Ullmann Coupling Reaction of Nitro-Substituted Aryl Halides with Phenols under Mild Conditions: Micro-/ Mesoporous Hierarchical LaAIPO-5 Zeolite Catalyst

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Heterogeneous catalytic reactions of aromatic organic molecules over zeolite catalysts present many challenges because of the shape selectivity of the micropores of conventional zeolites that limits the diffusion of aromatic molecules. Herein, Ullmann coupling reactions of phenols with nitro-substituted aryl halides were catalyzed by rare-earth-doped mesoporous AIPO-5 zeolites in the absence of ligands. The AIPO-5-MAIPO-5-M zeolites had a pure AFI structure and consisted of spherical particles assembled by nanofibers. The rare-earth elements

Introduction

Diaryl ether compounds often exist in medicines, natural products, and fine chemicals. The Cu-assisted Ullmann coupling of phenols with aryl halides is a valuable and important chemical reaction for the synthesis of diaryl ethers. However, harsh reaction conditions, such as a high reaction temperature (>150 $^{\circ}$ C), the requirement for stoichiometric equivalents of Cu, and low to moderate yields have limited its commercial utilization.^[1-3] Ullmann coupling reactions can be catalyzed efficiently by $Pd^{II}_{,}$ (4-6) $Cu^{I}_{,}$ (7-15) and $Ni^{II}_{,}$ compounds with ligands, such as Ndimethylglycine,^[13] salicylaldimine,^[14] and atropisomeric dipyridyl diphosphine, in the presence of organic additives^[16] under mild conditions (90-120°C). Simple and ligand-free catalytic systems that are recoverable and reusable have received increasing attention, for example, copper fluorapatite,^[17] copper oxide on alumina,^[18, 19] copper ferrite nanoparticles,^[20] nano-CuO,^[21,22] Au-Pd alloy nanoclusters,^[23] and Cu-USY.^[24]

Zeolite molecular sieves are solid porous materials with a high stability that are used widely as adsorbents and catalysts.^[25-27] Compared with microporous aluminosilicate zeolites, aluminophosphate zeolites (AIPO-n) exhibit more attractive properties, and its AI and/or P atoms can be replaced by Si to form SAPO-n materials, and by other metals to form metaldoped aluminophosphate (MeAIPO-n) materials.^[28-33] The interaction between these metal species, framework acid sites, and

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were highly dispersed in the AIPO-5-MAIPO-5-M samples. The LaAIPO-5-MAIPO-5-M zeolite is an excellent catalyst for UIImann coupling reactions of phenols and nitro-substituted aryl halides. Mesoporous LaAIPO-5 has an excellent stability and recyclability in the UIImann coupling of *p*-X-nitrobenzene (X = CI, Br, and I) with 2-naphthol. These results are important in the exploration of attractive UIImann coupling reactions and in the development of mesoporous zeolite catalysts for other organic reactions.

unique pores make the MeAIPO-n molecular sieves important materials in the design of new catalysts. Relative to other microporous zeolites, the large microporous channels (0.73 nm) of AIPO-5 facilitate the diffusion of aryl compounds with a large size. However, the diffusion of some bulky aryl molecules in the micropores of AIPO-5 is still difficult, which is an important challenge for the application of MeAIPO-5 catalysts in organic syntheses. Therefore, only mesoporous zeolites can catalyze the reactions of bulky molecules efficiently.

Catalytic materials based on rare earths (RE) are used widely in the water gas shift,^[34,35] oxidative dehydrogenation,^[36–38] aldol condensation,^[39] and other reactions^[40] because of their specific chemical properties.^[41–43] We reported that Ce-doped AlPO-5 materials exhibit a high catalytic performance for the oxidation of cyclohexane^[44,45] and the oxidation of styrene over La-MCM-48^[46] and Ln-MCM-41 (Ln=La, Ce, Sm, Yb)^[47] catalysts. Herein, RE-doped mesoporous AlPO-5 (LnAlPO-5-MAlPO-5-M) catalysts were prepared and used to catalyze Ullmann coupling reactions of phenols with nitro-substituted aryl halides in the absence of ligands for the first time. The prepared micro-/mesoporous LaAlPO-5-MAlPO-5-M zeolites exhibit an excellent catalytic performance for the Ullmann coupling reactions of *p*-X-nitrobenzene (X = Cl, Br, and I) with 2-naphthol under mild conditions (80 °C) with good operational stability.

