer Mechanism for the N-Alkylation Reaction of Amines with Alcohols Mediated by Transition Metal-Based Materials**

![Scheme 1](https://example.com/scheme1.png)
Benzyl Alcohol.

The mechanistic experiments were performed in 2 mL glass-vessel reactors equipped with a magnetic bar. The corresponding amount of Hf-MOF-808_H2O (10.03 mg, 12 mol % Hf) was weighed in the reactors together with the different benzyl alcohols (PhClOH and PhCH2OD, 0.2 mmol), aniline (0.20 mmol, 18.6 mg) and/or N-benzylidenеanine (0.20 mmol, 36.2 mg), and o-xylene (0.45 mL). The mixtures were placed in an aluminum heating block at 120 °C under magnetic stirring during 5 h. The reaction mixtures were filtered with a PTFE syringe filter, diluted with toluene-d8 and analyzed by 1H NMR spectroscopy.

**N-Alkylation Substrate Scope.** The scope reactions were performed in 2 mL glass-vessel reactors equipped with a magnetic bar. The corresponding alcohols and amines (0.60 mmol of each of them), dodecane (0.22 mmol, 37.40 mg) as an external standard, and o-xylene (11.16 mmol, 1.35 mL) as solvent were added to each reactor containing the corresponding amount of Hf-MOF-808_H2O (30.10 mg, 12 mol % Hf). The mixtures were placed in an aluminum heating block at 120 or 140 °C with magnetic stirring. Approximately 50 μL alcohols were taken at different times, diluted with ethyl acetate, and centrifuged. The supernatant obtained from batch reactions was analyzed using gas chromatography in an instrument equipped with a 25 m capillary column of 5% phenylmethylsilicone.

**Mechanistic Study for the N-Alkylation Reaction of Aniline with Benzyl Alcohol.** The mechanistic experiments were performed in 2 mL glass-vessel reactors equipped with a magnetic bar. The corresponding amount of Hf-MOF-808_H2O (10.03 mg, 12 mol % Hf) was weighed in the reactors together with the different benzyl alcohols (PhClOH and PhCH2OD, 0.2 mmol), aniline (0.20 mmol, 18.6 mg) and/or N-benzylidenеanine (0.20 mmol, 36.2 mg), and o-xylene (0.45 mL). The mixtures were placed in an aluminum heating block at 120 °C under magnetic stirring during 5 h. The reaction mixtures were filtered with a PTFE syringe filter, diluted with toluene-d8 and analyzed by 1H NMR spectroscopy.

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**RESULTS AND DISCUSSION**

**Synthesis and Characterization of MOF-Type Materials.** Recently, the green preparation of different MOF-type materials, particularly Uio-66 and MOF-808, has been described via modulated hydrothermal synthesis (MHT). In these cases, water is used as the solvent during their crystallization, avoiding the use of N,N-dimethylformamide (DMF), a common and highly toxic solvent in the traditional solvothermal syntheses. Interestingly, it has been shown that the relative amount of defective –OH groups within the metallic nodes in MOFs can be substantially increased when the MOF preparation is carried out via MHT synthesis compared to the more classical solvothermal approach, a fact that unavoidably influences the adsorption and catalytic properties. Based on these recent results, we propose here to study different Zr- and Hf-MOF type materials, UiO-66 and MOF-808, prepared via both hydrothermal and solvothermal syntheses, as well as the catalytic implications that these different synthesis approaches would have for the tandem N-alkylation reaction between amines and benzyl alcohols.

