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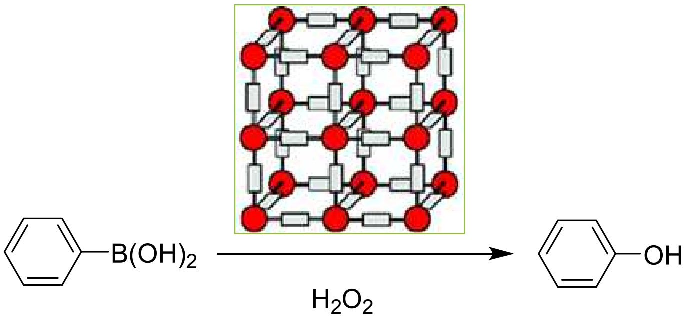
TOC Graphic



This work describes the use of $Cu_3(BTC)_2$ as heterogeneous catalyst to promote the oxidative hydroxylation of arylboronic acids to the corresponding phenols by H_2O_2 at room temperature. $Cu_3(BTC)_2$ can be reused with no significant drop in the activity.

$Cu_3(BTC)_2$ as heterogeneous catalyst for the room temperature oxidative hydroxylation of arylboronic acids

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Abstract

A well known copper based-metal organic framework (MOF), namely $Cu_3(BTC)_2$, is a suitable heterogeneous catalyst to promote the oxidative room-temperature hydroxylation of arylboronic acids to the corresponding phenols by H_2O_2. Using 0.5 eq. of H_2O_2, $Cu_3(BTC)_2$ exhibits 80% conversion in 60 min that is higher than 70% conversion achieved with Fe(BTC) under the same conditions and reaction time. $Cu_3(BTC)_2$ is reusable with no significant drop in the activity. Furthermore, powder XRD of the reused $Cu_3(BTC)_2$ shows no changes in crystallinity compared to the fresh $Cu_3(BTC)_2$, indicating catalyst stability is maintained under reaction conditions. The scope of $Cu_3(BTC)_2$ as heterogeneous catalyst for the oxidative hydroxylation was studied for various phenylboronic acids.

Keywords: Metal-organic frameworks; $Cu_3(BTC)_2$; phenylboronic acid; oxidation; hydrogen peroxide.

1. Introduction

Phenols and their derivatives exhibit many important chemical and biological activities and are present in numerous natural products.[1] Further, they are potential precursors for the synthesis of pharmaceuticals, polymers, and naturally occurring compounds.[2] Therefore, novel synthetic procedures for the preparation of this type of compounds are of continued interest. Among the numerous reactions reported, nucleophilic aromatic substitution of aryl halides, copper-catalyzed transformation of diazoarenes and protocols based on the intermediacy of benzyne are dominant.[3-5] However, these methods suffer from disadvantages such as harsh reaction conditions or lack of control of diazotation of the amino groups to aryldiazonium ions. Conversion of aryl bromides and chlorides into phenols in the presence of palladium-based catalysts and phosphine ligands is another approach.[6,7] Aryl iodides can also be converted into the corresponding phenols in the presence of a copper catalyst using non-phosphine ligands at elevated temperature.[8,9] More recently, the photochemical conversion of arylboronic acids into the corresponding phenols has been reported.[10-12] Arylboronic acids have become valuable synthetic precursors in a wide range of organic transformations.[13] On the other hand, phenols have been reported as by-products in several metal-catalyzed coupling reactions of arylboronic acids as substrates.[14,15]

Metal organic frameworks (MOFs) are crystalline porous materials constituted by metallic nodes of a single metal ion or a cluster with a few metal ions that are coordinated by Coulombic and metal-ligand coordination forces with rigid bi- or multipodal organic linkers.[16] MOFs have been prepared for virtually all transition metals and even alkali earth and heavy metals have been used in the preparation of MOFs. Aromatic polycarboxylates and nitrogenated heterocycles are the most common organic linkers.[17]