Results and Discussion

As shown in the XRD pattern (Figure 1 a), the AIPO-5-MAIPO-5-M sample has an AFI structure and high crystallinity.^[41-43] In the N₂ sorption isotherm of AIPO-5-MAIPO-5-M (Figure 1 b), there is a step at $P/P_0 = 0.4-0.9$, which is typical of mesostructures. Its mesopore size is 2–10 nm, and the most probable pore size is 3.97 nm (Figure 1 b, inset). The SEM image (Figure 1 c) shows



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Figure 1. a) XRD pattern, b) N₂ sorption isotherm, c) SEM image, and d) TEM image of AIPO-5-M.

that its morphology is spherical with a particle size of 20– 50 μ m, which is composed of bread-shaped fibers (inset). The TEM image (Figure 1 d) shows that the AIPO-5-MAIPO-5-M sample has hierarchical mesopores of 2–10 nm, some of which are interconnected, which can be corroborated by the TEM image of a thin-section of AIPO-5-MAIPO-5-M sample (Figure S1 of the Supporting Information).

AIPO-5-MAIPO-5-M and LnAIPO-5-MAIPO-5-M (AI/Ln = 50, Ln = La, Ce, Sm, and Yb) were synthesized, and their textural parameters are presented in Table 1. Notably, the LnAIPO-5-

Table 1. BET surface areas (S_{BET}), micropore and mesopore volumes (V_{micro} and V_{meso}), and mesopore diameters (d_{meso}) of LnAIPO-5-M samples (Ln = La, Ce, Sm, and Yb, Al/Ln = 50).								
Ln	Ln loa [wt Solution	ading :%] Solid	S_{BET} [m ² g ⁻¹]	$V_{ m micro}$ [cm ³ g ⁻¹]	V _{meso} [cm ³ g ⁻¹]	d _{meso} [nm]		
La	2.5	2.1	281	0.08	0.22	4.43		
Ce	2.5	2.4	301	0.11	0.23	4.42		
Sm	2.5	1.5	262	0.07	0.18	4.53		
Yb	2.5	< 0.001	270	0.08	0.19	3.71		
-	0	0	354	0.10	0.24	5.02		

MAIPO-5-M samples have similar BET surface areas (262–301 m²g⁻¹) and mesopore volumes (0.18–0.23 cm³g⁻¹). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) showed that the Ln doping amounts in LaAIPO-5-MAIPO-5-M, CeAIPO-5-MAIPO-5-M, and SmAIPO-5-MAIPO-5-M are ~2.1, 2.4, and 1.5 wt%, respectively. However, the amount of Yb in YbAIPO-5-MAIPO-5-M is less than the limit of detection (<0.001 wt%). Analysis of the XRD patterns shown in Figure S2

shows that the LnAIPO-5-MAIPO-5-M (Al/Ln = 50) samples possess the typical AFI structure with a high crystallinity. The diffraction peaks of lanthanide oxides are not observed in the XRD patterns, which shows that the Ln elements are highly dispersed in the AIPO-5-MAIPO-5-M samples and that some Ln species are trapped inside zeolite cavities.

UV/Vis spectra of LaAIPO-5-M samples with different ratios of Al/La are shown in Figure 2. The absorption peak at $\lambda = 256-300$ nm (Figure 2 a) for LaAIPO-5-M (Al/La = 50) is assigned to four-coordinate La^{III} in the sample framework and six-coordinated extra-framework La species.^[45] The peak at $\lambda \sim 220$ nm (assigned to La₂O₃) can hardly be observed, which is in agreement with the XRD results. For LaAIPO-5-M (Al/La = 25), a peak at $\lambda \sim 220$ nm from La₂O₃ can be seen clearly (Figure 2 b). This



Figure 2. UV/Vis spectra of LaAIPO-5-M with Al/La of a) 50 and b) 25 (in the synthesis solution).



indicates the formation of $\mathrm{La}_2\mathrm{O}_3$ in the LaAlPO-5-M sample if the La amount is high.