The detailed synthesis descriptions of the different metal-containing MOFs can be found in the Experimental Section. Those materials have been adequately characterized by amounts of benzyl alcohol (0.43, 0.33, 0.22, and 0.10 mol·L⁻¹) and aniline (0.33, 0.30, 0.23, and 0.13 mol·L⁻¹) in o-xylene (11.16 mmol, 1.35 mL), Hf-MOF-808_H2O (30.10 mg, 12 mol % Hf) as catalyst and dodecane (0.22 mmol, 37.40 mg) as external standard were added to each reactor. The mixtures were placed in an aluminum heating block at 120 °C with magnetic stirring. Approximately 50 μL alcohols were taken at different times, diluted with ethyl acetate, and centrifuged. The supernatant obtained from batch reactions was analyzed using gas chromatography in an instrument equipped with a 25 m capillary column of 5% phenylmethylsilicone.
different techniques to unravel their physicochemical properties. The powder X-ray diffractograms of the different solids reveal the formation of the pure crystalline MOF-808 or UiO-66 phases in all cases (see Figure 1).

The interaction of the organic ligands with the different metallic clusters has been studied by FTIR spectroscopy (see Figure 2). The spectra of the different MOFs present a clear shift of the $\sim 1700 \text{ cm}^{-1}$ signal assigned to the carbonyl stretch $\text{C}=\text{O}$ of the free carboxylic acid group toward lower frequencies, as well as the appearance of a signal centered at $\sim 700–600 \text{ cm}^{-1}$, which is assigned to the vibration mode frequency of the $\text{M}–\text{O}$ linkages.

The textural properties of the as-obtained MOF samples have been analyzed from the $\text{N}_2$ adsorption–desorption isotherms (see Figure 3). The entire MOFs exhibited a type-I isotherm with a minor hysteresis between adsorption and desorption branches.\(^\text{53}\)

The surface area calculated by the BET method, following Rouquerol’s criterion, for the Zr-MOF-808 $\text{H}_2\text{O}$ sample is considerably higher than for the Hf counterpart (see Table 1, entries 1 and 2, respectively), a fact that can be explained by the higher density of the Hf-MOF-808 $\text{H}_2\text{O}$ sample.\(^\text{54}\) Moreover, the Hf-MOF-808 prepared via hydrothermal and solvothermal syntheses presents similar BET surface areas (see Table 1, entries 2 and 3, respectively). Finally, the Hf-UiO-66-$\text{NH}_2$-$\text{H}_2\text{O}$ shows a measured BET surface area analogous to those reported previously for this material in the literature,\(^\text{49}\) but this value is lower compared to Hf-MOF-808 samples (see Table 1, entry 4). The higher cluster connectivity of UiO-66 (12-connected) together with the smaller pore size (8 and 11 Å) of this structure compared to MOF-808, which presents a
6-connectivity and adamantane-type apertures of ~18.4 Å, would explain this difference.

The chemical composition and stability of the hydrothermal and solvothermal catalysts have been studied by ICP, elemental analysis, and TGA analysis (Table 1 and Figure S1). The M/C molar ratios obtained for the Hf and Zr-MOFs are consistent with their molecular formulas. Moreover, the TGA analysis reveals that all MOFs have high thermal stability under oxidant atmospheres and would be stable up to 350 °C (see Figure S1).

Finally, the morphology of the MOF materials has been evaluated by field-emission scanning electron microscopy (FE-SEM, see Figure 4). The samples prepared by the MHT synthesis present a quasi-spheroidal morphology (see M-MOF-808 and Hf-MOF-808 in Figure 4), while the Hf-MOF-808 prepared by the solvothermal approach shows an octahedral morphology (see Hf-MOF-808). The different crystal morphologies achieved clearly indicate the influence of the applied synthetic method on the final nucleation and crystallization processes.55 In addition, Hf-MOF-808_H2O material shows a smaller particle size (~300 nm, see Figure 4) compared to Zr-MOF-808_H2O (~900 nm, see Figure 4). Despite Hf and Zr exhibiting similar ionic radii, it has been broadly described in coordination chemistry that Hf performs in a sluggish way compared to Zr,56 maybe influencing the overall crystal growth of the MOF particles.