One of the most promising applications of MOFs is as heterogeneous catalysts since these materials encompass large surface area, high metal content and some of them are stable under catalytic conditions.[18,19] One of the MOFs that has been most widely studied as heterogeneous catalysts is $Cu_3(BTC)_2$ (BTC: 1,3,5-benzenetricarboxylic acid). The structure of $Cu_3(BTC)_2$ has a dimeric Cu unit that is coordinated with four BTC units defining octahedra around each Cu^{2+} ion with a paddle wheel shape.[20] One coordination position of each copper is occupied by a solvent molecule such as DMF or water that upon removal releases a free coordination position around each Cu^{2+} ion allowing the interaction of catalytically active Cu^{2+} with substrates and reagents. While $Cu_3(BTC)_2$ has been used as solid catalysts for a large variety of reactions including cyanosilylation of aldehydes,[21] alcohol oxidation[22] and benzylic hydrocarbon oxidation[23] among others,[24,25] one of its main drawbacks is its relatively low stability that is not compatible with the use of some reagents like thiols[26] or amines.[27]

Aqueous H_2O_2 is considered an environmentally friendly oxidizing reagent from the green chemistry point of view, since water is the resulting byproduct of the oxidation.[28] There are numerous reports in the literature showing the feasibility of the oxidative hydroxylation of phenylboronic acid to the corresponding phenol in the presence of an oxidant and additives and several of them have used H_2O/H_2O_2 as oxidant.[29,30] However, they employ an excess of H_2O_2, homogenous catalysts or temperatures above the ambient. Other procedures involve the use of light, such as the use of $[Ru(bpy)_3Cl_2]\cdot 6H_2O$ (bpy = bipyridine) in the presence of Et_3N and air under visible light irradiation[12] or employing Zr-based MOF with tetrakis(carboxyphenyl)-porphyrin groups as photocatalyst and Et_3N as electron donor using green LED light as irradiation source.[10] Other catalysts and oxidants that have also been used for the transformation of arylboronic acids into phenols include Pd-based complex/O_2/Et_3N,[31] solid poly(N-vinylpyrrolidone)/H_2O_2,[32] poly(4-vinylpyridine)/H_2O_2,[32] UiO-67-

$[Ru(bpy)_3]_{0.1}$/i-Pr_2NEt,[11] lactic acid/H_2O_2,[33] PhI/$NaIO_4$,[34] $CuCl_2/O_2$,[35] Cu_2O/NH_4OH,[36] Cu^{II}–β-cyclodextrin complex,[37] $CuSO_4$/phenanthroline/KOH,[38] Amberlite IR-120/H_2O_2,[39] biosilica/H_2O_2,[40] Ag nanoparticles supported on K10-montmorillonite/H_2O_2,[41] and Cu nanoparticles/ellagic acid composite among others.[42] In the present manuscript, we report that commercially available $Cu_3(BTC)_2$ is a convenient and efficient catalyst to convert arylboronic acids to the corresponding phenols using H_2O_2 as oxidant.

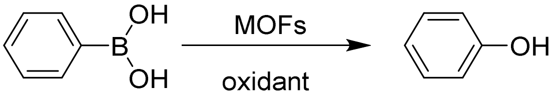
The advantages of the present procedure compared to the earlier methods are the heterogeneous nature of the catalyst, allowing easy recovery and recycling, mild reaction conditions and short reaction times. This commercially available Cu MOF does not require any post-synthetic modification. In addition, this catalytic system does not rely on noble or critical metals and exhibits a high catalytic activity and broad substrate scope.

2. Results and Discussion

Phenylboronic acid was initially selected as model substrate to screen the conditions for the room temperature oxidative hydroxylation to phenol using 30% aqueous H_2O_2 added at the starting time. The catalytic activity of a series of different MOF catalysts was tested. In the absence of H_2O_2 or in the presence of H_2O_2 in the absence of catalyst no conversion of phenylboronic acid was observed at room temperature under the reaction conditions used. Fe(BTC) and $Cu_3(BTC)_2$ exhibited 70 and 80% conversions of phenylboronic acid, respectively at room temperature with 0.5 mmol of H_2O_2 (Table 1, entries 3 and 4). Quantitative conversion of phenylboronic acid was achieved after 1 h at room temperature using 1 mmol of H_2O_2 in the presence of Fe(BTC) or $Cu_3(BTC)_2$ (Table 1, entries 5 and 6). Furthermore, Fe(BTC) and $Cu_3(BTC)_2$ did not show any conversion of phenylboronic acid using air as oxidant at room temperature after 2 h (Table 1, entries 10 and 11). Most of the reports in the literature have promoted the reaction with the presence of a base that was considered essential in this transformation. For example, Xu and coworkers have reported copper-catalyzed oxidative hydroxylation of arylboronic acid[38] in the presence of potassium hydroxide as a base and 1,10-phenanthroline as ligand. Hence, a further development would be to find a catalytic system which avoids the use of base or any additive as cocatalyst to promote this transformation.