Solid-state ²⁷Al and ³¹P magic-angle spinning (MAS) NMR spectra of the LnAIPO-5-M (AI/Ln=50) samples are shown in Figures S3 and S4. The signal at $\delta = 39-40$ ppm in the ²⁷AI MAS NMR spectra of the LnAIPO-5-M samples is assigned to tetrahedral AI in the crystalline aluminophosphate framework; this chemical shift is $\delta = 2-3$ ppm higher than that of the AIPO-5 sample ($\delta = 37$ ppm).^[42,43] This is convincing evidence for the doping of Ln^{3+} in the framework (Figure S3). In the ³¹P MAS NMR spectra of the LnAIPO-5-M samples, the signal at $\delta = -5$ to -13 ppm, ascribed to P(3Al, 1Ln) can be observed clearly, which further proves the presence of Ln³⁺ species in the framework (Figure S4). No lanthanide oxide was detected in the XRD patterns, which confirms that some Ln species were trapped inside zeolite cavities (Figure S2). The atomic ratios of P/Ln were estimated from the simulation of the ³¹P MAS NMR spectrum of LnAIPO-5-M as the NMR spectra reflect the amount of Ln that occupies framework Al sites (Figure S4). The XPS spectra of LaAIPO-5-M are shown in Figure 3. The surface atom concentrations of LnAIPO-5-M (AI/Ln=50) were obtained based on the XPS data and are shown in Table S1. For the LaAIPO-5-M sample, P/La was 63.8:1, higher than the theoretical value of 59:1 in the gel; for CeAIPO-5-M, P/Ce was 55.8:1, and P/Sm was 127.3/1 for SmAIPO-5-M.

Although many highly efficient catalytic systems have been developed for the Ullmann reaction,^[9, 10, 14] many catalysts are

promoted by ligands or noble metals, which increases costs. Therefore, the development of simple catalyst systems for the Ullmann reaction without ligands and noble metals is a challenge.^[17,18] Herein, the Ullmann coupling of *p*-bromonitrobenzene and *p*-cresol was used as a model reaction, and the catalytic performances of the LnAIPO-5-M (Al/La = 50) catalysts are shown in Table 2.

The results show that the CeAIPO-5-M catalyst with K₂CO₃ as the base additive and DMSO as the solvent led to 32% product yield at 40 $^\circ\text{C}$ for 12 h (Table 2, entry 1); if the temperature was increased to 130° C, the yield increased to >99% (Table 2, entry 3). If we used the LaAIPO-5-M catalyst, the most efficient catalyst among the Ln-doped AIPO-5 catalysts, the yield reached > 99% at 80 °C (Table 2, entry 4). As the Yb amount in the YbAIPO-5 catalyst was very low, the product yield over this catalyst was the lowest (17%; Table 2, entry 6). Notably, 24% yield was obtained over the AIPO-5 catalyst (Table 2, entry 7), and the blank run without LnAIPO-5-M or AIPO-5 catalysts yielded no desired products as detected by GC (Table 2, entry 8). These results show that the Ln species are the efficient catalytically active components for the coupling reactions. The nature of the base is crucial in the Ullmann coupling reaction, and the effect of the base additive (K₃PO₄, KOH, and NaOtBu) on the yield of the coupling reaction of p-bromonitrobenzene with p-cresol was investigated (Table 2). Compared with that of K_2CO_3 (>99%; Table 2, entry 4), the use of K_3PO_4 ,