Scheme 2. N-Alkylation Reaction of Aniline 2a with Benzyl Alcohol 1a to Afford the N-Benzylaniline Product 4a

| Table 1. Physicochemical Properties of the Different Zr- and Hf-MOFs |
|---|---|---|---|---|---|---|---|
| entry | sample | C (%) | H (%) | N (%) | M (%) | BET surf. area (m²/g) | micro. area (m²/g) | microp. vol. (cm³/g) |
| 1 | Zr-MOF-808_H2O | 22.8 | 3.0 | - | 26.5 | 1540 | 1475 | 0.7 |
| 2 | Hf-MOF-808_H2O | 15.4 | 3.9 | - | 44.5 | 1109 | 1052 | 0.5 |
| 3 | Hf-MOF-808_DMF | 17.9 | 2.1 | 2.1 | 36.2 | 1135 | 1093 | 0.5 |
| 4 | Hf-UiO-66-NH2_H2O | 22.2 | 3.6 | 2.4 | 37.2 | 848 | 812 | 0.4 |

“Determined by elemental analysis. “Determined by ICP-OES analysis.

N-Alkylation Reaction of Aniline with Benzyl Alcohol.

The different Zr- and Hf-containing MOFs have been tested as catalysts for the one-pot synthesis of the N-benzylaniline (4a) with aniline (2a) and benzyl alcohol (1a) as starting materials (see Scheme 2). A preliminary optimization of the reaction conditions has been first carried out, in which the metal loading of Hf-MOF-808_H2O and the reaction temperature were varied. The highest yield toward the desired N-benzylaniline has been obtained at 120 °C and with 12 mol % Hf after 2 h of reaction (~85%, see blue triangles in Figure S2), where complete benzyl alcohol conversion has been reached. Moreover, the catalyst loading could be reduced to even 8 mol % to achieve similar 4a yield after 5 h (see black squares in Figure S2A). However, neither at 110 °C nor at 100 °C does the benzyl alcohol conversion exceed 20% after 2 h of reaction (see black squares and red circles in Figure S2B, respectively). Furthermore, the kinetic curves show a sigmoidal shape that indicates the presence of an induction period where the active phase of the catalyst is being formed (see Figure S2). This initial induction period could be minimized if Hf-MOF-808_H2O is previously activated with benzyl alcohol for 2 h at 120 °C, and after that period, an equimolar amount of aniline was added.
is then injected (see Figure S3). A complete benzyl alcohol conversion and high N-benzylaniline yield (≈86%) are achieved after only 0.75 h at 120 °C (see Figure S3), suggesting that benzyl alcohol would have an important role in the N-alkylation reaction mechanism.

An additional optimization of the N-alkylation reaction conditions using Hf-MOF-808·H$_2$O as catalyst has been performed by studying different solvents at 120 °C. From this second set of experiments, polar solvents, as DMF and DMSO, do not afford the corresponding 4a product after 2 h (see Table S1, entries 1 and 2, respectively). The same trend is observed when moderate polar solvents, such as butyl acetate or 2-methoxyethanol, which contain carbonyl and alcohol groups in their structures, respectively, were used (see Table S1, entries 3 and 4, respectively). The undesired adsorption of these solvent molecules on the metallic nodes of the MOF catalyst could block the access of the reaction substrates to the active sites. The best catalytic results have been obtained using 1,2-dichlorobenzene and o-xylene as solvents (see Table S1, entries 5 and 6, respectively). Particularly, o-xylene shows the highest catalytic activity after 2 h at 120 °C with an ≈85% yield of the N-benzylaniline product (see Table S1, entry 6). The different activity shown as a function of the solvent polarity and structure could be tentatively attributed to the chemical environment created around the active sites. This behavior has been observed previously in enzymes$^{57}$ and other inorganic solids, such as zeolites,$^{58}$ where well-defined confined spaces promote high activities and selectivities toward the desired product. In our case, the nonpolar solvent could facilitate the promotion of hydrophobic or cage effects since the reagent substrates have polar groups within their structures. The nonpolar environment would allow the pre-organization of the reactants close to the active sites, which would be electronically decompensated due to the defects in the metal–organic framework, enabling the interaction between them and, consequently, the formation of the desired N-alkylation reaction product.