In the present work, it has been found that oxidative hydroxylation of phenylboronic acid with H_2O_2 in the presence of triethylamine is catalyzed by $Cu_3(BTC)_2$ reaching complete conversion of phenylboronic acid (Table 1, entry 8). Furthermore, the reaction also exhibited quantitative conversion using $Cu_3(BTC)_2$ with 1 mmol of H_2O_2 in the presence of 4-NH_2-TEMPO (Table 1, entry 9), thus ruling out a reaction mechanism involving of carbon centred radical reaction intermediates. In the literature there are several reports describing the use of hydrogen peroxide in combination with different catalysts/promoters to promote the conversion of phenylboronic acid to phenol (Table 1, entries 12-16) with high yield. However, the major drawback in these systems is the excess use of hydrogen peroxide required. Hence, progress in this reaction requires development of a catalytic process in where a minimum amount of hydrogen peroxide is used as oxidant for this transformation. Furthermore, the present data show that the conversion of phenylboronic acid to phenol catalyzed by $Cu_3(BTC)_2$ takes place without the addition of base or additive, thus increasing the environmental benignity and the economic competitiveness of the entire chemical process.

Table 1. Oxidative hydroxylation of phenylboronic acid to phenol catalyzed by MOFs.[a]



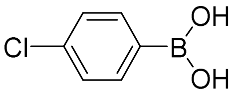
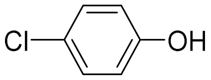
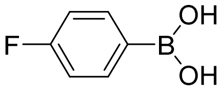
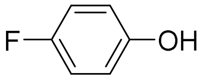
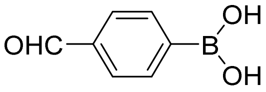
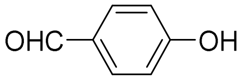
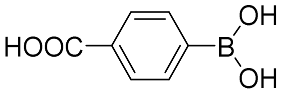
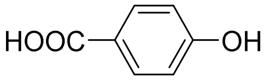
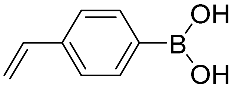
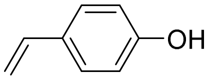
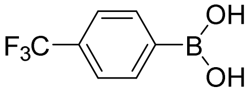
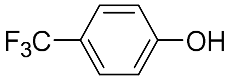
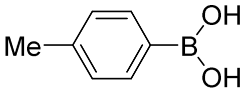
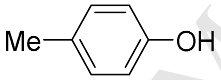
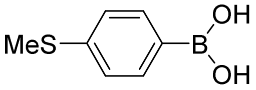
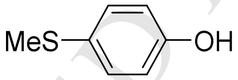
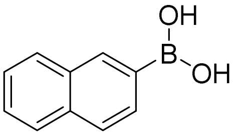
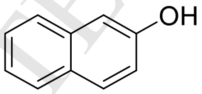
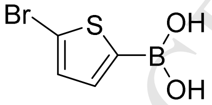
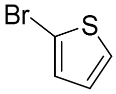
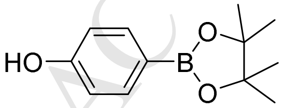
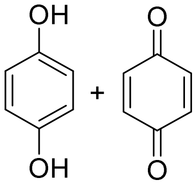
S. No	Catalyst	Time (min)	Oxidant	Oxidant	Conversion