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Table 2. Ulimann coupling reaction of <i>p</i> -bromonitrobenzene with p - cresol over the LnAIPO-5-M catalysts							
O _o N ²	Br +	\sim^{OH} Ln.	AIPO-5-M	$\bigcirc^{\circ}\bigcirc$			
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Entry	Catalyst	Base	T/t	Yield ^[a]	TOF		
			[°C/h]	[%]	$[h^{-1}]$		
1	CeAIPO-5-M	K ₂ CO ₃	40/12	32 (26)	-		
2	CeAIPO-5-M	K ₂ CO ₃	100/12	77 (71)	-		
3	CeAIPO-5-M	K ₂ CO ₃	130/12	>99	-		
4	LaAIPO-5-M	K ₂ CO ₃	80/12	>99 (91)	8.75 ^[e]		
5	SmPO-5M	K ₂ CO ₃	80/12	83 (78)	-		
6	YbPO-5M	K ₂ CO ₃	80/12	17 (10)	-		
7	AIPO-5-M	K ₂ CO ₃	80/12	24 (20)	-		
8	-	K ₂ CO ₃	80/12	n.d.	-		
9	LaAIPO-5-M	K₃PO₄	80/12	49 (44)	-		
10	LaAIPO-5-M	КОН	80/12	71 (65)	-		
11	LaAIPO-5-M	NaOtBu	80/12	55 (50)	-		
12	La/AIPO-5-M	K ₂ CO ₃	80/12	56 (51)	-		
13 ^[48]	Nano-CeO ₂ ^[b]	KOH	110/2	72	12		
14	LaAIPO-5-M ^[b]	K ₂ CO ₃	100/12	>99 (87)	-		
15 ^[49]	Cu ^{II} /silica	KF	130/16	88	1.1		
16 ^[50]	Cul/ligand ^[c]	Cs ₂ CO ₃	110/21	88	0.4		
17	LaAIPO-5-M ^[c]	K ₂ CO ₃	80/12	>99 (89)	-		
18[51]	Cu-Fe-HT ^[d]	-	140/10	95	-		
19	LaAIPO-5-M ^[d]	K ₂ CO ₃	80/12	>99 (92)	-		
Reaction conditions: LnAIPO-5-M (100 mg), <i>p</i> -bromonitrobenzene							

(0.1 mmol), *p*-cresol (0.15 mmol), base additive (2.5 equiv.), DMSO (2 mL), 40–130 °C, GC yield. [a] The value in the parentheses is the isolated yield. [b] Coupling of *p*-cresol with *p*-chloronitrobenzene. [c] Coupling of phenol with *p*-iodonitrobenzene. [d] Coupling of phenol with *p*-bromonitrobenzene. [e] TOF calculated based on 1 mmol reaction, reaction time 1 h (yield of 17.5%).



KOH, and NaOtBu resulted in lower yields (49–71%; Table 2, entries 9–11).

In comparison with reported results (72–95% yield; Table 2, entries 13, 15, 16, and 18),^[48–51] the catalytic performance of LaAIPO-5-M (>99% yield; Table 2, entries 4, 14, 17, and 19) is superior. The excellent catalytic performance of LaAIPO-5-M for the Ullmann coupling reaction is attributed to the high and uniform dispersion of La species because of the large surface area and the abundant mesopores, which facilitate the diffusion of the reactant and product molecules.

The catalytic performances of LaAIPO-5-M for the Ullmann coupling reaction of bulky 2-naphthol with *p*-X-nitrobenzene (X = Cl, Br, and I) are listed in Table 3, and the results for the reaction with other halide substituents are listed in Table S2. If Br- (or I-)*para*-substituted nitrobenzenes were used, high yields of 91% (88%) were obtained at 80 °C (Table 3, entries 1 and 3). For the reaction of 2-naphthol with *p*-nitrochlorobenzene at 80 °C, only a trace of product was obtained (Table 3, entry 4); if the reaction temperature was increased to 100 °C, a high yield (89%) was obtained (Table 3, entry 5). Meanwhile, good to excellent isolated yields were obtained for the Ullmann coupling reaction of 2-naphthol with COH- (or OCH₃-)*para*-substituted bromobenzenes over LaAIPO-5-M (Table S2, entries 1–2).