At this point, the one-pot reaction between aniline 2a and benzyl alcohol 1a has been studied under the above optimized reaction conditions (T = 120 °C and o-xylene as solvent), using the different Zr- and Hf-metal–organic materials synthesized and characterized in this work, together with other homogeneous and heterogeneous catalysts (see Table 2).

| entry | sample | alcohol conversion (%) | 3a (%) | 4a (%) |
|-------|--------|------------------------|--------|--------|
| 1     | Hf-MOF-808·H$_2$O | 98.6 | 0.6 | 85.3 |
| 2     | Hf-MOF-808·DMF | 56.5 | 17.5 | 17.2 |
| 3     | Zr-MOF-808·H$_2$O | 99.0 | 1.5 | 83.2 |
| 4     | Hf-Uio-66-NH$_2$·H$_2$O | 22.6 | 1.5 | 0.9 |
| 5     | HfOCl$_4$ | 6.4 | 0.0 | 0.4 |
| 6     | HCl$_4$ | 24.1 | 0.3 | 0.4 |
| 7     | HfOCl$_4$·8H$_2$O | 8.6 | 0.0 | 0.3 |
| 8     | ZrO$_2$·np | 4.5 | 0.0 | 0.8 |
| 9     | HfBTC | 4.4 | 0.0 | 0.4 |

$^a$Reaction conditions: benzyl alcohol 1a (0.60 mmol), aniline 2a (0.60 mmol), catalyst (12 mol % M), o-xylene (11.16 mmol, 1.35 mL), dodecane as external standard (0.22 mmol, 37.40 mg), T = 120 °C, 2 h. $^b$Conversion and yield were determined by gas chromatography.

The two M-MOF-808·H$_2$O (M: Hf and Zr) materials, which have been prepared under hydrothermal conditions, present the highest catalytic performance for the N-alkylation reaction, with complete alcohol conversion after 2 h (see Table 2, entries 1 and 3, respectively). Selectivities of ≈85% toward N-benzylaniline 4a have been determined for both materials, detecting only traces of the corresponding imine 3a.

However, the Hf-MOF-808·DMF catalyst prepared via solvothermal synthesis shows much lower catalytic activity for the N-alkylation reaction compared to the two M-MOF-808 prepared via hydrothermal synthesis (see entry 2 in Table 2 and Figure 5).

![Figure 5. N-alkylation reaction between benzyl alcohol and aniline catalyzed by Hf-MOF-808·H$_2$O (■) and Hf-MOF-808·DMF (●).](https://doi.org/10.1021/acssuschemeng.1c04903)

Recently, we have determined that the Hf-MOF-808 synthesized via the hydrothermal method contains a much higher concentration of defective –OH sites than the same sample prepared via the solvothermal approach, which undoubtedly plays an important role in the final activity of this material for specific catalytic reactions.$^{42,46}$ Thus, the different catalytic behaviors observed between the MOF-808 samples prepared via modulated hydrothermal and solvothermal approaches could be tentatively assigned to the fact that the defective –OH species would facilitate the hydride formation due to the proton uptake of the alcohol group (step 1 in Scheme 1). To determine the relative concentration of –OH sites, FTIR spectroscopic studies of CO as the probe molecule have been carried out. For both Hf-MOF-808 samples, IR peaks at 2134, 2154, and 2180 cm$^{-1}$ assigned to CO physisorbed and interacting with slight acid –OH groups and Hf Lewis acid sites, respectively, were detected (see Figure 6).$^{39}$

However, the relative ratio between the integrated signals referred to Brønsted and Lewis acid sites (2154 and 2180 cm$^{-1}$, respectively) is at least two times higher for the Hf-MOF-808·H$_2$O sample than for the Hf-MOF-808·DMF, suggesting that the relative concentration of defective –OH sites is considerably higher in the Hf-MOF-808 synthesized via the hydrothermal method (see Figure 6).