				(mmol)	(%)[b]
1	Fe(BTC)	-	-	-	-
2	$Cu_3(BTC)_2$	-	-	-	-
3	Fe(BTC)	60	H_2O_2	0.5	70
4	$Cu_3(BTC)_2$	60	H_2O_2	0.5	80
5	Fe(BTC)	60	H_2O_2	1	>99
6	$Cu_3(BTC)_2$	60	H_2O_2	1	>99
7	$Cu_3(BTC)_2$	60	H_2O_2	1	>99[c]
8	$Cu_3(BTC)_2$	60	H_2O_2	1	98[d]
9	$Cu_3(BTC)_2$	60	H_2O_2	1	97[e]
10	Fe(BTC)	60	Open air	-	-
11	$Cu_3(BTC)_2$	60	Open air	-	-
12	Lactic acid[33]	5	H_2O_2	2[f]	95[g]
13	Biosilica[40]	5	H_2O_2	17.6[f]	93[g]
14	Ag^0/K10 mont.[41]	15	H_2O_2	4.4[f]	92[g]
15	H_3BO_3[43]	35	H_2O_2	35.2[f]	88[g]
16	NH_4HCO_3[44]	120	H_2O_2	2[f]	97[g]

[a]Reaction conditions: Phenylboronic acid (1mmol), catalyst (50 mg), acetone (3 mL), room temperature, 1 h; [b]Determined by gas chromatography; [c]Reaction was performed in $CDCl_3$ and the conversion was determined by ^1H-NMR; [d]With 0.2 mL of triethylamine; [e]With 120 mg of 4-NH_2-TEMPO; [f]mmol of H_2O_2 required to convert 1 mmol of phenylboronic acid; [g]Reported yield.

Although $Cu_3(BTC)_2$ and Fe(BTC) exhibited comparable activity for the transformation of arylboronic acids to phenols under the present experimental conditions, further studies were performed using $Cu_3(BTC)_2$ that exhibits somewhat higher catalytic activity than Fe(BTC) (Table 1, entries 3 and 4). Thus, the study of the catalytic activity of $Cu_3(BTC)_2$ as a heterogeneous catalyst for the oxidative hydroxylation of phenylboronic acid to phenol was expanded to phenylboronic acids substituted with electron donating or withdrawing groups under optimized reaction conditions. The results attained are given in Table 2. 4-Chlorophenylboronic acid and 4-fluorophenylboronic acid resulted in quantitative conversion with very high selectivity towards the corresponding phenols in 1 h time (Table 2, entries 1 and 2). 4-Formylphenylboronic acid and 4-carboxyphenylboronic acid gave 99 and 97% conversions in 45 and 60 min, respectively, without oxidation of the formyl group (Table 2, entries 3 and 4). Interestingly, the oxidation conditions are also compatible with the presence of C=C double bonds that are generally reactive under oxidation conditions at temperatures higher than ambient and, in this way, 4-vinylphenylboronic acid exhibited 99% conversion and complete selectivity to 4-hydroxystyrene in 45 min (Table 2, entry 5). This selectivity derives from the room temperature and short reaction times required for the $Cu_3(BTC)_2$ oxidation. Interestingly, 4-trifluoromethylphenylboronic acid also afforded the respective phenol in quantitative conversion with 99% selectivity in spite of the strong electron withdrawing effect of the $–CF_3$ group (Table 2, entry 6). 4-Methylphenylboronic acid and 4-methylthiophenylboronic acid showed 99 and 98% conversions in 60 min, respectively, with very high selectivities under optimized reaction conditions (Table 2, entries 7 and 8). The reaction also proceeds for condensed polycyclic arenes and in this way, 2-napthylboronic acid also gave 99% conversion with 99% selectivity of 2-naphthol in 60 min (Table 2, entry 9). In contrast, 2-bromo-5-thiophenylboronic acid resulted in the formation of 2-bromothiophene with 95% conversion and 96% selectivity (Table 2, entry 10). Finally, oxidation of 4-hydroxyphenylboronic acid pinacolyl ester resulted in the formation of a mixture of hydroquinone and quinone after 9 h (Table 2, entry 11). The requirement of longer reaction times in this case may be explained as due to the steric encumbrance of pinacolyl ester respect to boronic acids and the fact that the reaction is taking place inside the pores of $Cu_3(BTC)_2$.

Table 2. Scope of $Cu_3(BTC)_2$ as a heterogeneous catalyst for the oxidative hydroxylation of various phenylboronic acids to the corresponding phenols.

S. No	Substrate	product	Time (min)	Conversion (%)^b	Selectivity (%)^b
1			60	99	98
2			60	98	99
3			45	99	97
4			60	97	96
5			45	99	99
6			60	99	99
7			60	99	98
8			60	98	98
9			60	99	99
10			120	95	96
11			540	99	99^c

^{a}Reaction conditions: Phenylboronic acid (1 mmol), $Cu_3(BTC)_2$ (50 mg), acetone (3 mL), H_2O_2 (1 mmol), room temperature; ^{b}Determined by gas chromatography; ^{c}Corresponds to the combined selectivity to hydroquinone and quinine.