Table 3. Catalytic performance of LaAIPO-5-M for a series of Ullmann coupling reactions of p -X-nitrobenzenes (X = Cl, Br, and I) with 2-naphthol.									
0 ₂ 1	O_2N + $OH LaAIPO-5-M K_2CO_3 O_2N$ $O O O O O O O O O O O O O O O O O O O$								
Entry	Х	<i>T</i> [°C]		Yield	l in re	peated	d run	[%]	
			1st	2nd	3rd	4th	5th	6th	7th
1	Br	80	91	89	87	82	81	80	80
2 ^[a]	Br	80	25	-	-	-	-	-	-
3	I	80	88	88	85	85	83	83	82
4	Cl	80	trace	-	-	-	-	-	-
5	Cl	100	89	87	86	84	81	81	79
6 ^[b]	Br	80	91	92	92	90	89	87	87
7	Recycled	catalyst [mg]	100	96	94	88	85	83	80
8 ^[c]	Cl	100	63						
9 ^[c]	Br	80	trace						
10 ^[c]	I	80	trace						
Reaction conditions: LaAIPO-5-M catalyst (100 mg), aryl halide (0.1 mmol), 2-naphthol (0.15 mmol), K ₂ CO ₃ (2.5 equiv.), and DMSO (2 mL), 80 °C, 12 h, isolated yield. [a] LaAIPO-5 catalyst (100 mg); mesopore volume = $0.09 \text{ cm}^3 \text{g}^{-1}$. [b] The reaction conditions were the same as for entry 1, and the used catalyst was calcined at 550 °C for 3 h after each cycle. [c] The reaction was performed in the absence of zeolite catalyst.									

The lower reactivity of *p*-nitrochlorobenzene than that of *p*-nitrobromobenzene should be ascribed to the different C–X bond energies, such as the C–Cl energy of ~81 kcalmol⁻¹ and C–Br energy of ~70.2 kcalmol⁻¹. Interestingly, Taillefer et al.^[52] reported a 68% yield of diaryl ether from the reaction of *p*-io-donitrobenzene with 3,5-dimethylphenol at 90 °C for 18 h over a base catalyst instead of a metal catalyst. Although there is an approximately 63% yield of diaryl ether from the reaction of *p*-chloronitrobenzene with 2-naphthol at 100 °C (Table 3, entry 8),

$Ar^{2}-OH$ $K_{2}O$ $K_{2}O$ $Ar^{2}-OH$ Ln-AIPO-5-M $K_{2}O$ $Ar^{2}-O-Ar^{1}$

Solution

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Figure 4. Possible mechanism of the synthesis of diaryl ether.

only traces of diaryl ether were obtained in the reaction of *p*-bromo- and *p*-iodonitrobenzene with 2-naphthol at 80 °C without LnAlPO-5 (Table 3, entries 9 and 10). These results indicate that the pathway of Ullmann coupling is different from an S_NAr pathway. A possible synthesis mechanism of diaryl ether catalyzed by LnAlPO-5-M is shown in Figure 4.

As it is different from the LaAIPO-5-M mesoporous catalyst, the yield over the LaAIPO-5 microporous catalyst was only 25% (Table 3, entry 2) if *p*-bromonitrobenzene was used at 80°C. The significant differences of the catalytic performance of the microporous and mesoporous LaAIPO-5 catalysts suggest that the highly efficient Ullmann coupling reaction of bulky molecules should be attributed mainly to the mesoporous structure.

To verify the real heterogeneity of the LaAIPO-5-M zeolite, a Sheldon test was performed to evaluate possible metal leaching.^[53] Thus, after 2 h at 80 °C, the reaction mixture was filtered, and the filtrate was heated at 80 °C for an additional 2 h. The catalytic performance of the reused LaAIPO-5-M catalyst for Ullmann coupling reactions of *p*-bromonitrobenzene with 2-naphthol was also conducted at 80 °C for 4 h. These results are listed in Table 4. The obtained results indicated clearly that there is no appreciable leaching of La ions under the given reaction conditions (Table 4). Furthermore, La species were not detected in the liquid mixture (less than the ICP-AES detection limit of 10 ppm), which indicates negligible La leaching from the LaAIPO-5-M catalyst in this coupling reaction.