On the other hand, another MOF-type structure, UiO-66, containing Hf, has been prepared under hydrothermal syntheses. Hf-Uio-66-NH$_2$·H$_2$O, which has an additional basic group that may be able to capture/stabilize the proton of the benzyl alcohol molecule and, then, favor its dehydrogen-
ation, does not show any detectable catalytic activity for the N-alkylation reaction (see Table 2, entry 4). These differences observed between both types of MOFs, MOF-808 and UiO-66, may be ascribed to higher diffusional limitations along the UiO-66 structure, since this framework not only has higher theoretical organic ligand connections per metallic node than MOF-808 (12 and 6, respectively), but also smaller pore sizes (8–11 and 18.4 Å for UiO-66 and MOF-808, respectively).

Neither the heterogeneous catalyst bulk HfO$_2$ nor the homogeneous HfCl$_4$ and HfOCl$_2$ · 8H$_2$O show any activity for the N-alkylation reaction (see Table 2, entries 5, 6, and 7, respectively). In addition, ZrO$_2$-np (<100 nm) nanoparticles, even when they present remarkably smaller particle sizes than HfO$_2$ and, thus, larger external surface areas to facilitate the...
interaction with the reagents do not present an appreciable catalytic activity (see Table 2, entry 8). In the same way, H3BTC has been studied as a homogeneous catalyst, presenting low catalytic activity (see Table 2, entry 9) and, then, ruling out the possible contribution of the organic ligands during the catalytic process.

Kinetic and Mechanistic Studies for the $N$-Alkylation Reaction of Aniline with Benzyl Alcohol. To better understand the mechanism of the $N$-alkylation reaction when Hf-MOF-808_H2O is employed as catalyst, different kinetic and mechanistic studies have been carried out. The three reaction steps required in the $N$-alkylation reaction are described in Scheme 1, where it was assumed that each one could, in principle, be the overall rate-determining step with the other two reactions being in equilibrium. Following this, the resultant kinetic rate equations are presented in Table S2.10

To discriminate among the three kinetic expressions, the initial concentration of benzyl alcohol was varied (0.43, 0.33, 0.22, and 0.10 mol L$^{-1}$) while the concentration of aniline was kept constant (0.43 mol L$^{-1}$) (see Figure 7A), and the initial reaction rates were measured. The same procedure was applied but varying the concentration of aniline (0.33, 0.30, 0.23, and 0.13 mol L$^{-1}$) and maintaining constant the concentration of benzyl alcohol (0.43 mol L$^{-1}$) (see Figure 7B).

The entire kinetic experiments show sigmoidal curves (see Figure 7A,B), clearly indicating the presence of an induction period in all cases. To evaluate the dependence of the initial reaction rate with reactants, the initial reaction rates have been estimated, without considering the induction period, (see slopes in Figure 7A,B). This kinetic analysis suggests a dependence of the initial reaction rate with the concentration of benzyl alcohol (see Figure 7C), where the initial reaction rate increases exponentially with the concentration of benzyl alcohol until reaching a maximum concentration. This would explain why the induction period of the kinetic curves could be suppressed with a previous thermal treatment of the Hf-MOF-808_H2O catalyst with benzyl alcohol (120 °C for 2 h, see Figure S3), facilitating the in situ benzaldehyde formation before introducing aniline. In contrast, the reaction order of aniline is $\sim 0$ (see Figure 7D). Thus, according to the rate
equations shown in Table S2, only the benzyl alcohol dehydrogenation reaction (see eq 1) depends exclusively on the concentration of benzyl alcohol, indicating that this could be the rate-limiting step. Similar theoretical and experimental results supporting the fact that the benzyl alcohol dehydrogenation reaction is the rate-limiting step for the $N$-alkylation reaction have been recently reported using metal-containing zeolites as catalysts.30

Subsequently, we conducted deuterium-labeling experiments using $^1$H NMR spectroscopy (see Figure 8). To unravel the nature of the metal hydride, two isotopically labeled benzyl alcohols $1b$ and $1c$ were employed as starting materials in the $N$-alkylation reaction (see Figure 8A,B, respectively). The obtained $^1$H NMR spectra confirm that the hydrogen borrowed by the catalyst is the one contained in the methylene position of benzyl alcohol and does not proceed from the hydroxyl group of benzyl alcohol.