One of the main advantages of the heterogeneous catalysts is the possibility to recover the solid from the reaction mixture, allowing its reuse in subsequent runs. In this context, $Cu_3(BTC)_2$ was reused as catalyst. After completion of the reaction, the catalyst was filtered, washed with acetone, dried in an oven, and reused for the next run. The catalytic activity of $Cu_3(BTC)_2$ showed no significant change in its activity after two reuses. The $Cu_3(BTC)_2$ stability under the oxidation conditions was further confirmed by the absence of leached copper in the reaction mixture as evidenced by ICP-OES elemental analysis of the liquid phase after the reaction. Figure 1 shows the powder XRD of the fresh and two times used $Cu_3(BTC)_2$. It was observed that the crystallinity of the reused solid coincides with that of the fresh catalyst, thus confirming the stability of the catalyst under the present oxidation conditions. Furthermore, Figure 2 shows EPR spectra of fresh and two times reused $Cu_3(BTC)_2$. The oxidation state of Cu in the reused catalyst is still +2, although it seems that the intensity of the peak is reduced. This may be due to the adsorption of some reactants or products in the pore of $Cu_3(BTC)_2$ or to partial reduction of some Cu(II) ions to Cu(I) by H_2O_2 as reducing agent in low extent without resulting in noticeable collapse of the $Cu_3(BTC)_2$ structure.

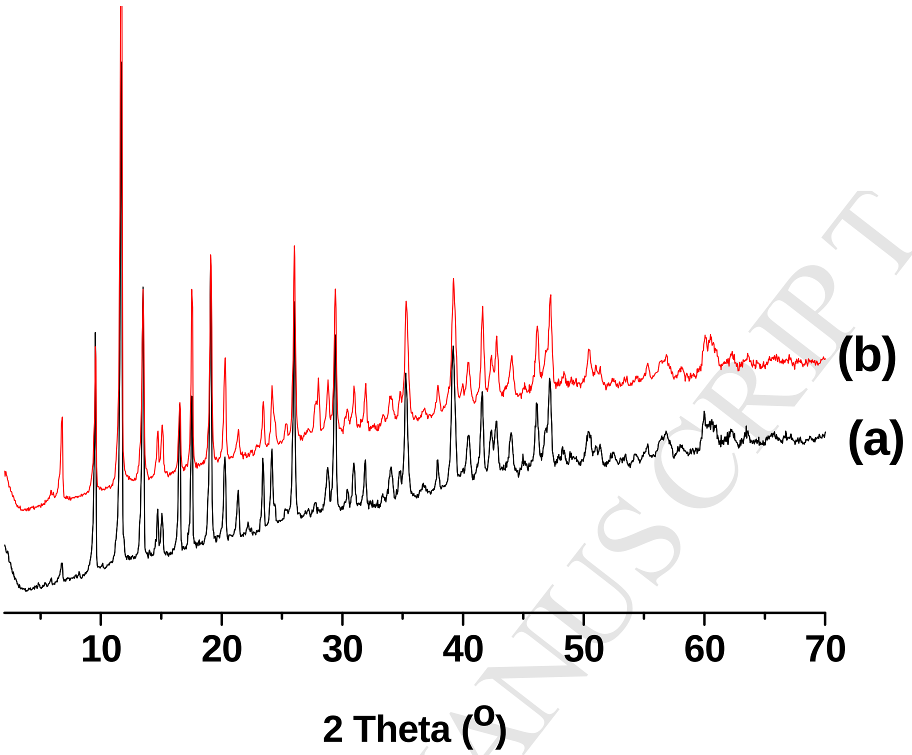


Figure 1. Powder XRD of (a) fresh $Cu_3(BTC)_2$ and (b) two times reused $Cu_3(BTC)_2$.