To investigate the stability of the LaAIPO-5-M catalyst, Ullmann coupling was performed on the recycled catalyst





(Table 3). After the catalyst was recycled seven times, the yield of 2-(4-nitrophenoxy)naphthalene was still maintained at 80% (Table 3, entry 1). The slight decrease in product yield is attributed to the loss of catalyst during recovery (separation by centrifugation and washing with ethanol three times) and/or deactivation. After it was used repeatedly seven times, the catalyst mass was reduced to 0.08 g (Table 3, entry 7).

To clarify whether the LaAIPO-5-M catalyst had changed during the reaction, the fresh and used catalysts (LaAIPO-5-M-R after recycling seven times) were analyzed by thermogravimet-ric analysis (TGA; Figure 5). The fresh catalyst underwent a mini-



Figure 5. TGA curves of fresh LaAIPO-5-M and LaAIPO-5-M-R used seven times.

mal weight loss (~3% at 600°C), and the used catalyst exhibited ~10% weight loss in the same temperature range, which indicates that the LaAIPO-5-M-R catalyst suffered a degree of coke formation. After the used catalyst was calcined at 550°C for 3 h, its catalytic activity could be recovered to the initial activity (Table 3, entry 6), which indicates that coke formation is a key factor that results in catalyst deactivation.

Ullmann coupling reactions of aryl halides with phenols were performed over the LaAIPO-5-M catalysts, and the results are listed in Table 5. Phenol derivatives can react well with aryl halides that have electron-rich or electron-poor substituents in the benzene ring to form the desired products in excellent yields (Table 5, entries 1–7). This indicates that the electronic nature of the phenol substrate does not affect its reactivity remarkably.

In addition, we investigated Ullmann reactions of nitrobenzenes with Cl, Br, and I at the *para* position systematically with a series of phenols. As *p*-nitrochlorobenzene is less reactive than *p*-nitrobromo/iodobenzene, a lower yield (63%) of the product was obtained at 80°C (Table 5, entry 8); if the reaction temperature was increased to 100°C, the isolated yield reached 91% (Table 5, entry 9). For the reaction of 2-nitrobromobenzene with phenol, only 34% conversion was obtained at 80°C (Table 5, entry 14), which implied the presence of steric hindrance for the aryl halides in the Ullmann coupling. If the reaction temperature was increased to 120°C, the isolated yield was enhanced to 85% (Table 5, entry 15). Similar to the Ullmann coupling reaction of iodobenzene, 2-nitrobromoben-

Table .		J ×	+ R ²		LaAIPO-5-M K ₂ CO ₃		
Entry	R ¹	х	R ²	T [°C]	Conversion [%]	Selectivity [%]	Isolated yield [%]
1	4-NO ₂	Br	4-Me	80	100	>99	91
2	4-NO ₂	Br	4-Cl	80	100	>99	91
3	4-NO ₂	Br	3-Me	100	100	>99	90
4	4-NO ₂	Br	Н	100	100	>99	92
5	4-NO ₂	L	н	80	100	>99	89
6	4-NO ₂	I.	4-Me	80	100	>99	89
7	4-NO ₂	I.	4-Cl	80	100	>99	92
8	$4-NO_2$	CI	4-Cl	80	65	>99	63
9	4-NO ₂	CI	4-Cl	100	100	>99	91
10	4-NO ₂	CI	4-Me	100	100	>99	87
11	4-NO ₂	CI	3-Me	100	100	>99	86
12	4-NO ₂	CI	2-Me	100	100	>99	88
13	4-NO ₂	CI	н	120	100	>99	90
14	$2-NO_2$	Br	Н	80	34	>99	30
15	2-NO ₂	Br	н	120	100	>99	85
16	2-NO ₂	Br	4-Me	120	75	>99	67
Reaction conditions: LaAIPO-5-M (100 mg), aryl halide (0.1 mmol), phenol (0.15 mmol), K_2CO_3 (2.5 equiv.), and DMSO (2 mL). For the isolated yield, the conversion and selectivity were calculated from GC–MS data.							