To corroborate this hypothesis, the hydrogenation of $N$-benzylideneaniline $3a$ with the two isotopically labeled benzyl alcohols $1b$ and $1c$ has been studied (see Figure 9A,B, respectively). It can be observed in the $^1$H NMR spectra that the hydrogenation of the imine $3a$ with PhCD$_2$OH ($1b$) also favors the fully incorporation of deuterium in the methylene position of the amine product $4b$ (see Figure 9A), whereas the deuterium from dehydroxyl group of $1c$ is not able to hydrogenate the imine (see Figure 9B).

This evidence suggests that the Hf Lewis acid sites are able to borrow the hydrogen from the methylene position of benzyl alcohol to hydrogenate the imine group. Finally, the influence of the isotopic exchange in the methylene position of benzyl alcohol on the initial reaction rate has been studied, confirming an isotopic effect of $k_H/k_D = 3.03$ (see Figure S4). This isotopic effect result, complemented with the previous kinetic experiments, would further suggest that the alcohol dehydrogenation must be involved in the rate-determining step of the catalytic cycle.

With all the information obtained from kinetic and mechanistic studies, we tentatively propose a possible catalytic route for the $N$-alkylation of aniline with benzyl alcohol using Hf-MOF-808_H2O as catalyst based on the borrowing
hydrogen pathway (BH) (see Scheme 3):5 (1) The first step consists in the alcohol deprotonation by the metallic cluster with the defective −OH group and the consequent dehydrogenation. (2) After the alcohol deprotonation and dehydrogenation processes, a benzaldehyde molecule is produced at the same time that the Hf-hydride is generated. (3) Subsequently, the benzaldehyde adsorbed on the Hf site, which increases its electrophilicity and, therefore, its reactivity, instantly undergoes a nucleophilic addition by the amino group of the aniline, giving rise to the corresponding imine. This process involves the loss of a water molecule. (4) Finally, the Hf-hydride generated in the first stage hydrogenates the imine group at the same time that the proton captured by the defective −OH group is taken by the imine nitrogen to give rise to the corresponding N-benzylaniline product, while the active site is regenerated.

**N-Alkylation Substrate Scope.** To determine the generality of the method developed for the N-alkylation reaction with Hf-MOF-808_\(H_2O\) as catalyst, different benzyl alcohols and substituted anilines have been studied as starting materials (see Table 3).

Under the optimal conditions, the method appears to be applicable in terms of catalytic performance and selectivity toward the desired N-benzylaniline products when the nature and position of the substituents on the benzyl alcohol (see Table 3, entries 1, 2, 3, 4, and 5) and aniline ring (see Table 3, entries 8, 9, 10, and 11) are varied. Interestingly, halogen substituents, including Br and Cl (see Table 3, entries 4, 9, and

### Table 3. N-Alkylation Substrate Scope Using Different Amines and/or Alcohols

| Reaction | Product | Yield (%) |
|----------|---------|-----------|
| 1. 4d: 74% (70%) | 2. 4e: 79% | 8. 4k: 97% (90%) |
| 3. 4f: 77% (74%) | 4. 4g: 85% (81%) | 9. 4i: 91% (85%) |
| 5. 4h: 78% (72%) | 6. 4i: 52% (45%) | 10. 4m: 71% (64%) |
| 7. 4j: 73% | 11. 4n: 89% (83%) | 12. 4o: 75% (64%) |
| 13. 4p: 8% | 14. 4q: 11% |  |