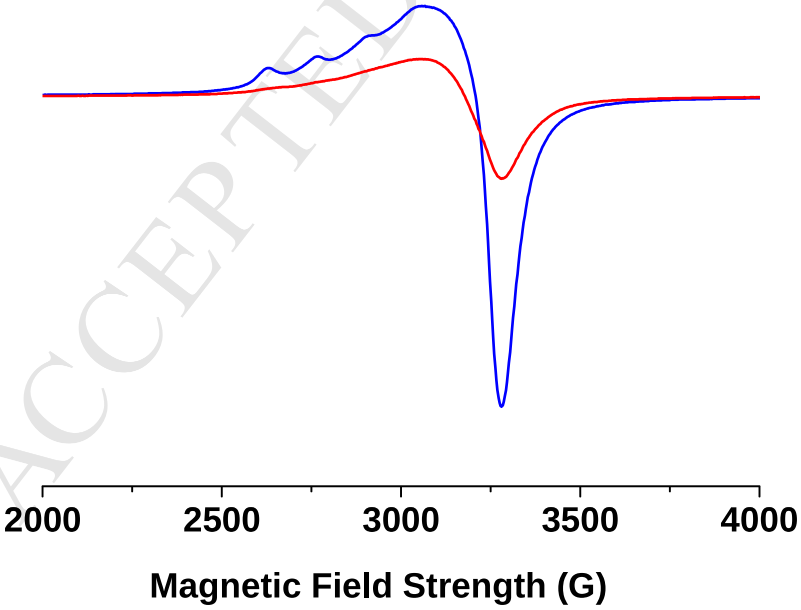


Figure 2. EPR spectra of fresh $Cu_3(BTC)_2$ (blue line) and two times reused $Cu_3(BTC)_2$ (red line).

3. Conclusions

In conclusion, the catalytic activity of $Cu_3(BTC)_2$ as heterogeneous catalyst for the oxidative hydroxylation of phenylboronic acids to the corresponding phenols using H_2O_2 as oxidant at room temperature is described. The main advantages of $Cu_3(BTC)_2$ as catalyst is that no base or additives are required. Furthermore, the reaction is highly selective towards the formation of phenol and products derived from other oxidation processes are not observed, even when the compound contains substituents able to undergo oxidation. This catalyst can be reused without significant drop in its activity. Although Fe(BTC) exhibits also notable catalytic activity, its performance is somewhat lower than that of $Cu_3(BTC)_2$.

4. Experimental

4.1. Materials

$Cu_3(BTC)_2$ and Fe(BTC) are commercially available from Sigma Aldrich as Basolite C 300 (31.5% of Cu) and F 300 (25.2% of Fe) MOFs, respectively. Phenylboronic acid and its derivatives (95-99% purity) and 35% H_2O_2 were purchased from Sigma Aldrich and used as received. Solvents used in the present study were purchased from Sigma Aldrich and are AR grade.

4.2 Instrumentation

Powder XRD diffraction patterns were measured in the refraction mode in a Philips X'Pert diffractometer using the CuKα radiation (λ = 1.54178 Å) as the incident beam, PW3050/60 (2 theta) as Goniometer, PW 1774 spinner as sample stage, PW 3011 as detector, incident mask fixed with 10 mm. PW3123/10 for Cu was used as a monochromator. PW3373/00 Cu LFF was used as X-ray tube with power scanning of 45 kV and 40 mA current. The sample powder was loaded into a holder and levelled with a glass slide before mounting it on the sample chamber. The specimens were scanned between 2° and 70° with the scan rate of 0.02°/s. ESR spectra were recorded by using a Bruker EMX spectrometer, with the typical settings (frequency 9.80 GHz, sweep width 30.6 G, time constant 80 ms, modulation frequency 100 kHz, modulation width 0.2 G, microwave power 200 mW).

4.3 Reaction procedure

In a typical reaction, 50 mg of catalyst was added to 3 mL of acetone containg 1 mmol of phenylboronic acid. This reaction mixture was stirred at room temperature for the required time as indicated in Tables 1 and 2. The reaction progress was monitored by gas chromatography and after completion of the reaction, the mixture was washed twice with acetone and filtered. Then, the solvent was removed and the product is analyzed by gas chromatography for its purity and selectivity. Conversion and selectivity were determined by Agilent gas chromatography using internal standard method. ^{1}H-NMR spectra were recorded with 400 MHz using tetramethylsilane as internal standard. The same procedure is followed for the reusability experiments.

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