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zene exhibited a low reactivity, and only if the reaction temperature was increased to 120 °C did the yield reach 90% (Table 5, entry 13).

Conclusions

Mesoporous AIPO-5 zeolites doped with rare earths (LnAIPO-5-M, Ln=La, Ce, Sm, Yb) were prepared successfully. These LnAIPO-5-M zeolites have high BET surface areas (262-301 m^2g^{-1}) and mesoporous volumes (0.18–0.23 cm³g⁻¹). The results show that the mesoporous AIPO-5 zeolite is an effective catalyst for Ullmann coupling reactions, and modification with rare earths can improve the catalytic performances of mesoporous AIPO-5 zeolites significantly. Among the LnAIPO-5-M samples, the LaAIPO-5-M catalyst exhibited the best catalytic performance for the Ullmann coupling reaction of p-bromonitrobenzene with p-cresol. In the Ullmann coupling reactions of halonitrobenzenes with 2-naphthol and aryl halides with phenols, the LaAIPO-5-M zeolite catalyst possessed excellent catalytic performances: the yields reached > 99% at 80–100 °C after 12 h. After the LaAIPO-5-M catalyst was recycled seven times in the reaction of 2-naphthol and 4-nitrobromobenzene, the product yield decreased slightly from 91 to 80%, which should be attributed to the catalyst loss during the catalyst recovery and surface coke formation. After the used catalyst was calcined at 550 °C for 3 h, its catalytic activity could be recovered. The LaAIPO-5-M catalyst, which possesses a hierarchical micro-/mesoporous structure, exhibits an excellent catalytic performance in terms of a high catalytic activity, excellent recyclability, and negligible metal leaching, and therefore, presents a promising alternative for Ullmann coupling. The hierarchical micro-/mesoporous zeolite catalyst was used here to catalyze the reactions of bulky molecules, which provides valuable



guidance for the future development of other organic transformations.

Experimental Section

Materials

Orthophosphoric acid and $Ln(NO_3)_3 - 6H_2O$ (Ln = La, Ce, Sm, Yb) were obtained from the Sinopharm Chemical Reagent Co., Ltd. (China). Aluminum isopropoxide (98%) was purchased from the Aladdin Reagent Database Inc. (China). Tetramethylguanidine (TMG, 99.2%) was supplied by the Xinhua Wanbo Company (China). All reagents were used without further purification.

Synthesis of AIPO-5 and AIPO-5-M

AIPO-5-M samples were synthesized hydrothermally from an aluminophosphate gel in the presence of TMG and a silane $[(C_2H_5O)_3SiC_3H_6N(CH_3)_2C_{18}H_{37}]Br$ (TPOAB); the composition was 1 P₂O₅:0.8 Al₂O₃:0.6 TMG:0.12 TPOAB:33 H₂O. Typically, aluminium isopropoxide (9.155 g) was added to deionized water (15.8 mL), followed by addition of TPOAB (2 mL) and H₃PO₄ (3.6 mL) under stirring. TMG (2.2 mL) was then introduced into the gel under stirring. All operations were performed at RT. Finally, the gel was transferred to an autoclave to be crystallized hydrothermally at 150 °C for 6 h. The formed solid was collected by filtration, dried at 100 °C overnight, and calcined at 550 °C for 5 h. AIPO-5 was prepared using the same method above without the addition of TPOAB.