“Reaction conditions: alcohol (0.60 mmol), amine (0.60 mmol), Hf-MOF-808_\(H_2O\) (12 mol % Hf), o-xylene (11.16 mmol, 1.35 mL), dodecane as external standard (0.22 mmol, 37.40 mg), \(T = 120^\circ C\), 3 h. Yield determined by gas chromatography. Isolated yield in parentheses. \(^5\)1.5 h. \(^6\)\(T = 140^\circ C\), \(P_m = 5\) bar, 23 h. \(^7\)23 h.
heterogeneity and stability of Hf-MOF-808\_H\textsubscript{2}O under the being reused in successive catalytic cycles. Thus, the entitmates them from their homogeneous counterparts is their fundamental aspects of heterogeneous catalysts that di

Reaction of Aniline with Benzyl Alcohol.

the reaction has been followed by gas chromatography until 2 out after 30 min (see Figure 10A). After that, the evolution of the reaction has been followed by gas chromatography until 2 h. During this period, no increment in the yield of product 4a has been observed. These results reflect the catalyst heterogeneity and, therefore, the absence of leaching processes of active species from the catalyst to the reaction media. Furthermore, Hf-MOF-808\_H\textsubscript{2}O could be reused successfully up to 4 consecutives catalytic cycles without a significant decrease of the N-benzylaniline 4a yield (see Figure 10B).

The recovered material after the successive catalytic cycles has been analyzed by several techniques including powder X-ray diffraction, FE-SEM and TEM/EDX microscopy, solid-state \textsuperscript{13}C MAS NMR and FTIR spectroscopies, TGA, and elemental analysis. The PXRD pattern reveals the integrity of the crystalline structure of MOF-808, while FE-SEM images show the preservation of the crystal morphology (see Figure S5). Moreover, through TEM/EDX analysis, similar Hf contents and distribution have been obtained for the fresh and recovered material (25 and 23\%, respectively), also corroborating the structural integrity of the MOF sample under the studied reaction conditions (see Figure S6).

However, an increment of the organic content is observed by TGA and elemental analysis in the recovered Hf-MOF-808 material (see Figure S7 and Table S3, respectively), suggesting that some organic substrates are retained within the MOF-type catalyst. To elucidate the nature of the adsorbed products, solid-state \textsuperscript{13}C MAS NMR and FTIR spectroscopies have been employed. The characteristic bands of the N-benzylaniline product are clearly detected in both cases (see Figures S8 and S9, respectively). Moreover, \textsuperscript{1}H NMR and GC-MS spectra of the digested Hf-MOF-808\_H\textsubscript{2}O sample with a mixture of D\textsubscript{2}SO\textsubscript{4}/DMSO-\textsubscript{d}\textsubscript{6} elucidate the N-benzylaniline nature of the adsorbed organic substrate (see Figures S10 and S11, respectively).

Finally, through the elemental analysis of the reused solid, an additional 1.16\% of N was detected (Table S3). Taking into account that the extra-nitrogen amount must be associated with the N-benzylaniline product adsorbed during the catalytic process, the overall real product yield value obtained toward 4a would be 92\% instead of 85\%.

**CONCLUSIONS**

The results presented in this work reveal the excellent ability of the hydrothermally synthesized Hf-MOF-808, denoted as Hf-MOF-808\_H\textsubscript{2}O, to catalyze the N-alkylation reaction of

Figure 10. (A) Hot filtration test and (B) recyclability test for Hf-MOF-808\_H\textsubscript{2}O catalyst after 4 successive cycles for the N-alkylation reaction of aniline with benzyl alcohol, where a 2 h reaction is performed for each catalytic cycle.
aniline with benzyl alcohol. The presence of defective –OH groups on the metallic nodes together with the Hf Lewis acid sites enhances the catalytic behavior of this material for the N-alkylation reaction. Through kinetic and deuterium-labeling experimental studies, it has been demonstrated that the mechanism occurs via a borrowing hydrogen pathway, in which the dehydrogenation step has been determined as the rate-determining step. Moreover, the method described in this study is adequate for a wide range of aniline and benzyl alcohol deri
vates. Finally, Hf-MOF-808_H2O could be used in at least four consecutive catalytic cycles without observing a significant catalytic activity loss.

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**Notes**

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