Synthesis of LaAIPO-5, LnAIPO-5-M, and La/AIPO-5-M

LaAlPO-5 was synthesized from a gel of $1P_2O_5$:0.8 Al₂O₃:0.034 La:0.6 TMG:33 H₂O and the LnAlPO-5-M samples (Ln = La, Ce, Sm, Yb) were synthesized from a gel of $1P_2O_5$:0.8 Al₂O₃:0.034 Ln:0.6 TMG:0.12 TPOAB:33 H₂O. All experimental procedures and conditions were the same as those used for the synthesis of AlPO-5 and AlPO-5-M, apart from the addition of Ln to the synthesis solution before TMG addition.

For comparison, La was supported on AIPO-5-M by impregnation with an aqueous solution of lanthanum or cerium nitrate, followed by drying at 100 °C, and calcination in air at 550 °C for 5 h. These samples are denoted as La/AIPO-5-M. The loading amount of rare-earth metal was ~2.5 wt %.

Catalytic activity testing

A solution of aryl halide (0.15 mmol), phenol (0.1 mmol), catalyst (50 mg, ~2.5 wt %, 0.009 mmol), K₂CO₃ (40 mg, 0.3 mmol), and dimethyl sulfoxide (DMSO; 2 mL) was sealed in a 25 mL Schlenk tube at 80 °C for 12 h. After cooling to RT, the catalyst was separated by centrifugation at 8000 rpm for 5 min. The filtrate was diluted with diethyl ether (~5 mL) and washed twice with water (~5 mL). Before purification of the products by silica-gel chromatography with an eluent consisting of diethyl ether and petroleum ether, the reactant conversion and product selectivity were determined by using GC (Agilent 7890) equipped with a flame ionization detector and a HP-5 column (30 m×0.25 mm), and the product yields are based on isolated yields. The products were then characterized by ¹H and ¹³C NMR spectroscopy.

Catalyst recycling

LaAlPO-5-M (100 mg), *p*-halonitrobenzene (0.15 mmol), 2-naphthol (0.1 mmol), DMSO (2 mL), and K_2CO_3 (40 mg, 0.3 mmol) were added to the reactor. The mixture was stirred at 80 °C for 12 h and then cooled to RT. The LaAlPO-5-M catalyst was separated by centrifugation, washed three times with ethanol, and dried at 100 °C for 12 h. The catalyst was reused directly.

Catalyst characterization

N₂ adsorption-desorption isotherms were measured at 77 K by using a Micromeritics ASAP 2020 surface area and porosity analyzer. Before the measurements, the sample was degassed for 4 h at 350 °C. The BET method was used to calculate the specific surface areas of the samples. The pore size distributions of the samples were calculated by Barrett-Joyner-Halenda method from the desorption branches of the isotherms. The XRD patterns of the samples were obtained by using a Rigaku Ultima IV diffractometer using CuK_a radiation. TGA was performed by using a PerkinElmer Pyris Diamond instrument with a WCT-2 thermal analyzer at 10°C min⁻¹ from RT to 850°C. TEM images of the samples were obtained by using a FEI Tecnai G2 F30 S-Twin microscope operated at 300 kV. SEM images were obtained by using a high-resolution field-emission scanning electron microscope (JSM6700F, JEOL) operated at 15 kV. The samples were coated with a thin layer of Pt to prevent charging before scanning. The amounts of rare-earth elements in AIPO-5-M were determined by using ICP-AES (Varian 710-ES). X-ray photoelectron spectroscopy (XPS) was performed by using a Thermo ESCALAB 250 with AlK_a radiation ($h\nu = 1486.6$ eV) operated at 150 W under 10⁻⁹ mbar in the analytical chamber. All binding energies were determined with respect to the C1s line (284.7 eV) that originates from adventitious carbon. Solid-state Al and P MAS NMR spectra were recorded by using an AVANCE 500 NMR spectrometer at 130.3 and 202.1 MHz, respectively. The products were characterized by using ¹H (500 MHz) and ¹³C NMR (125 MHz) spectroscopy. NMR spectra were recorded at 20 °C using CDCl₃ as the solvent. Chemical shifts are given in ppm relative to tetramethylsilane as the internal standard.

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Keywords: doping · heterogeneous catalysis · mesoporous materials · rare earths · zeolites

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